Determination of the glass transition temperature of poly(cyclohexyl acrylate) from oxygen permeability measurements

V. Compañ*, M. L. Lopez and L. Monferrer
Department of Experimental Sciences, Universitat Jaume I, Apdo. 224, 12080 Castellón, Spain

and J. Garrido
Department of Thermodynamics, Universitat de València, 46100 Burjassot, Valencia, Spain

and E. Riande and J. San Roman
Instituto de Ciencia y Tecnología de Polimeros, CSIC, 28006 Madrid, Spain
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The glass transition temperature (T_g) of poly(cyclohexyl acrylate) (PCA) has been obtained from measurements of the oxygen permeability ($P=0.60$ barrers, $T_g=23.5\pm2.0°\mathrm{C}$) using a potentiostatic electrochemical sensor, and from the oxygen diffusion coefficient ($D=0.12\times10^{-8}\,\mathrm{cm^2\,s^{-1}}$, $T_g=24.0\pm1.8°\mathrm{C}$) by the time-lag method. A T_g of $25\pm1°\mathrm{C}$ was found by differential scanning calorimetry and a T_g of $25.0\pm3.5°\mathrm{C}$ was obtained from the specific volume by dilatometry. The fractional free volume (v_f) at T_g is 0.020 ± 0.002, which is slightly below ($\sim20\%$) most glassy polymers. A linear correlation has been observed between $\ln D$ and the reciprocal of v_f, which suggests that the polymer morphology is not influenced by the presence of oxygen. The diffusion coefficient of oxygen through PCA membranes follows Arrhenius behaviour and has an activation energy of $26\pm2\,\mathrm{kcal\,mol^{-1}}$, a surprisingly high value considering that the range of activation energies observed in most systems is 1–$20\,\mathrm{kcal\,mol^{-1}}$.

(Keywords: glass transition temperature; diffusion; membrane transport; polymer films)

INTRODUCTION

The temperature of a polymer determines to a great extent its mechanical, chemical and permeation properties. These properties undergo a great change at the glass–rubber transition temperature[1]. As a consequence, the determination of the glass transition temperature, T_g, is very important for predicting the performance of polymeric materials.

It is widely accepted that the glass transition in polymers is governed by kinetics. The studies reported in the literature clearly show this behaviour, although they have not proved conclusively whether it is a purely thermodynamic glass transition or not[2].

Glass transition in polymers has been shown by measuring different parameters, such as free volume, tensile modulus, heat capacity, dipolar correlations, permeability, refractive index, degree of crosslinking, etc. The plots of these parameters *versus* temperature exhibit discontinuities at the T_g[3–9].

The dependence of penetrant diffusion on chain dynamics becomes clear if we consider that below T_g, where the chains are frozen and only short-range motions are permitted, the value of the diffusion coefficient is severely reduced with respect to that of the diffusion coefficient above T_g.

The purpose of this paper is to determine the T_g from measurements of apparent oxygen permeability and diffusion coefficient. The result is compared to the values of T_g obtained by other techniques[2], such as specific volume measurements and differential scanning calometry (d.s.c.). We study the effect on an amorphous polymer, poly(cyclohexyl acrylate) (PCA), when it is heated and a glassy–rubbery state appears.

The free volume measurements are carried out following the usual procedure[10]. Heat capacity measurements by d.s.c.[11], and also oxygen permeability and the oxygen diffusion coefficient measurements are based on electrochemical methods with an oxygen sensor[12,13]. The results are discussed in terms of the free volume at T_g.

EXPERIMENTAL

Synthesis of cyclohexyl acrylate

Cyclohexyl acrylate was synthesized by esterification of 0.5 mol acrylic acid with 0.55 mol cyclohexanol in a solution of 100 ml dry toluene, with an equimolecular mixture. *p*-Toluenesulfonic acid (1.0×10^{-3} mol) and boric acid (1.0×10^{-3} mol) were used as catalysts. Hydroquinone (0.1 g) was used as an inhibitor of polymerization. After refluxing the reaction mixture for 5 h and the azeotropic distillation of the water of esterification, the reaction product was chromatographed through a silica gel column (Kiesegel 60, Merck) using a mixture of chloroform/heptane (75:25 v/v) eluent. The residue after evaporation of the chloroform was distilled under reduced pressure (b.p. 45°C, 0.5 mmHg) to obtain

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* To whom correspondence should be addressed

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cyclohexyl acrylate (75% yield) of 99% purity. This was characterized by i.r. (Perkin-Elmer 457) and n.m.r. spectroscopy (Bruker AM-200) using 5% deuterated chloroform solutions, and was tested by high performance liquid chromatography.

