

Selectivity of Shear Rate on Chains in Polymer Combination Reaction

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ABSTRACT: The combination reaction of linear low density polyethylene initiated by Dicumyl peroxide at elevated temperature was investigated under different steady shear rates. Gel-permeation chromatography was used to determine the molecular weight distributions, and time-molecular weight superposition method was used to analyze the viscosity curves. The results showed that lower (or higher)

shear rate increased the reaction possibility of shorter (or longer) chains. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 839–842, 2006

Key words: combination; flow field; rheology; selectivity; shear

INTRODUCTION

Peroxide has been successfully used for enhancing the mechanical and heat performance of polyethylene.^{1–3} Focuses were mainly put on end products' properties and related processing parameters,⁴ such as temperature, type, concentration, and efficiency of peroxide. The microstructure changes of polyethylene were relatively less explored. Lem and Han⁵ related the viscosity evolution with molecular weight, Yamazaki and Seguchi⁶ studied the type of radicals in reaction, and later Zhou and Zhu⁷ proved that the combination of backbones is the dominant reaction. But, polyethylenes (and other polymers) all have a wide molecular weight distribution (MWD). The difference of reactivity between chains of different length is not distinguished until now, which will influence the reaction and properties of end products. On the other hand, during the reaction, shears are usually applied to improve the mixing effect and help to dissipate heat. Whether and how the shear flow field affects the reactivity of chains of different length is still not clear.

Dhavalikar and Xanthos⁸ studied the chain extension reaction of polyethylene terephthalate in a Brabender batch mixer and found that the rotating speed of rotors decided chain extension or degradation to take place. Fredrickson and Leibler⁹ investigated the influences of steady shear flow field on a polymer reaction system that is dilute in reactive sites. The rate

constant was related with the mean square gyration radius. Those works have noticed the difference in reactivity of chains with different length under flow field.

In this study, a typical combination reaction system (linear low-density polyethylene/low dose of dicumyl peroxide) was selected to study the effects of shear flow fields on the reactivity of polymer chains with different length.

Before experiment, the widely accepted three-step kinetics of radical combination reaction is concisely reviewed below.

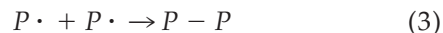
Step 1: Initiator decomposition and formation of primary radicals.



Step 2: Hydrogen abstraction and formation of macroradicals.



Step 3: Combination termination of macroradicals (disproportionation was ignored).



EXPERIMENTAL

Materials

Linear low-density polyethylene (LLDPE), grade 1004YB, with melt-flow index of 2.5 g/10 min (190°C, 2.16 kg, ϕ 2.095 mm) and density of 0.92 g/cm³ (20°C), was obtained from ExxonMobil Chemical, USA. The melt point of LLDPE is 116°C and the melt range is

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TABLE I
Shear Rate for Reaction, and GPC and Rheological Results of Reacted Samples

	Original LLDPE	S1	S2	S3	S4	S5
$\dot{\gamma}$ (s^{-1})	–	0.0015	0.0065	0.025	0.1	0.4
M_w (g/mol)	38,300	58,900	58,900	54,300	48,000	45,300
M_n (g/mol)	18,300	24,100	24,100	23,300	21,000	20,300
M_w/M_n	2.09	2.44	2.44	2.33	2.29	2.23
η_0 (Pa · s)	5540	12,270	12,270	11,500	11,000	10,500
$\eta_0(M_w)$ (Pa · s)	–	24,987	24,987	18,798	12,208	9969
α_M	1	4.51	4.51	3.39	2.20	1.80

110–120°C, measured by DSC. Dicumyl peroxide (DCP, molecular weight, 270 g/mol, chemical pure) and xylene (a mixture of *o*-, *m*- and *p*-xylene whose boiling point is ~140°C and density 0.87 g/cm³ at 20°C) were purchased from Shanghai Chemicals Factory, China. The decomposition rate constant of DCP is $1.53 \times 10^{-4} \text{ s}^{-1}$ and $1.37 \times 10^{-3} \text{ s}^{-1}$ at 130 and 150°C, respectively, provided by the supplier. The corresponding half-life time is 4530 and 530 s.

