

# The Effect of the Type of Purge Gas on the Solid-State Polymerization of Polyethylene Terephthalate

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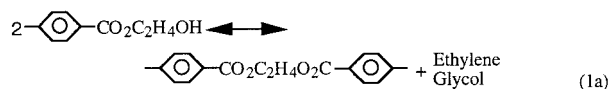
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**ABSTRACT:** Solid-state reactions of polyethylene terephthalate were conducted with various purge gases to reexamine the surprising results of Hsu.<sup>1</sup> In contrast to Hsu's work, we found that all tested purge gases (nitrogen, carbon dioxide, and helium) led to identical reaction behavior at a reaction temperature of 226°C. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* 69: 1789–1791, 1998

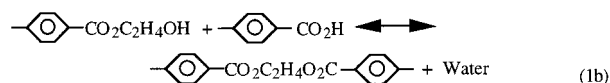
**Key words:** purge gas; solid-state polymerization; polyethylene terephthalate

## INTRODUCTION

PET (polyethylene terephthalate) is produced commercially primarily through an alcoholysis interchange reaction evolving ethylene glycol [eq. (1a)].



In addition to the alcoholysis reaction, residual carboxyl ends react with glycoyl ends producing linkages and water [eq. (1b)].



Because the equilibrium constants for eqs. (1a) and (1b) are near unity,<sup>2</sup> the concentrations of ethylene glycol and water must be reduced to low levels by mass transfer before high molecular weights can be achieved. In solid-state polymerization, ethylene glycol and water evaporate from the solid into an inert purge gas. The dilution effect of the purge gas keeps the partial pressure

of the condensates low and thereby enhances the driving force for mass transfer.

Hsu<sup>1</sup> reported that in addition to the expected dependence of the mass transfer rate upon the gas velocity, the chemical identity of the gas itself (nitrogen, carbon dioxide, and helium) also affects the final molecular weight achieved. For these three gases, Hsu reported the highest molecular weight for helium and the lowest for nitrogen. This ordering does not correspond to any physical property trends of the gases (Table I). In addition, the polymerizations were conducted at a much higher temperature than that used industrially. For these reasons, a reexamination of the purge gas effect on the polymerization rate was conducted under carefully controlled industrially relevant conditions.

## EXPERIMENTAL

### Material Preparation

PET was ground to particles that passed through a number 10 sieve and were retained on a number 12, yielding particles of approximately 1 mm in diameter.

### Equipment

The apparatus in Figure 1 was used for the polymerization. The polymer particles were supported

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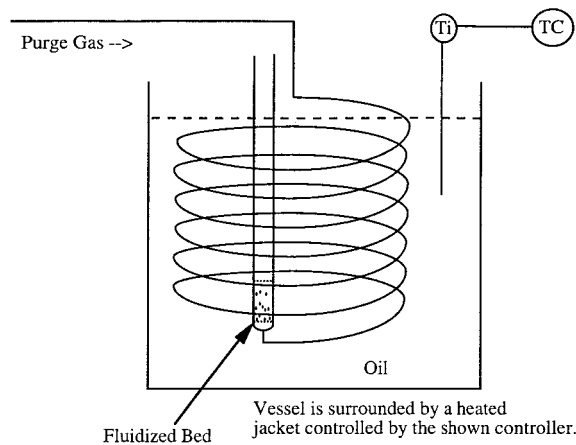
**Table I Purge Gas Properties at 500 K**

Purge Gas	Heat Capacity (J/mol/K) <sup>3</sup>	Conductivity (W/m/K) <sup>3</sup>	Thermal Diffusivity (cm <sup>2</sup> /s) <sup>3</sup>	Mass Diffusivity (cm <sup>2</sup> /s) <sup>4,5</sup>
Nitrogen	29.6	0.0386	0.535	0.43
Carbon dioxide	45.4	0.0323	0.295	0.36
Helium	20.8	0.211	4.16	1.59

on a fine screen at the bottom of the reactor tube. For particle confinement, an additional screen was added approximately  $\frac{1}{3}$  of the distance from the bottom. The top of the polymer bed was more than 10 cm below the surface of the oil bath (to avoid conduction effects). The bed radius was 0.5 cm (containing approximately 0.1 g of polymer). The polymerization vessel was immersed in a silicone oil bath at 226°C with the bath temperature controlled by a heated jacket.

### Polymerization and Analysis

To avoid polymer sticking, two precrystallization steps were conducted prior to polymerization. The reactor temperature (oil bath temperature) was raised to 120°C for 8 min, then to 180°C for 10 min, and finally to the reaction temperature (226°C) for 6 h. The purge gas rate was 3 L/min. Preliminary experiments for each purge gas showed that further increases in flow rate produced no effect. In addition, the outlet was throttled to ensure high exit vapor velocities sufficient to avoid oxygen entrance into the reactor. The molecular weight of the polymer product was determined by intrinsic viscosity in trifluoroacetic acid at 25°C.

**Figure 1** Equipment for solid-state polymerization.

### RESULTS AND DISCUSSION

In Hsu's work,<sup>1</sup> experiments were conducted in a chromatographic column. Due to the different heat capacities and thermal conductivities of the various purge gases, the gas type may affect the actual temperature, an effect seen in some preliminary experiments for this work in a Thermal Gravimetric Analyzer. By contrast, by forcing the gas to flow through a copper tube immersed in a constant temperature bath, all purge gases entered the reactor at the same temperature. Heat exchange calculations showed that the maximum deviation of the gas temperature from the oil bath temperature is expected to be less than 0.001°C.

Extrapolation to zero concentration of the dilute solution viscosities [eq. (2)] was conducted using a common Huggins constant ( $k'$ ) of 0.3262, somewhat higher than the reported value of 0.19.<sup>6</sup>

$$[\eta] = \eta_{sp}/c + k'[\eta]^2c \quad (2)$$

For the entire experiment involving both reaction and analysis, an overall experimental precision of  $\pm 0.03$  dL/g was found, corresponding to a molecular weight precision of approximately  $\pm 1500$ . From the intrinsic viscosities, the viscosity average molecular weight was calculated using the Mark-Houwink coefficients shown in eq. (3).<sup>6</sup>

$$[\eta] = 0.0014M_v^{0.64} \quad (3)$$

Table II compares the change in molecular weight for the gases with Hsu's results appended for comparison; the results represent the average of three experiments for nitrogen and two each for carbon dioxide and helium. Because the reactions were conducted at different temperatures than Hsu's work, the magnitude of the results cannot be compared. However, one would still expect to see the same trend. In the present work, polymer sticking problems did not allow operation at 250°C (and is not interesting industrially for the same

**Table II Experiments on Purge Gas Effect**

Purge Gas	Intrinsic Visc. (This Work)	Viscosity Molecular Weight (This Work)	Viscosity Molecular Weight (Hsu)
Nitrogen	1.173 dL/g	36,900	58,000
Carbon dioxide	1.169 dL/g	36,700	81,000
Helium	1.139 dL/g	35,300	90,000

Hsu reactions were at 250°C, reactions in this work at 226°C.

reason). The results of Table II show that equivalent molecular weights are achieved with the three different gases.

## CONCLUSION

The type of purge gas seems to have no significant effect on the solid-state polymerization of polyethylene terephthalate.

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