Polymerization of cyclohexyl acrylate

The cyclohexyl acrylate in benzene solution (1 mol l^{-1}) with 2,2′-azobisisobutyronitrile as initiator (1.5×10^{-2} mol l^{-1}), was placed in a Pyrex tube which was degassed under high vacuum (10^{-4} mmHg) under repeated freeze–thaw cycles and sealed. The polymerization was carried out in a thermostatic bath (60±0.5°C) for 6 h. The polymer was precipitated as white particles from its benzene solution by addition of excess of methanol. The polymer was decanted and washed repeatedly with pure methanol, and was filtered and dried under vacuum to constant weight (yield 95% by weight).

Films of PCA were cast from toluene solution (100 ml) on a Teflon plate, and the films were dried to constant weight in a desiccator under vacuum.

Oxygen permeability

The procedure for measuring the apparent oxygen permeability, P, is based on a previously described potentiostatic method: the oxygen sensor (Schema Versetae, Berkeley, USA) is covered by the polymer film which is separated from the cathode and anode by a thin layer of twice-distilled water[12–16].

The oxygen sensor cathode consists of a solid cylinder of gold (6 mm long, 4.25 mm i.d.). The anode is a hollow cylinder of silver (7 mm long, 10 mm o.d., 5 mm i.d.). Both the cathode and the anode are concentrically fixed in an epoxy resin cylinder. A constant electric potential difference (0.75 V) is maintained between the two electrodes.

The oxygen which reaches the cathode is reduced immediately as:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \qquad (1)$$

The reaction in the anode is:

$$4Ag + 4OH^- \rightarrow 4AgOH + 4e^- \qquad (2)$$

The electric current measured, I, is related to the amount of oxygen crossing the polymer film. At the steady state, I is related to P by[12,13,15]:

$$P = Dk = \frac{I(t \rightarrow \infty)L}{vFA\Delta p} \qquad (3)$$

where $L$is the polymer film thickness (0.0273 cm), v is the number of electrons transferred in the cathodic reaction, F is Faraday's constant (96 500 C mol^{-1}), A is the effective area of the membrane (same as the sensor surface, $(14.24 \pm 0.13) \times 10^{-2}$ cm^2) and $\Delta p = 155$ mmHg. The permeability, P (in barrers, 1 barrer $= 10^{-11}$ cm^3 of O_2 cm/cm^2 s mmHg) is the product of the oxygen diffusion coefficient D (cm^2 s^{-1}) and oxygen solubility coefficient k in water (Henry's law) (cm^3 STP/cm^3 mmHg).

The value of D was also determined by the time-lag method[17]:

$$D = \frac{L^2}{6\tau} \qquad (4)$$

where τ is the time lag.

To measure I as a function of time[18], the polymer film was placed on the sensor and an O-ring (10 mm i.d.) was placed over it. A vertical gas inlet tube was adjusted onto the O-ring. A small quantity (0.05 cm^3) of twice-distilled water was placed between the polymer film and the electrode. As the system was exposed to a process of deoxygenation by bubbling nitrogen through the tube, a sharp decrease in I was observed. Once the lowest intensity of current was reached, the nitrogen was substituted by atmospheric air flowing over the polymer film, and I began to increase. After 1–2 h a steady state was reached. A thermostatic bath (P Precis Term model 138) was used to maintain the system at constant temperature $t = 21$–35°C.

RESULTS AND DISCUSSION

The stereochemical composition of the PCA was determined from analysis of the ^{13}C n.m.r. spectrum of the polymer in a chloroform solution (Varian XL-300, at 75 MHz). The molar fraction of iso-, syndio- and heterotactic triads, determined from the CH and C=O signals, amounted to 0.21, 0.30 and 0.49, respectively. The number average molecular weight of the polymer determined with a Knanes high speed membrane osmometer was found to be 150 000 daltons.

Figure 1 shows the time evolution of I determined with the potentiostatic oxygen permeability cell and PCA film. Different curves are obtained for each temperature. Two types of behaviour can be distinguished in the curves shown in *Figure 1*. For temperatures of 25°C or below, I decreases with time. This expresses the impermeability of the oxygen through the polymer. For temperatures of 27°C or above, I increases until saturation. From these values, we calculated the oxygen permeability of the polymer using equation (1).

The oxygen permeability of PCA film *versus* time is shown in *Figure 2*. Non-zero values of P are fitted linearly (from 25 to 35°C). Thus we obtain:

$$P = (0.240 \pm 0.016)T - (5.2 \pm 0.5) \qquad (5)$$

The glass transition temperature ($T_g = 23.5 \pm 2.0$°C) corresponds to the intercept of two lines describing the relation between P and T.

