

Reaction Rate Enhancement During Swollen-State Polymerization of Poly(ethylene terephthalate)

MANOJ KUMAR PARASHAR, RAVI PRAKASH GUPTA, ANURAG JAIN, U. S. AGARWAL

Chemical Engineering Department, Indian Institute of Technology, Hauz Khas, New Delhi 110016, India

Received 6 February 1997; accepted 24 April 1997

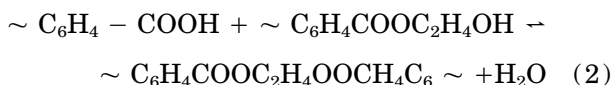
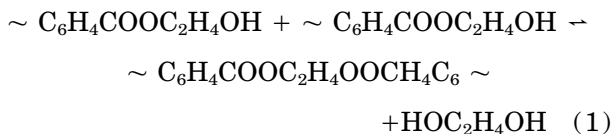
ABSTRACT: Experimental data are obtained for the extent of swelling and progress of the step-growth swollen-state polymerization (SwSP) of polyethylene terephthalate (PET). The SwSP is carried out in biphenyl and diphenyl ether mixture (26 : 74 w/w) solvent under appropriate conditions designed to understand the factors responsible for enhanced reaction rates. The kinetics rate constants, evaluated in terms of simple model, are found to be 2.5–5 times higher for SwSP as compared to the solid-state polymerization (SSP). As the diffusional/mass transfer effects are eliminated in our experiments, this increase in rate constants can be attributed to increased mobility of reactive chain ends. Polymerization rate is found to be further enhanced by addition of a polycondensation catalyst (Sb_2O_3) to the solvent during SwSP. © 1998 John Wiley & Sons, Inc. *J Appl Polym Sci* **67**: 1589–1595, 1998

Key words: poly(ethylene terephthalate); swollen-state polymerization; reaction rate enhancement

INTRODUCTION

Poly(ethylene terephthalate) (PET) is a commercially important polymer that is extensively used in the form of fibers, films, and as molding material. Its manufacture involves,¹ in the first step, the transesterification of dimethyl terephthalate with excess ethylene glycol (EG), or esterification of terephthalic acid with excess EG to form bis(hydroxyethyl) terephthalate (BHET).

In the second step, molecular weight increases as BHET undergoes polycondensation by the step-growth mechanism. During the melt polycondensation state, long chains with COOH and OH groups undergo the following reactions:



As these reactions proceed, the average molecular weight builds up. An important aspect of the reaction is the reversibility of the reaction, and, hence, the need for removal of the condensate products EG and H_2O for forward reaction to proceed. The mechanical properties of PET are strongly related to its molecular weight; and, hence, commercial applications of PET vary, depending on its molecular weight. PET of average molecular weight 15,000 to 25,000 is used in textiles applications. For injection and blow molding applications, PET with average molecular weight greater than 30,000

Correspondence to: U. S. Agarwal (uday@chemical.iitd.ernet.in).

Journal of Applied Polymer Science, Vol. 67, 1589–1595 (1998)
© 1998 John Wiley & Sons, Inc. CCC 0021-8995/98/091589-07

is required. It is produced by solid-state polymerization (SSP) of chips of PET obtained from the melt polymerization. Polymerization rates in the solid state are limited by the low diffusivity of water and EG out of the chips and by the low mobility of the reactive hydroxyl and carboxyl end groups of the polymer chains.²

A recent innovation for obtaining ultrahigh-molecular-weight (UHMW) PET is the swollen-state polymerization (SwSP).³⁻⁵ Here, the polymerization of PET chips is carried out by swelling in a suitable solvent that does not dissolve the chips. The enhanced rate of polymerization observed may be due to the increased surface area (high mass transfer rates of condensates), enhanced diffusivity of condensate molecules (enabling their easy removal), increased mobility of reactive chain ends (accelerating their col-

