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Sorption Properties of Methylene Chloride in Isotactic Polypropylene

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ABSTRACT: The sorption curves of methylene chloride vapor in different samples of isotactic polypropyllene were analyzed at 25 °C to investigate the effect of different parameters on the sorption mode. The investigated parameters were (a) molecular weight and molecular weight distribution, (b) aging, and (c) drawing to high draw ratio. The sorption isotherms were analyzed using some of the established isotherm equations derived on the basis of various sorption models. The Flory-Huggins interaction parameter, χ, derived for the different samples, shows that methylene chloride is a poor solvent for isotactic polypropylene (iPP). An attempt to correlate clustering of solvent molecules with the lowering of the upper T_g of iPP was performed.

Introduction

The study of the interactions between solvent systems and organic polymers in the solid state can help clarify many particulars about polymer structure.[1-5]

In the last years the equilibrium sorption and the diffusion of organic penetrants have been more and more frequently used to study the basic aspects of the polymer structure. In particular, the "mode of sorption", that is the manner by which penetrant molecules are sorbed within the polymer matrix, depends principally on the polymer chain segmental mobility, and this, in turn, can be affected by the presence of the penetrant, causing a change in the mode of sorption. The sorption modes of interest are random dispersion of free penetrant molecules, localization of penetrant molecules at specific polymer groups, and penetrant–penetrant molecule cluster formation. Each of these sorption modes is related to the particular structural and morphological situation of the polymer chains.

In the case of isotactic polypropylene (iPP), the molecular weight as well as the thermal and mechanical treatments greatly influences the transport properties, and there are many unsolved problems in the evaluation of the experimental data.[6-8]

The purpose of this work is to elucidate some properties and structural aspects of iPP through the study of the sorption modes of methylene chloride vapor in films of different molecular weight submitted to different treatments.

Table I
Density (g/cm^3), Amorphous Fraction, α_a, Interaction Parameter, χ, and Upper T_g Calculated from Eq 4, for the Different Samples

sample	density	α_a	χ	T_g^u, °C
A	0.9020	0.40	1.48	45
B	0.9050	0.36	1.46	45
C	0.9034	0.38	1.66	
D	0.9017	0.40	1.44	52

Experimental Section

Isotactic polypropylene of M_w = 307 000 and M_n = 15 600 was a product of RAPRA (Shrewsbury, Great Britain).

Films of this sample were obtained by heating pellets at 200 °C, pressing them into the film shape with a thickness 0.02 cm (sample A) and 0.005 cm (sample B), and cooling the melt quickly to 100–110 °C and then slowly to room temperature. Sample A was tested 2 mo after the preparation, sample B, after 16 mo.

A different film, quenched at 0 °C, was drawn at 110 °C up to a draw ratio of 15 and cooled to room temperature before being unhooked from the testing device (sample C).

A fourth sample (sample D) was obtained with the same procedure as sample A starting from pellets of iPP of M_w = 630 000 and M_n = 190 000 supplied by Himont, Italy.

Density measurements were obtained by floating the samples in a mixture of 1,2-diethoxyethanol and 2-ethoxyethane.

In Table I the samples and the corresponding densities are

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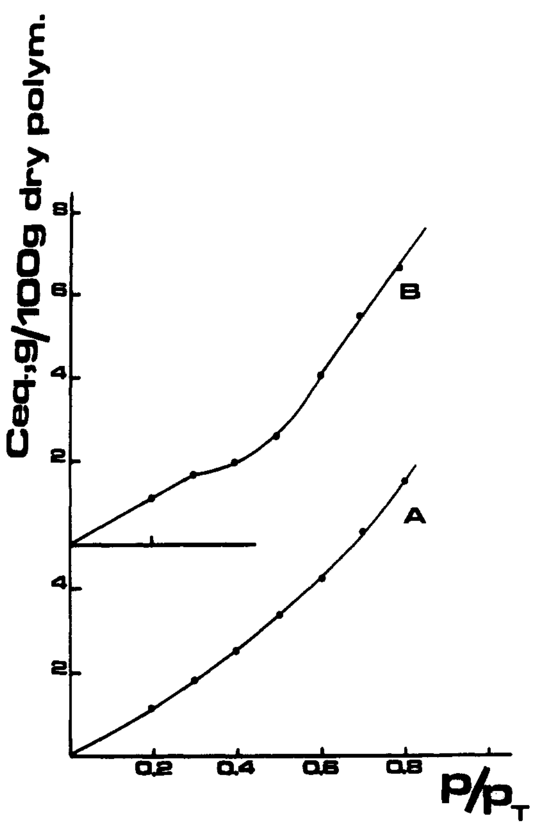

