

Molecular Weight Evaluation of Depolymerized Poly(ethylene terephthalate) Using Intrinsic Viscosity

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ABSTRACT: A series of poly(ethylene terephthalate) (PET) depolymerization experiments versus time was proceeded under optimal experimental conditions with microwave radiation, in which the temperature was 220°C, the pressure was 200 psi, the microwave power was 260 W, and the ratio of water to PET was 10 : 1. The relative viscosity of the feedstock PET grain and the residual solid products from depolymerization reaction at six different time, respectively, was measured in the solution of 60/40 (w/w) phenol/1,1,2,2-tetrachloroethane. Then the approximate intrinsic viscosity was calculated from linear and exponential extrapolation of reduced viscosity. Molecular weights were calculated by Mark-Houwink's equation,

with values of K and α taken from the literatures. The results show that the molecular weights fell dramatically with increasing of reaction time, namely the number average molecular weight from 2.57×10^4 of the feedstock PET to 372 of the remained solid product at 240 min, and the weight average molecular weight of the samples fell from 3.89×10^4 to 408 correspondingly. The intrinsic viscosity decreased greatly with reaction, while the distribution of molecular weight turned to be steady. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 109: 1294–1297, 2008

Key words: polyesters; degradation; viscosity; molecular weight distribution

INTRODUCTION

Determination of the molecular weight using intrinsic viscosity was a simple and inexpensive method, and widely used to determine the molecular weight of polymer, glucose, and cellulose.^{1–5} However, it was seldom used to determine the average molecular weight of poly(ethylene terephthalate) (PET),⁶ especially the molecular weight of the residual solid product from the depolymerization reaction of PET.

Viscosity depends on molecular weight distribution, pressure, temperature, and concentration. When the pressure and temperature are fixed, viscosity could be determined from a series of experiments versus concentration. In this article, the experiments were carried out at 25°C and 1 atm, and intrinsic viscosity was calculated from linear and exponential extrapolation to evaluate the molecular weight.

EXPERIMENTAL

Chemicals

Pure PET grain was obtained in the form of fiber-grade commercial chips supplied by LiaoYang Petrol Chemical Fiber Corp. (LiaoYang City, PRC). Six types of remained solid depolymerized product were obtained at 90, 120, 150, 180, 210, and 240 min, respectively, through microwave depolymerization reaction (using the discover system of CEM Corporation, Matthews, NC). Phenol and 1,1,2,2-tetrachloroethane used were of analytical grade.

Viscosity measurements

Phenol and 1,1,2,2-tetrachloroethane solution with weight ratio of 60/40 were carefully prepared. A clearly washed Ubbelohde type of capillary viscometer was used for the viscosity measurements, and flow time measurements were conducted with an equipped stopwatch. The solution of the feedstock PET grain and residual solid products at 90, 120, 150, 180, and 210 min were prepared with precisely weighted 0.10 g ground product and 25.00 mL solvent. The solution of the one at 240 min was prepared with precisely weighted 0.05 g product and 25.00 mL solvent, because of poor solvency. And each sample was measured with four different concentration, as for each concentration, the

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measurement was repeated at least three times to make sure the accuracy of the results.

RESULTS AND DISCUSSIONS

Determination of intrinsic viscosity

Relative viscosity (η_r), inherent viscosity (η_{inh}), specific viscosity (η_{sp}), and the intrinsic viscosity ($[\eta]$) of the solution could be determined by the flow time of the corresponding polymer solution and the pure solvent mixture using the following equations:

$$\eta_r = t/t_0 \quad (1)$$

$$\eta_{inh} = \ln \eta_r / C \quad (2)$$

TABLE I
Intrinsic Viscosity Measurement of PET Sample Obtained at Different Reaction Time

	Values of corresponding parameters				
	0.00 ^a	0.40 ^a	0.27 ^a	0.20 ^a	0.16 ^a
PET grain					
Flow time	78.12	100.07	92.34	88.51	86.23
η_r	1	1.281	1.182	1.133	1.104
$\ln \eta_r / C$	–	0.619	0.619	0.624	0.618
η_{sp}	0	0.281	0.182	0.133	0.104
η_{sp} / C	–	0.702	0.674	0.666	0.650
90 min					
Flow time	78.12	82.23	80.66	79.92	79.45
η_r	1	1.053	1.033	1.023	1.017
$\ln \eta_r / C$	–	0.129	0.120	0.114	0.105
η_{sp}	0	0.053	0.033	0.023	0.017
η_{sp} / C	–	0.133	0.122	0.115	0.106
120 min					
Flow time	78.12	81.40	80.15	79.45	79.14
η_r	1	1.042	1.026	1.017	0.013
$\ln \eta_r / C$	–	0.103	0.095	0.084	0.081
η_{sp}	0	0.042	0.026	0.017	0.013
η_{sp} / C	–	0.105	0.094	0.085	0.082
150 min					
Flow time	78.12	81.32	80.07	79.45	79.06
η_r	1	1.041	1.025	1.017	1.012
$\ln \eta_r / C$	–	0.100	0.091	0.084	0.075
η_{sp}	0	0.041	0.025	0.017	0.012
η_{sp} / C	–	0.101	0.091	0.084	0.074
180 min					
flow time	78.12	81.01	79.76	79.21	78.90
η_r	1	1.037	1.021	1.014	1.010
$\ln \eta_r / C$	–	0.091	0.077	0.070	0.062
η_{sp}	0	0.037	0.021	0.014	0.010
$\ln \eta_{sp} / C$	–	0.093	0.079	0.070	0.063
210 min					
Flow time	78.12	80.39	79.37	78.98	78.67
η_r	1	1.029	1.016	1.011	1.007
$\ln \eta_r / C$	–	0.071	0.059	0.055	0.044
η_{sp}	0	0.029	0.016	0.011	0.007
$\ln \eta_{sp} / C$	–	0.073	0.060	0.055	0.044