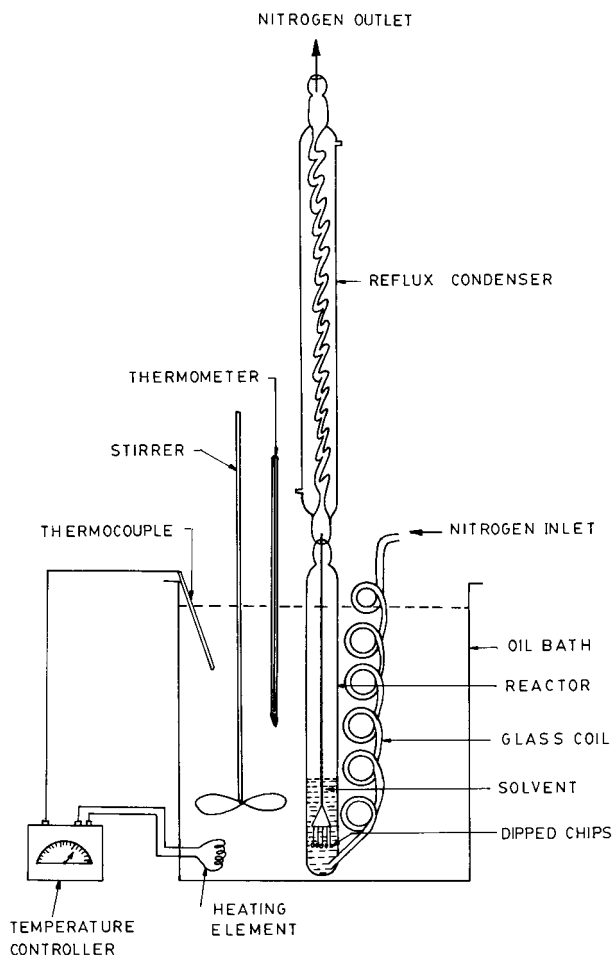


Figure 1 Experimental setup for polymerization.

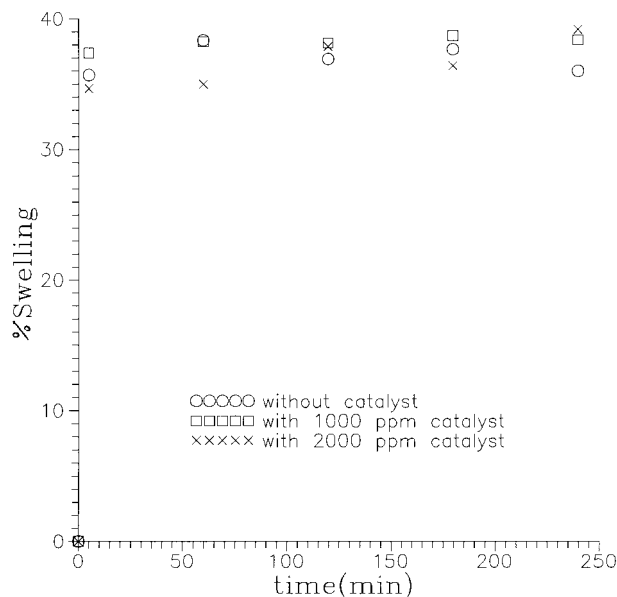


Figure 2 Percentage of swelling of PET chips in the solvent at 185°C.

lisions), and intrinsic catalytic effects of solvent presence/participation in reaction.

The only available kinetic analysis of swollen-state polymerization by Tate and Ishimaru⁴ was based on the kinetics of melt phase polycondensation of BHET given by Tomita,⁶ according to which the rate is given by

$$\frac{1}{\bar{n}} = \frac{1}{1 + k_p t} + \frac{2}{3} k_d t \quad (3)$$

where \bar{n} is the number-average degree of polymerization, k_p is a rate parameter for propagation reaction, and k_d is the rate parameter for degradation reaction. The only reaction considered for the propagation reaction was reaction (1). The following lacunae in such analyses are clear: (a) reaction (2) is ignored, (b) diffusional limitation is ignored, (c) reversible reactions are ignored without justification, and (d) the change in concentration due to swelling is not accounted.