Figure 1. Equilibrium sorption c_{eq} (g/100 g of dry polymer) as a function of vapor activity $a = p/p_T$ of CH_2Cl_2 in samples A and B.

reported. The amorphous fraction, derived from density, is also reported for all the samples.

The sorption measurements were obtained by a microgravimetric method, using a quartz spring balance, having an extension of 18 mm/mg. The penetrant used was methylene chloride at varying activity $a = p/p_T$, where p is the actual pressure to which the sample was exposed and p_T the saturation vapor pressure at the temperature of the experiment, T = 25 °C. The instrumentation and the methods used have been extensively described in a previous paper.[9] The volume fractions v_2 and v_1 of polymer and sorbed solvent in the amorphous regions at equilibrium were calculated from the experimentally determined weight fractions (m_i), by assuming that the solvent and the polymer volumes are additive on mixing and that sorption occurs only in the amorphous regions of the polymer. These conditions were verified for the solvent methylene chloride in iPP in a previous paper.[8] The density of the amorphous regions in the samples was assumed to be equal to that of the completely amorphous sample, i.e., 0.856 g/cm^3, and we used the equation

$$v_1 = \frac{m_1/d_1}{m_1/d_1 + m_2/d_2} = 1 - v_2 \quad (1)$$

Results

Figures 1 and 2 report the equilibrium sorption c_{eq} (g/100 g of dry polymer) as a function of vapor activity $a = p/p_T$ for the four different samples. The two samples with different molecular weight, obtained with the same thermal treatment and tested after 2 mo of aging, i.e., samples A and D, show the same mode of sorption, that is, first a linear dependence of c_{eq} on activity and, after a given activity, a positive deviation from Henry's law. This mode of sorption represents a preference for penetrant–penetrant pairs to be formed, such that the solubility coefficient increases continuously with pressure.[1] This behavior depends on the ability of the solvent to plasticize the polymeric matrix. Whereas in the case of sample A the deviation from linearity starts at low penetrant activity, for sample D Henry's law is followed up to a penetrant activity a = 0.4.

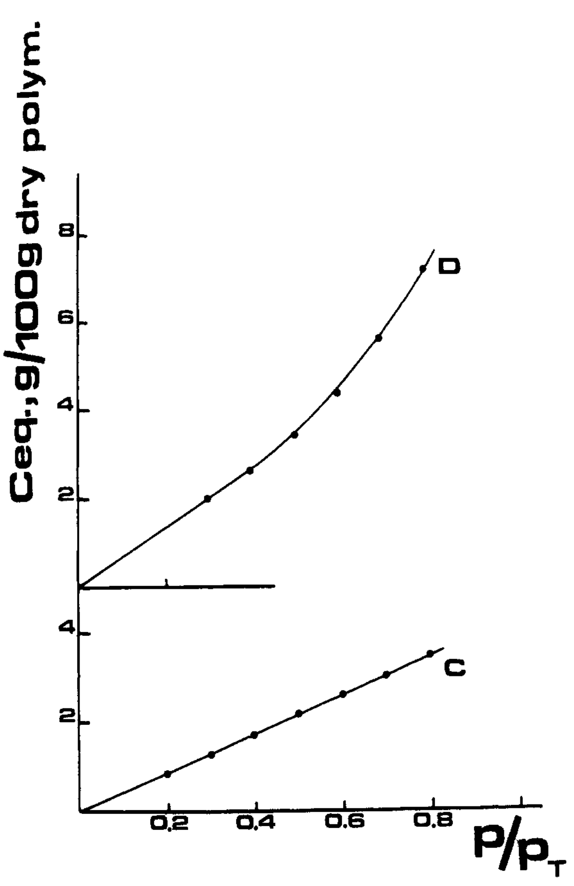

Figure 2. Equilibrium sorption c_{eq} (g/100 g of dry polymer) as a function of vapor activity $a = p/p_T$ of CH_2Cl_2 in samples C and D.