The measurement was carried out at 25°C and 1 atm.
^aConcentration of the remained solid product (g/dL).

TABLE II
Intrinsic Viscosity Measurement of Remained Solid Depolymerized Sample at 240 min

	Value of corresponding parameters				
	0.00 ^a	0.20 ^a	0.14 ^a	0.10 ^a	0.08 ^a
Flow time	78.12	78.82	78.48	78.35	78.28
η_r	1	1.009	1.005	1.003	1.002
$\ln \eta_r / C$	–	0.089	0.071	0.060	0.050
η_{sp}	0	0.009	0.005	0.003	0.002
η_{sp} / C	–	0.090	0.072	0.060	0.052

The measurement was carried out 25°C and 1 atm.
^aConcentration of the remained solid product (g/dL).

$$\eta_{sp} = \eta_r - 1 = t/t_0 - 1 \quad (3)$$

$$[\eta] = \lim_{c \rightarrow 0} \eta_{sp} / C \quad (4)$$

where t_0 (s) was the flow time of pure solvent mixture, t (s) was the flow time of the polymer solution, and c (g/dL) was the concentration of the polymer solution. The results of the measurement were calculated and listed in Tables I–III.

The values of intrinsic viscosity could be determined from Figures 1 and 2 by linear and exponential extrapolation. When $c = 0$, the value of η_{sp} / C approximately amounted to $[\eta]$ which was shown in Eq. (4). The value of the feedstock PET grain and the six samples was, respectively, 0.621, 0.092 at 90 min, 0.066 at 120 min, 0.061 at 150 min, 0.045 at 180 min, 0.029 at 210 min, and 0.028 dL/g at 240 min. It could be seen that the value of intrinsic viscosity becomes smaller and smaller with the increasing of reaction time, especially at the first 90 min, the value fell dramatically, and when the reaction time reached 210 min the value fell even more slowly and it began to turn to be steady. Meanwhile, it can be seen from Figures 1 and 2 that Huggins coefficient decreased obviously from the beginning to the reaction time of 90 min, and then it began to increase steadily from the reaction time of 120–240 min. The fact was led by the critical concentration, which was affected by the length of molecule chain. With the increasing of

TABLE III
 η_{sp} / C of Residual Solid Depolymerized Product at Different Time Versus Concentration

Reaction time (min)	η_{sp} / C			
	0.40 ^a	0.27 ^a	0.20 ^a	0.16 ^a
0	0.702	0.674	0.666	0.650
90	0.133	0.122	0.115	0.106
120	0.105	0.094	0.085	0.082
150	0.101	0.091	0.084	0.074
180	0.093	0.079	0.070	0.063
210	0.073	0.060	0.055	0.044

^aConcentration of the remained solid product (g/dL).

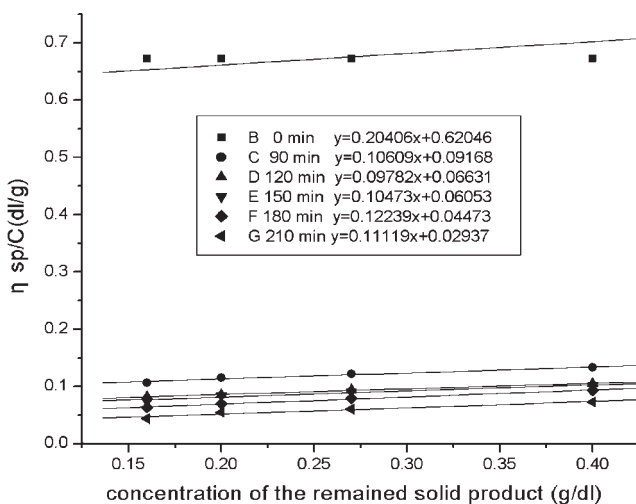


Figure 1 η_{sp}/C of the remained solid depolymerized product at different time versus concentration.

reaction time, the molecule chain reduced distinctly, then it easily reached the critical concentration, and the interaction between molecule chain became stronger and stronger, all of which led to the change.