In fact, it is not possible to judge if the faster intrinsic viscosity (*IV*) rise in SwSP is due to the increased diffusion of condensates or due to increased rate constants (which can be either due to increased mobility or due to intrinsic reactivity of the chain ends due to the presence of the solvent in the swollen polymer). Here, we report a systematic analysis of some

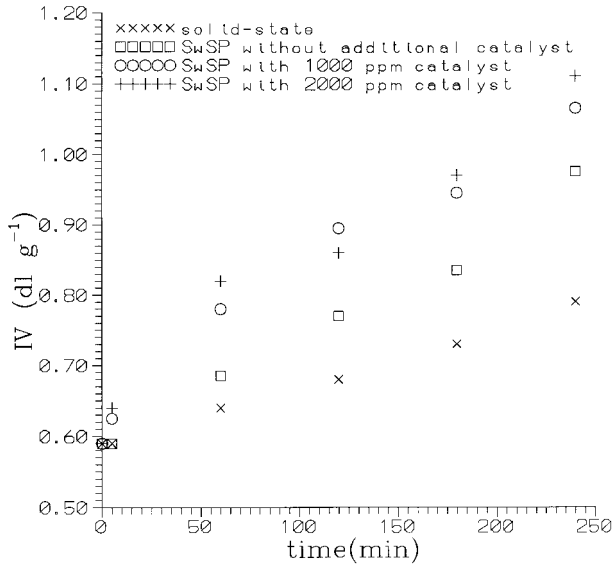


Figure 3 Increase in IV with time of polymerization at 185°C.

of these effects. For determining the true forward reaction rate constants for reactions (1) and (2), we follow the strategy of eliminating the reverse reaction by faster removal of the condensate products, EG and water. This is achieved by performing the polymerization of chips after pressing them to a disc shape of very small thickness.

REACTION KINETICS

The determination of the rate constants is done on the basis of previously reported models of SSP process.⁷⁻⁹ Only the ester interchange reaction (1) and esterification reaction (2) are considered. We assume that the diffusion of ethylene glycol and water is of the Fickian type under isothermal conditions. Further, we will carry out the polymerization under the conditions where there will be no significant change in volume of the chips during polymerization. Hence, the diffusivities of the condensates can be assumed to be constant (D_1 and D_2 for EG and water, respectively) during SwSP. For the unsteady-state diffusion process coupled with reactions, the concentration change of polymer end groups in a slab of thickness x_0 can be described by the following equations.

$$\frac{\partial g}{\partial t} = D_1 \frac{\partial^2 g}{\partial r^2} - \frac{1}{2} \left(\frac{\partial e}{\partial t} - \frac{\partial c}{\partial t} \right) \quad (4)$$

$$\frac{\partial e}{\partial t} = -2k_1 \left(e^2 - \frac{4gz}{K_1} \right) - k_2 \left(ec - \frac{2wz}{K_2} \right) \quad (5)$$

$$\frac{\partial w}{\partial t} = D_2 \frac{\partial^2 w}{\partial x^2} - \frac{\partial c}{\partial t} \quad (6)$$

$$\frac{\partial c}{\partial t} = k_2 \left(ec - \frac{2wz}{K_2} \right) \quad (7)$$

$$z = z_0 + \frac{(e_0 + c_0) - (e + c)}{2} \quad (8)$$

$$\bar{n} = \frac{2z}{e + c} \quad (9)$$

The relevant initial and boundary conditions are

$$e = e_0, \quad c = c_0, \quad g = g_0, \quad w = w_0$$

$$\text{at } t = 0, 0 < x < x_0 \quad (10)$$

$$g = g_s, \quad w = w_s \quad \text{at } t > 0, x = x_0 \text{ and } x = 0 \quad (11)$$

Here, x is the dimension along chip thickness; $e, c, z, g,$ and w are the concentrations of hydroxyl end groups, carboxyl end groups, diester groups, EG, and water, respectively; K_1 and K_2 are the equilibrium constants of ester interchange (1) and esterification (2) reactions; k_1 and k_2 are the respective forward rate constants; g_s and w_s are the concentrations of EG and water at the gas–solid interface; and the subscript zero represents the initial values.