Experiments

LLDPE and DCP (weight percentage, 0.2%) were mixed in a torque rheometer (Rheocord90, Haake Company, Germany) at 130°C with the rotor speed of 60 rpm. Mixing at 130°C can effectively decrease the decomposition of DCP. The torque decreased after the input peak and leveled off within 150 s. The samples were taken out at 200th second and compressed into sheet (thickness ≈ 1 mm) at 120°C under a pressure of 1.0 MPa. The sheet was cut into round discs with the diameter of 25 mm for reaction that was on-line monitored by rheometer. Time sweep tests under steady shear flow fields were carried out at 150°C on a rotating rheometer (Gemini200HR, Bohlin Instruments, UK) with parallel-plate geometry (gap = 1 mm). Five steady shear rates ($\dot{\gamma}$) were chosen (Table I) to illustrate the effects of flow field on reactions. The viscosity evolution was recorded, as shown in Figure 1. The viscosity of original LLDPE (without DCP) kept constant during the test time (not shown in Fig. 1) revealed the existence of combination reactions induced by DCP. After sufficient time of reaction, the viscosity became constant, which denoted the end of reaction. Then, steady rate sweep tests were carried out to measure the shear rate dependent viscosity of completely reacted LLDPE. After that, the samples were taken off for gel-content measurement by using Soxhlet extraction cycle for 24 h, with xylene as the solvent, at 140°C. The molecular weight distribution (MWD) of original LLDPE and reacted samples were measured by gel-permeation chromatography (GPC2000, Waters, Milford, MA; solvent, 1,2,4-trichlorobenzene, temperature, 150°C).

RESULTS AND DISCUSSIONS

The gel content, g , was obtained by

$$g = \frac{\text{the mass after extraction}}{\text{the mass before extraction}} \quad (4)$$

The gel content of original and five reacted LLDPE are all zero, which means that no gel (or crosslinking networks), but only branched chains, were formed in the recombination reaction, because the content of DCP is very low.

The viscosity curve of S1 (at $\dot{\gamma} = 0.0015 \text{ g}^{-1}$) is very close to that of S2 (at $\dot{\gamma} = 0.0065 \text{ g}^{-1}$), though the former is more scattered probably due to the sensitivity of the instrument. This means the reaction kinetics is not influenced by shear rate when it is low enough.

Figure 2 shows the shear viscosity of completely reacted LLDPE/DCP. The viscosity curves of all reacted systems (S1–S5) are higher than those of the original one, which manifest the occurrence of combination reactions. Moreover, the viscosity curve of S1 and S2 almost superimpose, which also confirms that extremely low shear rate has little influences on reactions. The viscosity curves decrease with the increase of preshear rate. The zero shear viscosities (η_0) of reacted samples are listed in Table I.

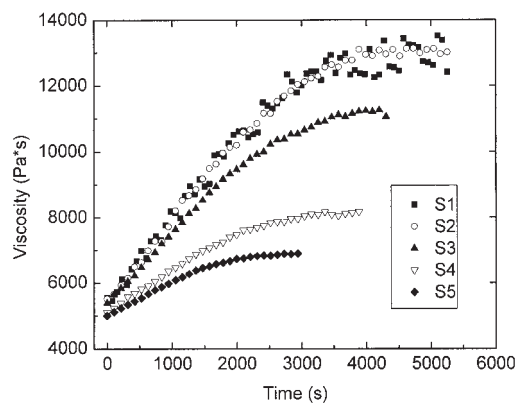


Figure 1 Shear viscosity evolution of LLDPE/DCP (DCP = 0.2%) at 150°C.