Evaluation of the molecular weight

According to the Mark–Houwink equation [Eq. (5)], the viscosity average molecular weight could be determined possibly⁷ by virtue of the values described earlier.

$$[\eta] = KM^\alpha \quad (5)$$

where the values of K and α were specific when the conditions were fixed, which could be found in the literatures.^{6,8,9} For the condition such as PET/60/40 (w/w) phenol/1,1,2,2-tetrachloroethane at 25°C,

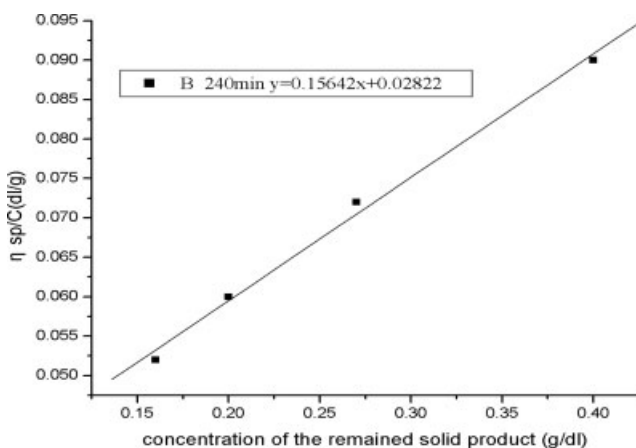


Figure 2 Intrinsic viscosity measurement of remained solid depolymerized product at 240 min.

TABLE IV
Average Molecular Weight Distribution of PET Versus Time

Reaction time (min)	$[\eta]$ (dL/g)	$\overline{(M_n)}$ ($\times 10^4$)	$\overline{(M_w)}$ ($\times 10^4$)	$\overline{(M_n)}/\overline{(M_w)}$
0	0.62	2.57	3.89	1.51
90	0.092	0.19	0.23	1.23
120	0.066	0.12	0.14	1.20
150	0.061	0.11	0.13	1.20
180	0.045	0.071	0.083	1.18
210	0.029	0.039	0.044	1.12
240	0.028	0.037	0.041	1.10

the following equations can also be found in these literatures.

$$[\eta] = 3.72 \times 10^{-4} \overline{(M_n)}^{0.73} \quad (6)$$

$$[\eta] = 4.68 \times 10^{-4} \overline{(M_w)}^{0.68} \quad (7)$$

So the values of number average molecular weight ($\overline{(M_n)}$) and weight average molecular weight ($\overline{(M_w)}$) of the samples at each reaction time could be calculated from the two equations above and the results were shown in Table IV.

CONCLUSIONS

The results showed that the molecular weights fell dramatically with the increasing of reaction time, namely the number average molecular weight fell from 2.57×10^4 of the feedstock PET to 372 of the remained solid product at 240 min, and the weight average molecular weight of the samples fell from 3.89×10^4 to 408 correspondingly. The intrinsic viscosity decreased greatly with reaction time, while

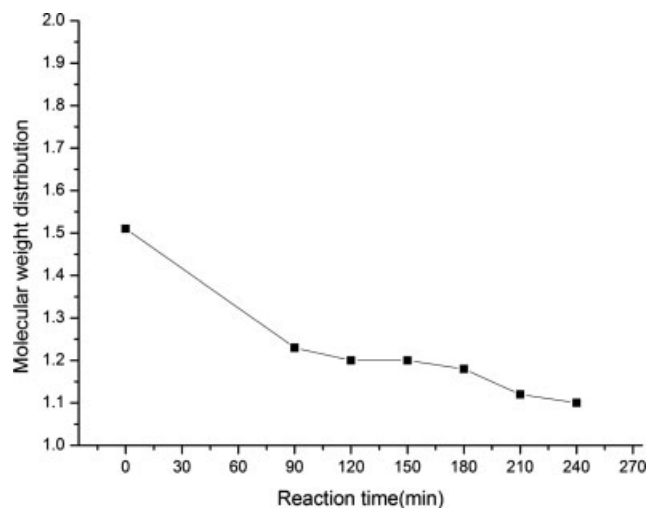


Figure 3 Molecular weight distribution versus reaction time.

the distribution of molecular weight turned to be steady (as shown in Fig. 3). Moreover, PET could be effectively depolymerized to lower molecular resins and radical materials within optimal reaction time, which could be important for experiments, especially for industrial production.

References

1. Nishida, K.; Kaji, K.; Kanaya, T.; Fanjat, N. *Polymer* 2002, 43, 1295.
2. Burkus, Z.; Temelli, F. *Carbohydr Polym* 2003, 54, 51.
3. Yang, D.; Adams, P. N.; Mattes, B. R. *Synth Metals* 2001, 119, 301.
4. Togrul, H.; Arslan, N. *Carbohydr Polym* 2003, 54, 63.
5. Vega, M. P.; Lima, E. L.; Pinto, J. C. *Polymer* 2001, 42, 3909.
6. Sanches, N. B.; Dias, M. L.; Pacheco, E. B. A. V. *Polym Test* 2005, 24, 688.
7. Kurata, M.; Tsunashima, Y.; Iwama, M.; Kamada, K. In *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; Wiley: New York, 1975; p IV-1.
8. Fakirov, S. In *Handbook of Thermoplastics*; Olabisi, O., ed.; Marcel Dekker: New York, 1994; p 451.
9. Jabarin, S. A. *J Appl Polym Sci* 1987, 34, 85.