Reaction Rate Controlling Model

During SwSP, the PET chips are dipped in solvent. The solvent (and, hence, the chip surface) is maintained free of EG and water by continuously bubbling nitrogen. If the chips are pressed into a disc shape of small thickness (that is, $x_0 \ll \sqrt{\frac{D}{kC}}$; see Ravindranath and Mashelkar⁹) as we

do here, then diffusion resistance to water and EG is negligible; and their concentration in the chip can be assumed to be zero.^{2,9-12} Further, the reverse reactions for which H_2O and EG are reactants are negligible. The kinetic equations now simply reduce⁷ to

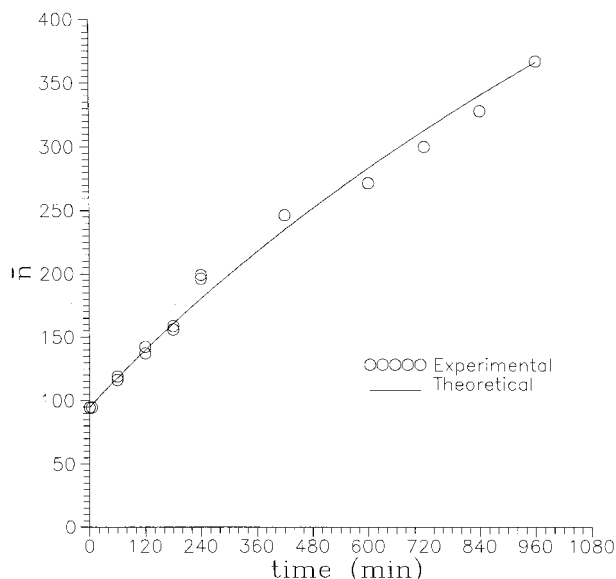


Figure 4 Increase in \bar{n} with time for SwSP at 185°C without an additional catalyst.

$$\frac{\partial e}{\partial t} = -2k_1e^2 - k_2ec \quad (12)$$

$$\frac{\partial c}{\partial t} = -k_2ec \quad (13)$$

with initial conditions at $t = 0$ being

$$c = c_o, \quad z = z_o = \frac{\rho_{sw}}{192},$$

$$\bar{n} = \bar{n}_o, \quad e = e_o = \frac{2z_o}{\bar{n}_o} - c_o \quad (14)$$

where ρ_{sw} is the mass concentration of polymer in the swollen chips. For any assumed values of the rate constants k_1 and k_2 , these two coupled differential equations are solved using Runge–Kutta, Gill technique to give the values of e and c at any desired time of reaction. If $\bar{n}(t_i)$ is the calculated value of \bar{n} at time t_i , and $\bar{n}_e(t_i)$ is the corresponding experimental observed values, the error corresponding to the assumed values of k_1 and k_2 can be represented as

$$E(k_1, k_2) = \frac{\sum_{i=1}^p \left(\frac{\bar{n}_e(t_i) - \bar{n}(t_i)}{\bar{n}(t_i)} \right)^2}{p} \quad (15)$$

where p is the number of experimental data points

in a single experiment. k_1 and k_2 values, giving minimum error $E(k_1, k_2)$, are taken as the best fit values of k_1 and k_2 .

EXPERIMENTAL

Reagents

Cylindrical PET chips (average weight ≈ 0.017 g) of intrinsic viscosity $IV = 0.59$ dL g⁻¹, $\bar{n}_o = 94.45$, and carboxyl group concentration $c_o = 26 \times 10^{-6}$ mol g⁻¹ were obtained from Garware Polyester Ltd. (Aurangabad). The chips were flattened to a thickness of 0.15–0.2 mm by pressing between two heated stainless steel plates at 140°C for 15 s. These pressed chips were then dried by heating in vacuum at 120°C for 1 h. Biphenyl (BDH Chemicals Ltd., U.K.) is dried under vacuum for 2 h. Diphenyl ether (PYE-KEM Laboratories, Delhi) is purified¹³ by vacuum distillation over anhydrous calcium chloride and stored over molecular sieves (5X type, BDH Chemicals Ltd.). Biphenyl and diphenyl ether are mixed in the ratio of 26 : 74 w/w and used as the solvent for SwSP. Polycondensation catalyst antimony oxide (Sb₂O₃) was obtained from a user industry. Nitrogen (IOLAR-II grade, moisture < 4 ppm) was obtained from Indian Oxygen Limited.