In the case of sample B, that is, a thin crystalline film aged for more than 1 yr, the sorption curve, after a linear part, displays a region of negative curvature, and after activity 0.4 shows a positive deviation as in the case of samples A and D.

The sorption curve of sample C, that is, the highly drawn sample, shows a linear dependence of sorption on penetrant activity. Therefore, Henry's law is obeyed, and the solubility coefficient is a constant independent of sorbed concentration.

To examine more thoroughly the different sorption modes, the isotherm data were analyzed using some of the established isotherm equations that have been derived on the basis of various sorption models.

In the case of samples A and D, for which a positive curvature in the sorption curve is observed, we can relate the activity of solvent in a solution of amorphous polymer with the volume fractions of solvent and polymer (v_1 and v_2, respectively) according to the Flory–Huggins equation

$$\ln a_1 = \ln v_1 + v_2 + \chi v_2^2 \quad (2)$$

where χ is the interaction parameter.[10,11] This equation is applicable to semicrystalline polymers in the absence of swelling or strong specific interactions. The interaction parameter, χ, was found to vary with the activity a_1 in a narrow range for the two samples. In fact, for sample A its value varies from 1.46 (at activity 0.2) to 1.50 (at activity 0.8). For sample D it varies from 1.42 to 1.468 respectively, at activity 0.2 and 0.8. The average value of the χ parameter in all the investigated range of activ-

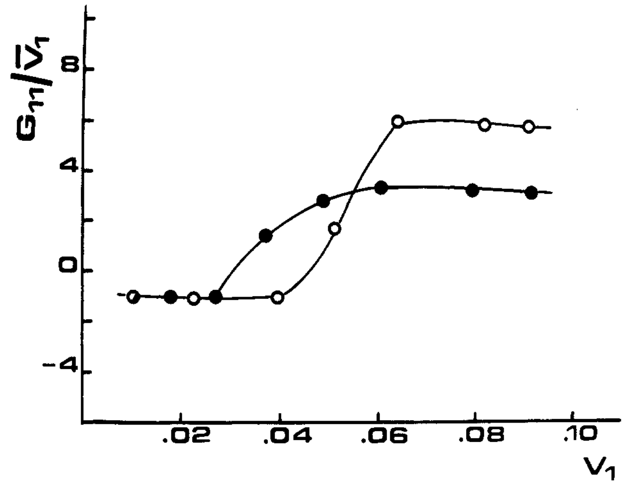

Figure 3. Cluster function $G_{11}/\bar{v}_1$ as a function of CH_2Cl_2 volume fraction v_1 for samples A (●) and D (○).

ities is reported in Table I. The quite high value indicates the lack of specific strong interactions of the penetrant with the polymer.

For sample C the χ parameter was derived from Henry's formulation

$$a_1 = v_1 \exp(1 + \chi) \qquad (3)$$

and its value, also reported in Table I, is very similar to the other cases. It is independent of the activity a_1.