Figure 3 shows oxygen diffusion values obtained by the time-lag method, from the measurements of I given in *Figure 1*. Linear fitting gives:

$$D = (1.13 \pm 0.07)10^{-8}T - (27 \pm 2)10^{-8} \qquad (6)$$

As for *Figure 2*, we obtained $T_g = 24.0 \pm 1.8$°C, which is in good agreement with the value obtained from the permeability results.

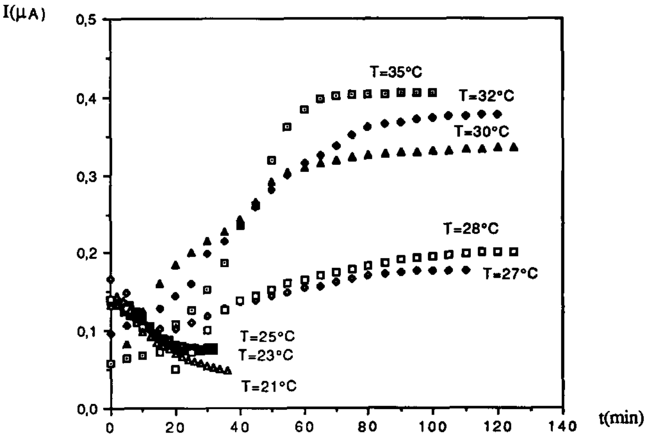

Figure 1 Electric current *versus* time in the diffusion processes

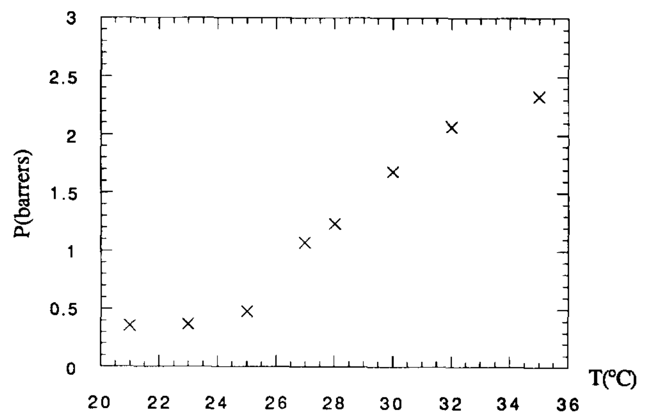

Figure 2 Apparent oxygen permeability obtained from electric current in the steady state *versus* temperature

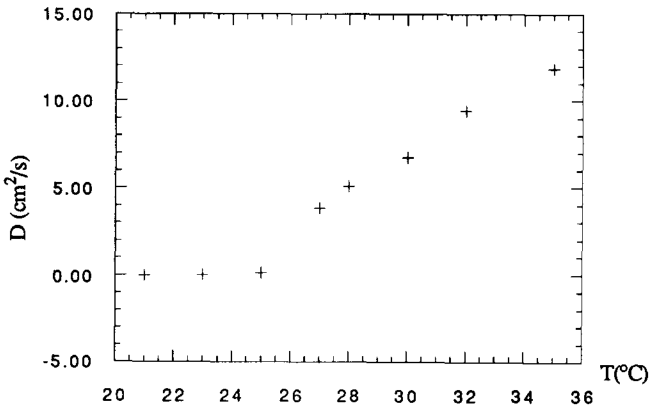

Figure 3 Diffusion coefficient obtained by time-lag method *versus* temperature

D.s.c. and free volume

The T_g of PCA obtained from P and D determined at different temperatures can be confirmed by measuring the heat capacity and the specific volume of the polymer. The heat capacity from -20 to 70°C, determined by d.s.c., is given in *Figure 4*. The polymer changes from the glassy to the rubbery state at about 25°C.

The specific volumes *versus* temperature measured by dilatometry are given in *Figure 5*. The data can be fitted to two straight lines of slopes 2.8×10^{-4} and 7.03×10^{-4} cm^3 g^{-1} °C^{-1}. The intercepts of the two straight lines is at 25.0 ± 3.5°C, which is in good agreement with the T_g obtained above.

The free-volume theory approach has proved particularly useful for a description of the effect of various factors on D in polymers above T_g through the corresponding changes in the fractional free volume of the polymer, v_f. The following empirical equation describes the change in viscoelastic properties of polymers and plasticization for the penetrant molecules above T_g[19–21]:

$$v_f = v_f(T_g) + \Delta\alpha(T - T_g) \qquad (7)$$

where $\Delta\alpha$ is the change in the thermal expansion coefficient at T_g. From *Figure 5* we have calculated these parameters for the PCA polymer: $\Delta\alpha = (4.23 \pm 0.04) \times 10^{-4}$ cm^3 g^{-1} °C^{-1} and $v_f(T_g) = 0.020 \pm 0.002$. This v_f value is about 20% below the values found for other glassy polymers[10].