Swollen-State Polymerization

As shown in the Figure 1, the reaction apparatus used here is a 20 cm long glass tube of diameter 3 cm fitted with a helical coil for bubbling nitrogen (1 L min⁻¹) to remove the condensates. The tube is dipped into an oil bath maintained at desired reaction temperature. The helical coil allows sufficient time for heating the incoming nitrogen to the bath temperature before being bubbled. The reactor is connected to a reflux condenser to reflux back the solvent entrained with nitrogen.

Pressed PET chips are hung independently from metallic wires and then dipped into the solvent maintained at reaction temperature. At each designated time of reaction, four chips are withdrawn with the help of the metallic wires. Their surface is cleaned with filter paper to remove the excess solvent at the surface and then weighed. The swollen PET chips are now dried under vacuum for 2–3 h at 140°C to remove all the solvent and then weighed again. The average swelling is determined by measuring the weights of the swol-

Table I Rate Constants ($1 \text{ mol}^{-1} \text{ min}^{-1}$) for Polymerization at 185°C

Rate Constant	Solid-State Polymerization	Swollen-State Polymerization		
		Without Catalyst	With Catalyst	
			1000 ppm	2000 ppm
k_1	0.0106	0.0265	0.0540	0.0589
k_2	0.0052	0.0180	0.0198	0.0180

len and the dried polymer. The IV of PET chips is measured by using an Ubbelohde viscometer at 30°C in a mixture of phenol and 1,1,2,2-tetrachloroethane (60 : 40, v/v). The number-average molecular weight $\bar{M}_n = 192 \bar{n}$ is determined using the following equation⁴:

$$IV = 7.5 \times 10^{-4} (\bar{M}_n)^{0.68} \quad (16)$$

Swollen-State Polymerization with Additional Catalyst

In order to evaluate the effect of polycondensation catalyst (Sb_2O_3) on SwSP, experiments were carried out by adding the catalyst to the swelling medium (solvent) just before dipping the pressed chips in the solvent at 185°C . Though the catalyst is not completely soluble in the solvent, the nitrogen bubbling keeps the excess catalyst in suspension. It is envisaged that the catalyst would diffuse into the swollen chips and enhance the polymerization rates. Experiments were carried out with catalyst concentrations of 1000 and 2000 ppm (based on solvent). As compared to the method of Kokkalas et al.¹⁴ for catalyst-assisted solid-state polymerization, the present method in SwSP has the advantage in case of SwSP of eliminating the need of melting the PET chips to mix the catalyst.

Solid-State Polymerization

To evaluate the efficiency of swollen-state polymerization in enhancing the reaction rates, the polymerization of the pressed chips was also carried out under identical conditions but in the solid-state in absence of the solvent.

RESULTS AND DISCUSSION

The rate constants k_1 and k_2 may be dependent on the reactive chain end mobility, which, as well

as the condensate diffusivities, may depend on the extent of swelling during SwSP. If the extent of swelling changes during the reaction, then the condensate diffusivities and reaction rate constants keep changing, making the determination of the kinetics difficult. Further, the concentration of the reactants will also be continuously affected by continuous change in swelling. Thus, it is desirable that the extent of swelling is maintained constant during a polymerization experiment.

We found that at the desired reaction temperature, the maximum swelling is attained rapidly (within 2 min) before significant extent of reaction can take place, and then no more change in swelling takes place during most of the reaction period (Fig. 2). Here, % swelling is defined as weight of solvent uptake as fraction of final dry weight of chips. We found that the % swelling was 35 and 49, and the weight loss (dissolution) was low (4 and 8%, respectively) for reaction at 185 and 190°C .

For polymerization at 185°C , the experimental results for rise in IV with time for SSP and SwSP (with and without additional catalyst) are plotted in Figure 3. The experimental and the best-fit results for the SwSP without additional catalyst are presented in Figure 4. The best-fit k_1 and k_2 values are presented in Table I. Table I also presents the best-fit rate constants values for SSP and SwSP (with additional catalyst). We find that values of k_1 and k_2 are 2.5–3 times higher for SwSP (without additional catalyst) compared to SSP at same temperature. Further examination of Table I shows that the ester interchange rate constant k_1 is about two times higher in the presence of additional Sb_2O_3 catalyst, as compared to the situation without additional Sb_2O_3 catalyst. However, the esterification rate constant k_2 is not affected significantly by the addition of Sb_2O_3 . This is because Sb_2O_3 is a catalyst for ester interchange reaction