The sorption mode of sample B calls for a particular attention. The negative curvature of the sorption curve, evident at activity 0.3–0.4, is generally explained with a dual sorption theory.[12,13] Sorption is visualized as a process in which there are dual modes: either the penetrant molecule is normally dissolved and is free to diffuse or it is immobilized in particular sites of the polymer matrix. This behavior is characteristic of a glassy polymer for which the particular sites are microcavities or holes entrapped in the matrix. Sample B is a very thin crystalline sample aged more than 1 yr. It is well-known that iPP undergoes a phenomenon of aging when stored at room temperature.[14-18] Struik ascribed the aging of iPP to a phenomenon of physical aging due to the amorphous chains more disturbed by the presence of the crystals.[17] The undisturbed regions have the same T_g as the atactic polymer, but that of the disturbed regions will be higher. Although this causes a distribution of T_g's in the semicrystalline polymer, the experimental results of aging can be explained by assuming the existence of an upper T_g. This is in agreement with the hypothesis of a double glass transition due to Boyer.[19] This author, analyzing many experimental results on thermal expansion and mechanical loss data, hypothesized the presence of two glasslike transitions in iPP, due the presence of different types of amorphous material. Wunderlich and Grebovicz,[20,21] studying the thermal properties of isotactic polypropylene, also found a double glass transition, with the "upper transition" occurring most prominently on slowly cooled samples stored for longer times at room temperature.

The basic property that changes during aging is the segmental mobility, and therefore an increase of the relaxation times is observed. For the well-aged sample B, the sorption behavior characteristic of a glassy polymer can be ascribed to the amorphous chains whose T_g is higher than the temperature of the experiment, becoming less and less mobile with the aging time. After activity 0.4, when the equilibrium concentration in the polymer reaches the value of 2%, the sorption curve resembles that of samples A and D at high activities: that is, we observe an increase of sorption with activity. The interaction with the solvent causes a change toward a mode of sorption which represents a preference for penetrant–penetrant pairs to be formed. Such behavior is generally observed when a particular concentration of penetrant lowers the T_g to the temperature of the experiment; the system becomes plasticized, and therefore subsequent sorption of vapor can result in the formation of solvent clusters within the polymer matrix and therefore a solubility coefficient increasing more than linearly with the activity. According to this hypothesis, we can calculate the upper T_g of the aged sample from the Kelley–Bueche equation[22] for the lowering of T_g due to the presence of the solvent, setting the T_g of the polymer after sorption of 2% of methylene chloride, as the temperature of the experiment, 298 K

$$T_{gm} = \frac{\Delta\alpha_2 v_2 T_{g2} + \alpha_1 v_1 T_{g1}}{\Delta\alpha_2 v_2 + \alpha_1 v_1} \qquad (4)$$

where α_1 is the solvent expansion coefficient ($\alpha_1 = 1.2 \times 10^{-3}$), $\Delta\alpha_2$ the change in polymer expansion coefficient at T_g, the solvent $T_{g1} = T_m - 50$ K = 126 K, and v_1 and v_2 are the volume fractions of solvent and polymer, respectively.

Using for $\Delta\alpha_2$ of iPP an average value of 4×10^{-4},[23] we find for T_g^u, a value of 45 °C, which is in very good agreement with the upper T_g reported by Boyer for samples of iPP having the same density as sample B.[19]

In order to further clarify the difference of sorption properties between the different samples, the effect of solvent clustering was analyzed, using the clustering function equation derived by Zimm and Lundberg[24]

$$G_{11}/v_1 = -v_2[\mathrm{d}(a_1/v_1)/\mathrm{d}a_1]_{P,T} - 1 \qquad (5)$$

where v_1 is the partial molecular volume, v_1 is the penetrant volume fraction, a_1 the thermodynamic activity of the penetrant, and G_{11} the cluster integral. The cluster function G_{11}/v_1 is a measure of the clustering tendency of penetrant molecules in the mixture. When the activity coefficient does not vary with the concentration, as in the case of an ideal solution, G_{11} equals $-v_1$; that is, $G_{11}/v_1 = -1$. If the solvent molecules are inclined to aggregate or to avoid one another, G_{11} assumes a large positive or a negative value, respectively. Values of the clustering function G_{11}/v_1 were calculated from the sorption of CH_2Cl_2 in isotactic polypropylene by assuming volume additivity. The volume additivity in the system iPP–methylene chloride was verified in a previous work.[8] In Figures 3 and 4 the cluster function G_{11}/v_1 is reported as a function of CH_2Cl_2 volume fraction v_1, for samples A and D (Figure 3) and samples B and C (Figure 4).