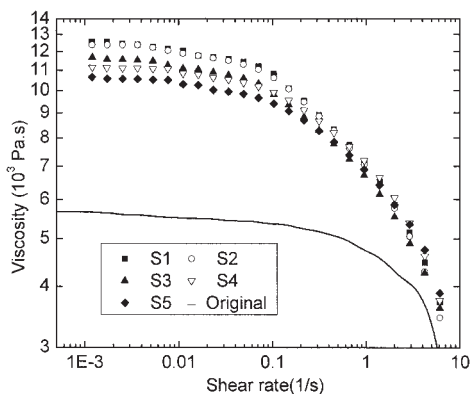


Figure 2 Shear viscosity of reacted and original LLDPE at 150°C.

The MWD of original LLDPE and reacted LLDPE are shown in Figure 3. The MWD curves shift to high-molecular weight direction after reaction, but their shapes are similar. The weight averaged value (M_w), number averaged value (M_n), and their ratios (polydispersity index) are summarized in Table I.

The ideal zero shear viscosity ($\eta_0(M_w)$) of reacted LLDPE at a given M_w (if they are linear) can be estimated by a widely acceptable relation

$$\eta_0(M_w) = kM_w^n \quad (5)$$

Taken k as a constant and $n = 3.5$ (because the MWD are similar), and taken original LLDPE as reference, $\eta_0(M_w)$ can be calculated by

$$\eta_0(M_w) = \eta_0(M_{\text{ref}}) (M_w/M_{\text{ref}})^{3.5} \quad (6)$$

where $M_{\text{ref}} = 38,300$ g/mol, is the weight-average molecular weight of original LLDPE, M_w is that of reacted samples (shown in Table I), and $\eta_0(M_{\text{ref}}) = 5540$ Pa s is the zero shear viscosity of original LLDPE. $\eta_0(M_w)$ was calculated and shown in Table I. The real zero shear viscosities (η_0) differ from the ideal viscosities of linear chains ($\eta_0(M_w)$), which might contribute

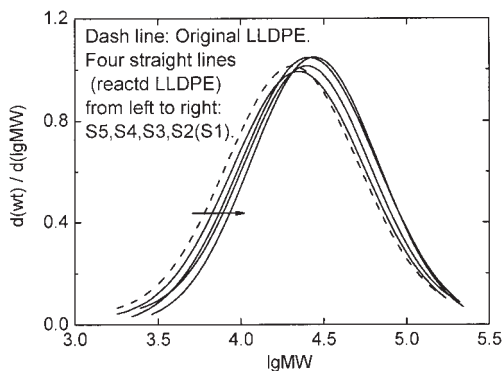


Figure 3 MWD of reacted and original LLDPE.

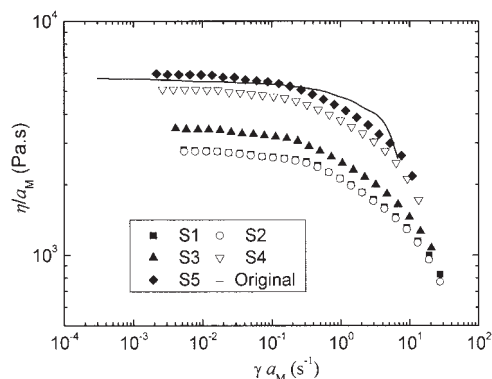


Figure 4 Shifted viscosities of reacted LLDPE.

to the nonlinearity of polymer chains, that is, the molecular weight, MWD, and the length of branches. MWD are similar as shown before, so it is necessary to distinguish another two factors to obtain the effect of shear rate on the reactions.

Wood-Adams and Dealy¹⁰ used viscosity data and MWD curve to determine the long chain branch (LCB) content in polyethylene. For unknown reasons, that method predicts all our samples' LCB contents are zero, which might be contributed to the differences in branched chains. In our experiment, the branched chains are original polymer chains with a MWD. But, in Wood-Adams and Dealy' study, the branched chains were formed in the synthesizing process. The former are more complex in structures and length. So, another method, time-molecular weight superposition,¹¹ was used to remove the influence of molecular weight from the viscosity curve. The superposition is applied by using the shift factor, α_μ

$$\alpha_M = \eta_0(M_w) / \eta_0(M_{\text{ref}}) \quad (7)$$

The shift factors are calculated from the data in Table I and also shown in the same table.