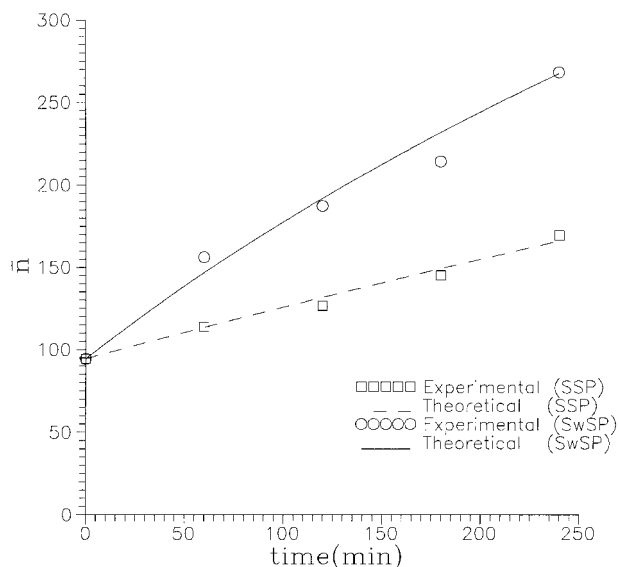


Figure 5 Increase in \bar{n} with time for polymerization at 190°C.

(1) only.¹⁴ Again, as seen in Figure 3, increasing the additional Sb_2O_3 concentration from 1000 to 2000 ppm in the solvent does not affect the kinetics significantly. This is also seen in comparison of the best fit rate constants values for 1000 and 2000 ppm catalyzed SwSP cases. This is expected since Sb_2O_3 acts as a catalyst and is not consumed in the reaction; hence, its concentration in excess of certain value does not further enhance the reaction rate.

Similarly, results for SSP and SwSP (without catalyst) at 190°C are plotted in Figure 5. Again, as seen in Table II, we find that the rate constants are four to five times higher for SwSP as compared to SSP.

As the condensate diffusional effects are absent in the above experiments, the observed enhancement in polymerization rate constants by a factor of 2.5 to 5 for SwSP, as compared to SSP at 185–190°C, can be attributed to the increase in chain end mobility or the enhancement in intrinsic reactivity due to presence of solvent.

As both k_1 and k_2 are higher during SwSP, it is not likely that this enhancement is due to the action of the solvent in enhancing the intrinsic reactivity since the same solvent is not likely to have a catalytic effect on both the reactions. Thus, the indications are that the rate constant enhancement during SwSP is due to enhanced mobility of chain ends. This is further supported by the following experiment.

Table II Rate Constants ($1 \text{ mol}^{-1} \text{ min}^{-1}$) for Polymerization at 190°C

Rate Constant	Solid-State Polymerization	Swollen-State Polymerization without Catalyst
k_1	0.0150	0.0700
k_2	0.0113	0.0390

The pressed PET chips are first swollen at 190°C for 2 min to % swelling equal to 49. Then, SwSP of these chips is carried out at 185°C, during which the swelling is found not to change from 49%.¹⁵ These polymerization results are compared in Figure 6 with the results for direct SwSP at 185°C (% swelling is equal to 35). We notice that the reaction rate is higher when the % swelling is higher. The solvent is present in high concentration in both the cases. Therefore, it is unlikely that any catalytic action (if present at all) of the solvent will be enhanced if its concentration is increased in the present range. Hence, we feel that the observed rate enhancement seen in Figure 6 is due to the increased chain end mobility at higher swelling.