Simulation techniques have been developed which permit the simulated sampling of static representative conformations of the chains in the glassy state from which v_f can be obtained[22]. These methods have been extended to evaluating D for small molecules diffusing through membranes in the rubbery state[23]. The model predicts Arrhenius behaviour for D or a linear correlation between the $\ln D$ *versus* the reciprocal of v_f. A linear correlation was found between D and the reciprocal of v_f (*Figure 6*). We may assume that this is a consequence of the great changes that take place in the amplitude of the oscillating mode with increasing temperature. It seems that once the

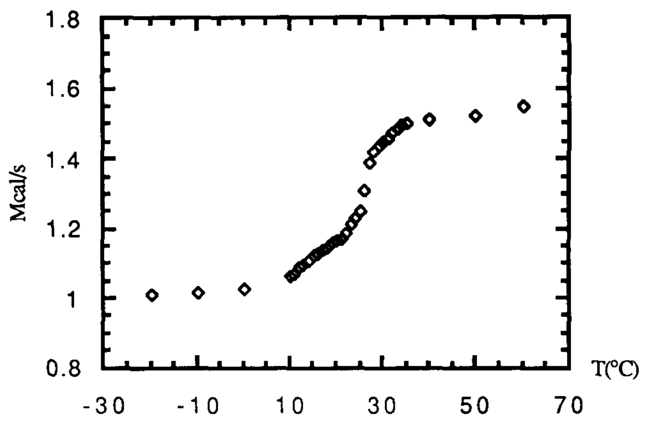

Figure 4 Heat capacity obtained by d.s.c. *versus* temperature

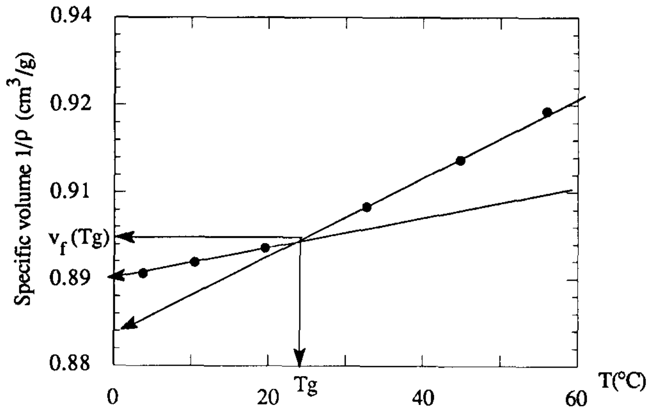

Figure 5 Specific volume obtained by dilatometry *versus* temperature

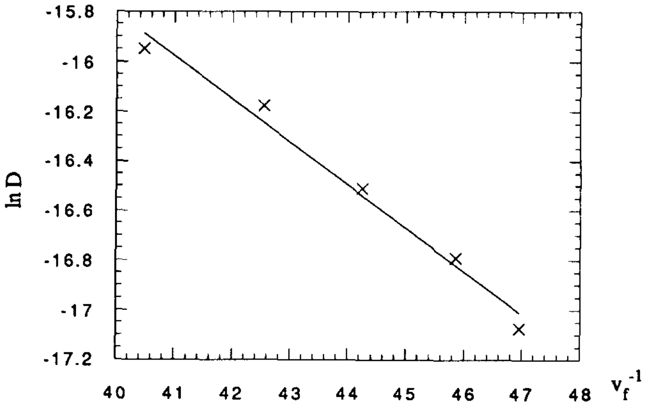

Figure 6 Correlation between the oxygen diffusion coefficient and the reciprocal of the fractional free volume. ——, $\ln D = -8.8457 +$ $-0.17388 v_f^{-1}$, correlation coefficient = 0.99128

penetrant is trapped within a hole, thermal motion of the chains is required to permit its escape. A similar behaviour has been reported for a number of systems. This suggests that the diffusivity of a given (non-interacting) gas molecule can be obtained from density measurements, because the polymer morphology is not influenced by the presence of the oxygen[23–26]. In this sense the behaviour of PCA is very similar to that of other glassy polymers. Furthermore, a molecule diffuses across a polymer provided there is enough room; the mobility will depend on the probability of finding large enough holes. This mobility is related to the diffusion coefficient and varies depending on whether the polymer is in the glassy or rubbery state. Finally, the diffusion coefficient of oxygen through PCA membranes follows Arrhenius behaviour and has an activation energy of 26 ± 2 kcal mol^{-1}, a surprisingly high value considering that the range of activation energies observed in most systems[23] is 1–20 kcal mol^{-1}.

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