Molecular Weight Estimation by Pressure During Polymerization

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SYNOPSIS

Experimental studies for the mol wt estimation by pressure was performed with a batch polymerization of phthalic anhydride (PA) and ethylene glycol (EG). Experimental results show that the pressure in the reactor can be utilized to estimate the mol wt of products. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Unsaturated polyester resins have been used mainly as insulating and structural materials. For these uses, it is desirable to obtain low mol wt polymers with narrow mol wt distribution. In commercial processes, to realize the above conditions, polymerization is periodically stopped to measure the mol wt and its distribution. Though the condition is fulfilled by the above method, it is time consuming and, during the period of measurement, the reaction of unsaturated double bonds occurs, which produces undesirable byproducts. Thus, for the synthesis of the resins, establishment of an online method for monitoring the mol wt and its distribution in a short time was required. This article describes the results of mol wt estimation by pressure for the model system of phthalic anhydride (PA) and ethylene glycol (EG).

The following equation represents the polymerization scheme of PA and EG.
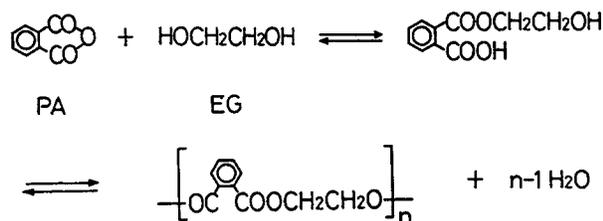
Since the industrial processes are batch processes, we examined the batch reaction. From the above equation, it is clear that in the closed batch system, removal of the water is necessary for the polymerization to proceed. Thus, during batch polymerization, the vapor of the reactor was periodically removed.

EXPERIMENTAL

Materials

The PA and EG used were industrial grade, obtained from Hitachi Kasei Co., Ltd.

Apparatus

Figure 1 shows the experimental apparatus used in the experiments. The reactor volume was 547.94 mL. The four thermocouples inserted in the reactor (numbered 1 to 4 from top to bottom, calibrated against a quartz thermometer) monitored the vertical temperature distribution in the reactor, and the temperature was controlled by the output of the lowest position thermocouples (No. 4), which monitored the temperature of the polymer solution. In the experiments RUN No. 1 and RUN No. 2, 1 mole (about 148 g) of PA and 1.1 mole (about 68 g) of EG were mixed in the reactor; in the experiments RUN No. 3 and RUN No. 4, 2 mole of PA and 2.2 mole of EG were used. The polymerization was conducted at 200°C for several hours, and the temperature regulation was within ±5°C. During the polymerization, the pressure in the reactor was measured by a pressure transducer, calibrated against a dead weight pressure gauge. Vapor phase over the polymer
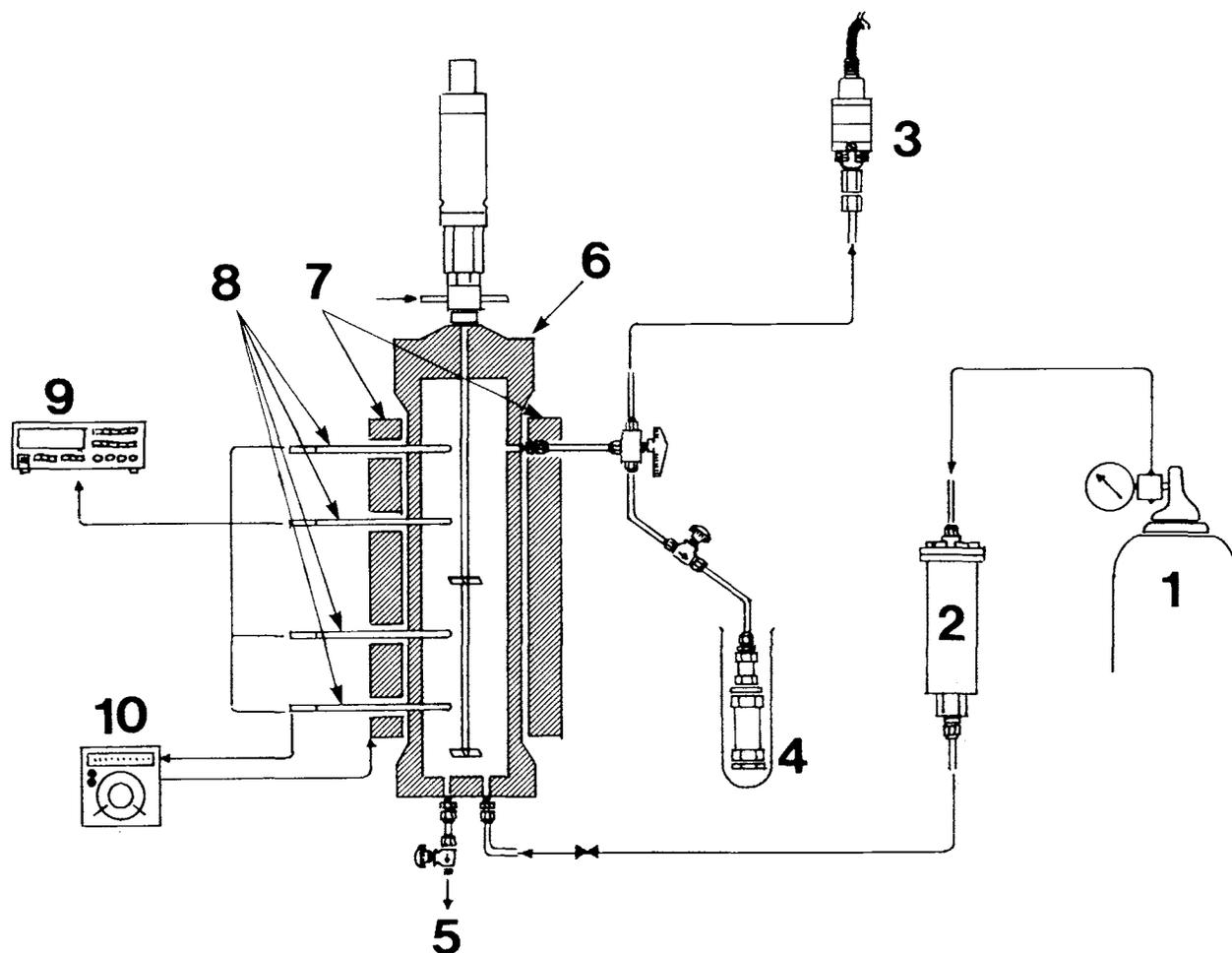
Figure 1 Schematic figure of the experimental apparatus. (1) N_2 Cylinder, (2) Reservoir, (3) Pressure Transducer, (4) Vapor Sampler, (5) Liquid Sampler, (6) Reactor, (7) Heater, (8) Thermocouples (Numbered 1 to 4 from top to bottom), (9) Digital Voltmeter, (10) Temperature Controller.