CONCLUSIONS

We have examined the kinetics of step-growth polymerization of PET in a solvent. As compared to the

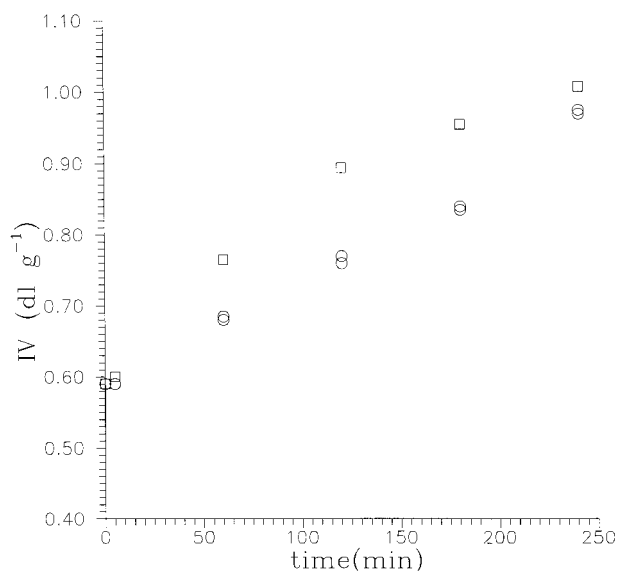


Figure 6 Increase in IV with time for (○) direct SwSP at 185°C (% swelling equals 35) and (□) initial % swelling equals 49 at 190°C for 2 minutes, followed by SwSP at 185°C.

conventional solid-state polymerization, the advantages can be (1) the faster removal of the condensates (due to enhanced diffusional and mass transfer reaction rates) and (2) the enhanced reactivity/mobility of reactive chain ends, resulting in faster polymerization. Here, we have carried out polymerization under conditions where diffusional and mass transfer limitations are eliminated, thereby allowing examination of the effect of solvent on chain end reactivity/mobility. The solvent used is a mixture of biphenyl and diphenyl ether (26 : 74 w/w). For 185°C polymerization of PET of $IV = 0.59 \text{ dL g}^{-1}$, the IV increased to 0.98 dL g^{-1} in 4 h during SwSP; while for SSP, it increased only to 0.8 dL g^{-1} . The kinetics results have been evaluated in terms of the simple models. The kinetic constants of the main reactions are found to be 2.5–5 times higher in the swollen-state as compared to the solid-state polymerization due to increased chain end mobility. Further, addition of a suitable catalyst antimony oxide to the solvent during the swollen-state polymerization is found to further enhance the ester interchange rate constant k_1 .

While these are the only effects visible in polymerization of thin samples, the enhancement in overall reaction rates may be even more in case of thicker samples where the reduced diffusional limitations are also likely to contribute. These effects will be analyzed in a future work.

REFERENCES

1. K. Ravindranath and R. A. Mashelkar, *Chem. Eng. Sci.*, **41**, 2197 (1986).
2. S. Chen and F. Chen, *J. Polym. Sci., Polym. Chem. Ed.*, **25**, 533 (1987).
3. A. L. C. Burke, G. Marier, and J. M. DeSimone, *Polym. Mater. Sci. Eng.*, **74**, 248 (1996).
4. S. Tate and F. Ishimaru, *Polymer*, **36**, 353 (1995).
5. S. Tate, Y. Watanabe, and A. Chiba, *Polymer*, **34**, 4974 (1993).
6. K. Tomita, *Polymer*, **14**, 50 (1973).
7. T. Zhi-Lian, Q. Gao, H. Nan-Xun, and C. Sironi, *J. Appl. Polym. Sci.*, **57**, 473 (1995).
8. I. Devotta and R. A. Mashelkar, *Chem. Eng. Sci.*, **49**, 1859 (1993).
9. K. Ravindranath and R. A. Mashelkar, *J. Appl. Polym. Sci.*, **39**, 2969 (1990).
10. S. Cheng, M. F. Sheu, and S. M. Chen, *J. Appl. Polym. Sci.*, **28**, 3289 (1983).
11. T. M. Chang, *Polym. Eng. Sci.*, **10**, 364 (1970).
12. F. C. Chen, R. G. Griskey, and G. H. Beyer, *AIChE J.*, **15**, 680 (1969).
13. D. D. Perrin and W. L. F. Armarego, *Purification of Organic Chemicals*, 3rd ed., Pergamon, U.K., 1993.
14. D. Kokkalas, D. Bikiaris, and G. Karyannidis, *J. Appl. Polym. Sci.*, **55**, 787 (1995).
15. J. S. Vrentas and C. M. Vrentas, *Macromol.*, **29**, 4391 (1996).