The shifted viscosity curves are shown in Figure 4. The shifted zero shear viscosities of reacted S1–S4 are all smaller than that of original LLDPE. This means that although their molecular weights increase, their viscosities are smaller than that of a linear polymer with the same molecular weight. The length of branches has a great effect on the zero shear viscosity. When compared to the linear polymer with the same molecular weight, long branches can significantly increase the zero shear viscosity, because they can entangle with each other.¹² But, the short branches decrease the zero shear viscosity because they cannot entangle with each other, and worse, their high mobility set hindrances to the entanglements between backbones. Critical molecular weight (M_c) distinguishes the long and short chains. For LLDPE, $M_c \approx 7000$ ¹³ or 8000.¹⁴

In the LLDPE/DCP branching products, it is conceivable that both long and short branches exist. These two kinds of branches have opposite effects on the zero shear viscosity. It is their competition of quantity that determines the zero shear viscosity. Therefore, from S1 to S5, the quantity of long branches increase and that of short ones decrease, which means that the increase of shear rate in reactions results in the increase of the content of long chain branches.

In our experiments, the highest shear rate is 0.4 s^{-1} , under which the flowing LLDPE melt still keeps lamellar, and the reaction is diffusion-controlled. When subjected to a low shear rate, the shorter chains have larger mobility and move faster than the longer ones. So, the shorter macroradicals have more reaction possibility. As the shear rate increases, the viscosity decreases, which might increase the mobility of all chains (especially the longer ones). So, the difference between the diffusion-controlled reactivity of chains with different length narrows, resulting in a comparatively higher reactivity of longer chains.

The selective effect of shear rate on the chains for reaction is valid for lamellar flow and diffusion-controlled reactions. Flow in complex geometries such as in internal mixer or extruder may have a different way in selecting chains for reactions, which needs more research.

CONCLUSIONS

The branching reaction of LLDPE initiated by a small amount of DCP was investigated under different steady shear rate. A time-molecular weight superposition of viscosity curve showed that higher (or lower) shear rate increased the reaction possibility of longer (or shorter) polymer chains. Such selectivity of shear rate on polymer chains for reaction was qualitatively explained by the influence of shear rate on chain mobility.

References

1. Kampouris, E. M.; Andreopoulos, A. G. *J Appl Polym Sci* 1987, 34, 1209.
2. Bremner, T.; Rudin, A. *J Appl Polym Sci* 1993, 49, 785.
3. Anbarasan, R.; Babot, O.; Maillard, B. *J Appl Polym Sci* 2004, 93, 75.
4. Kang, T. K.; Ha, C. S. *Polymer testing* 2000, 19, 773.
5. Lem, K. W.; Han, C. D. *J Appl Polym Sci* 1982, 27, 1367.
6. Yamazaki, T.; Seguchi, T. *J Polym Sci: Part A* 1997, 35, 279.
7. Zhou, W.; Zhu, S. *Macromolecules* 1998, 31, 4335.
8. Dhavalikar, R.; Xanthos, M. *J Appl Polym Sci* 2003, 87, 643.
9. Fredrickson, G. H.; Leibler, L. *Macromolecules* 1996, 29, 2674.
10. Wood-Adams, P. M.; Dealy, J. M. *Macromolecules* 2000, 33, 7481.
11. Doerpinghaus, P. J.; Baird, D. G. *J Rheol* 2003, 47, 717.
12. Gupta, R. K. In *Polymer and Composite Rheology*, 2nd ed.; Marcel Dekker: New York, 2000; Section 3.2.
13. Brandrup, J.; Immergut, E. H. *Polymer Handbook*; Wiley: New York, 1989.
14. Fred, W.; Billmeyer, Jr. *Textbook of Polymer Science*; Wiley: New York, 1984; Section 11.A.