solution was periodically removed from the reactor into a condenser cooled with ice and water. At the same time, a portion of polymer solution was sampled.

Characterization

Molecular weight and its distribution of products were measured by a GPC (Hitachi L-6000; Column R-420 + R-430 + R-440; THF), equipped with an IR monitor (Hitachi L-3000). Composition of vapor was also analyzed by a gas chromatograph (Hitachi-163).

RESULTS AND DISCUSSION

Time dependence of the temperature and the pressure in the reactor is shown in Figure 2. In all the figures, downward pointing arrows indicate the time when sampling was conducted. It is obvious that the pressure decreases as a result of sampling. The temperature distribution of RUN Nos. 1 and 2 was larger than of RUN Nos. 3 and 4. This occurance would be the effect of the initial amount of monomers. That is, when the amount of the polymerizing solution was small, not enough vapor would be generated to maintain the reactor temperature distribution uniformly. In fact, in the case of RUN No. 3 and RUN No. 4, after several samples were taken, the temperature distribution inside the reactor became larger.

Typical gas chromatogram for the sampled vapor phase is shown in Figure 3, which indicates that the major part of the vapor phase became water and EG as the polymerization proceeded. The increase in the EG concentration as time progressed would be explained as follows: At the initial stage of poly-
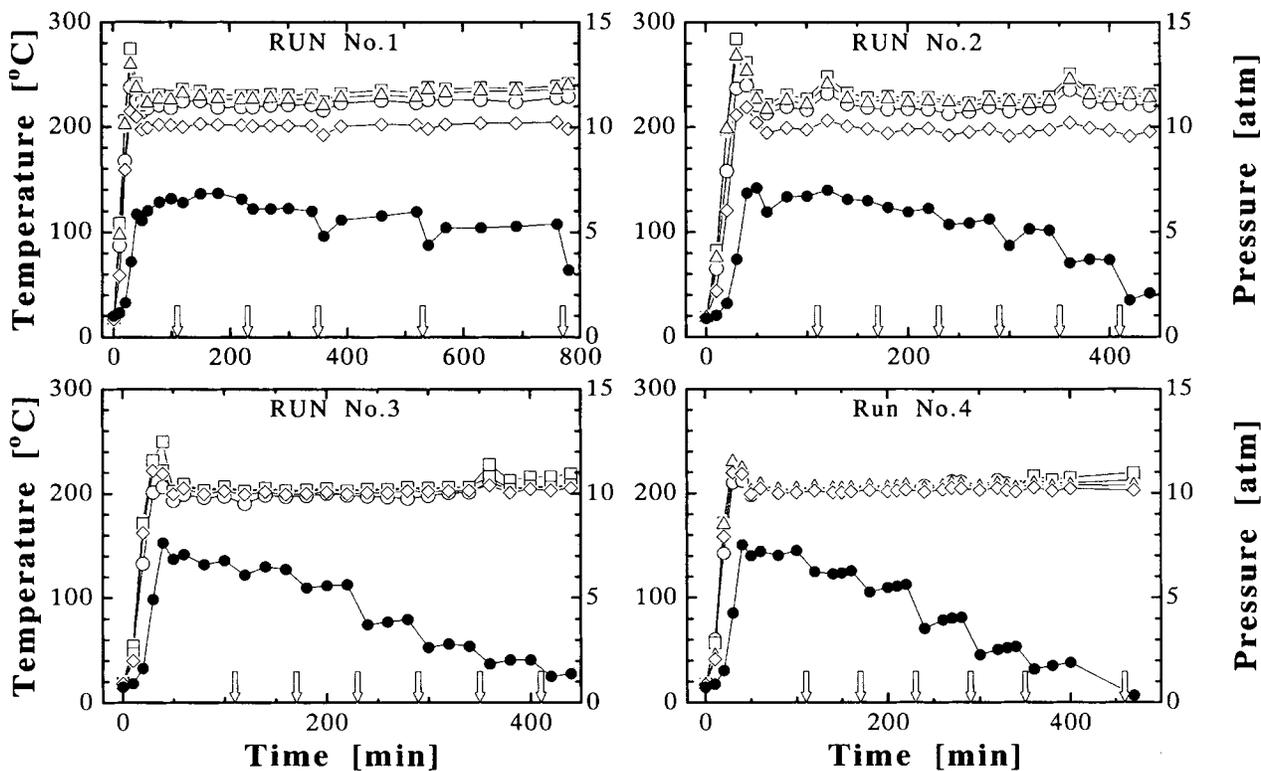
Figure 2   Time dependence of the temperature and pressure in the reactor. —O—: Thermocouples No. 1, —□—: thermocouples No. 2, —△—: thermocouples No. 3, —◇—: thermocouples No. 4, and —●—: pressure.
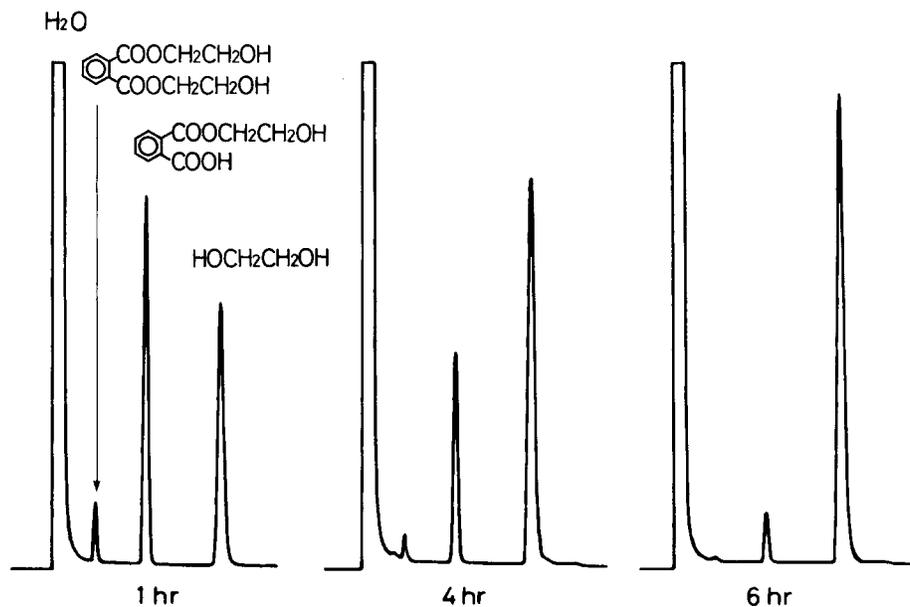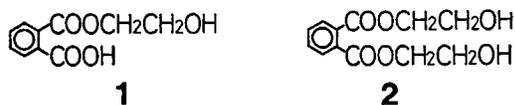

Figure 3   Typical gas chromatogram of the vapor removed from the reactor. (a) 1 h, (b) 4 h, (c) 6 h. Time in the figure refers that after the temperature had reached the experimental condition.

merization, low mol wt compounds **1** and **2**, shown below, were produced because of the excess amount of EG in the initial monomer mixtures.