The samples A and D of different molecular weight show the same trend of the cluster function. At low penetrant activity the solution behaves ideally; that is, $G_{11}/v_1 = -1$. This means that a penetrant molecule excludes its own volume to the other molecules without affecting their distribution. When the volume fraction of penetrant is higher than 0.035 (sample A) and 0.05 (sample D), a transition in the cluster function is evident. The value of G_{11}/v_1 greater than −1, at higher concentrations, indicates that penetrant clustering is occurring. We can suggest that penetrant clustering occurs when the upper glass transition is lowered by the presence of the solvent molecules to the temperature of the experiment, that is, 298 K. Once the amorphous chains are com-

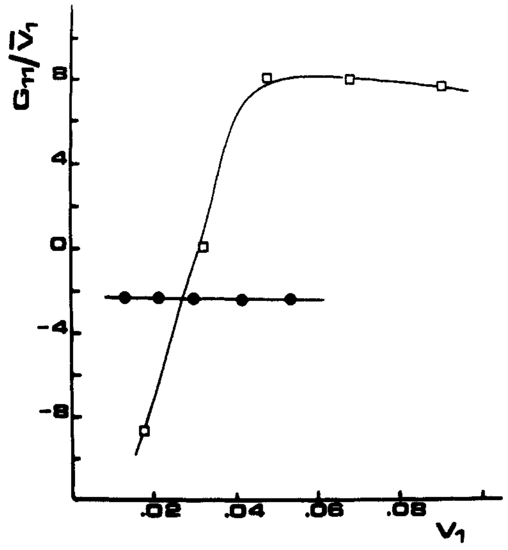

Figure 4. Cluster function $G_{11}/\bar{v}_1$ as a function of CH_2Cl_2 volume fraction v_1 for samples B (□) and C (●).

pletely plasticized and loosened, the solvent molecules are able to enter more easily in the neighborhood of the first molecules than to go elsewhere. We can calculate, according to eq 4, the upper glass transition in samples A and D. For sample A we obtain the same value as sample B; that is, $T_g{}^u$ = 45 °C. The difference in the sorption curve of these two samples is due to the aging of more than 1 yr of sample B. The aging decreases very much the mobility of the amorphous chains, and a sorption curve typical of a glassy polymer is obtained. As for sample D, a little higher value of $T_g{}^u$ is found; that is, $T_g{}^u$ = 52 °C. This higher value might be due to the higher molecular weight and a more narrow molecular weight distribution of sample D.

Also in Figure 4 the transition of the clustering function G_{11}/v_1 for sample B is evident. We observe that at lower penetrant concentrations the penetrants are sorbed at specific polymer sites as evidenced by G_{11}/v_1 values less than −1. The values of G_{11}/v_1 greater than −1, at higher concentrations, indicate again that penetrant clustering is occurring. Also in this case the attainment of the upper glass transition allows the system to behave as a plasticized polymer.

As for sample C, that is, the highly drawn sample, the cluster function has a constant value, a little smaller than −1, indicating that a penetrant molecule excludes its own volume to the other moelcules. This result agrees with the sorption curve, showing that Henry's law is followed in this case.

Conclusions

Analysis of the sorption isotherms of CH_2Cl_2 in isotactic polypropylene of different molecular weight indicates that there are two principal modes of sorption of the vapor. The first mode occurs at lower sorbed concentrations and corresponds to ideal solution. After a given activity, clustering of penetrant molecules occurs. We suggest that this phenomenon is due to the lowering of the upper glass transition of isotactic polypropylene. A higher value of $T_g{}^u$ is found for the higher and less disperse molecular weight (sample D).

The sample aged more than 1 yr shows two dominant modes of sorption: at low solvent concentration, there is penetrant localization at specific sites of the polymer matrix; at high concentration, clustering of penetrant molecules occurs. Also in this case the lowering of the upper glass transition to the temperature of the experiment allows a different mode of sorption.

The sorption curve of the highly drawn sample shows a linear dependence of sorption on activity, and the clustering function does not change in all the explored activity range. Due to the drawing process, the amorphous phase is so much constrained that it cannot be plasticized by the solvent.

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