COOCH2CH2OH
COOH
1

COOCH2CH2OH
COOCH2CH2OH
2

Then, as the polymerization proceeded, the compound **2** changed to **1** and the excess EG moved to the vapor phase. The figure indicates that the removal of the water could be carried out by the experimental procedure described above.

The relationship of the weight average mol wt of sampled products, with the total mass of vapor removed from the reactor, is shown in Figure 4(a). As seen from the figure, the mol wt of the products depended on the amount of vapor removed and on the initial mass of PA and EG.
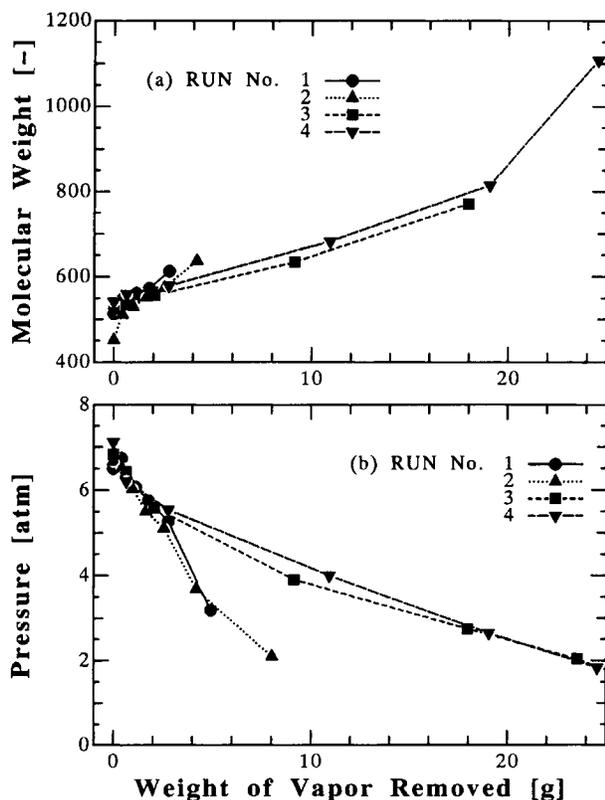

Figure 4   (a) Relationship of the weight average mol wt with the total mass of vapor removed from the reactor. (b) Relationship of the pressure with the total mass of vapor removed from the reactor.
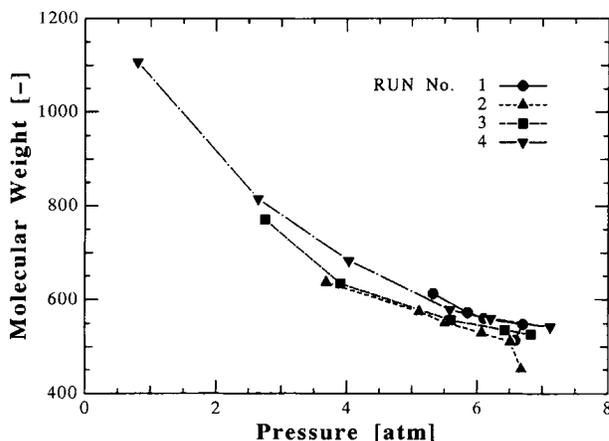

Figure 5   Pressure dependence of the weight average mol wt.

The relationship of the pressure in the reactor with the total mass of vapor removed is shown in Figure 4(b). The pressure also depended on the amount of vapor removed and on the initial amount of PA and EG.

As described above, both the mol wt and the pressure depended on the amount of vapor removed from the reactor. Thus, we plotted the weight average mol wt against the pressure in Figure 5. As can be seen from the figure, the mol wt and the pressure have a clear relationship, independent of the initial mass of monomers. This can be explained by the phase equilibria of the polymer solution. The pressure inside the reactor would be the saturated vapor pressure of polymer solution, and the saturated vapor pressure is thermodynamically determined by the mol wt of polymer and is independent of the mass of the solution.[1]

Recently, Simitzis showed that the amount of water removed from the solution is a good measure for the degree of polymerization.[2] However, our results indicate that in batch polymerization, the pressure in the reactor can be utilized as the controlling parameter for industrial operation.

REFERENCES

1. J. Simitzis, *Eur. Polym. J.,* **24**, 999 (1988).
2. P. J. Flory, *Principles of Polymer Chemistry,* Cornell University, Ithaca, New York, 1953, Chap. 12–13.