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Conversion measurement in polyethylene/peroxide coupling system under steady shear flow

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Abstract

The coupling reaction of melt linear low density polyethylene (LLDPE) initiated by dicumyl peroxide (DCP) in steady shear flow field was investigated. The conversion of DCP was measured by electron spin resonance (ESR) and chemical titration. An absolute method was proposed to calculate the actual conversion of DCP from rheological data. The coupling efficiency of DCP was obtained from those analyses, which was shown to increase at first, reach a maximum and then decrease in the end stage. A linear relationship between the coupling efficiency of DCP and the concentration of macroradicals was also found in the experiments.

Keywords: Conversion; Peroxide; Coupling efficiency

1. Introductions

Peroxide has been widely used in the modification of polyethylene [1–5]. Main focuses were put on the end products' properties and/or the optimization of related processing parameters. The changes of macroscopic properties (e.g. viscosity and modulus) during the processing can be readily monitored, but it is difficult to convert them to microstructural changes, such as molecular weight or molecular weight distribution. Lem and Han [6] recorded the viscosity evolution along with molecular weight increasing in DCP modificating polyethylene process, and Ramos et al. [4] qualitatively related the dynamic modulus with molecular weight and chain structure in polyethylene extrusion modification by DCP.

When it comes to the chemical reaction, Yamazaki and Seguchi [7] studied the type of radicals in reaction, and later Zhou and Zhu [8] proved that the combination of backbones is the dominant reaction. All these work were performed under static condition. But it is very difficult to determine the conversion evolution of peroxide under certain flow field. Therefore, several authors suggested calculating the relative conversion from the modulus [9] or viscosity [10]. This method can be summarized as:

$$\beta_{\mathrm{rel}} = \frac{X_t - X_0}{X_\infty - X_0} \tag{1}$$

where β_{rel} is the relative conversion at time t, X is the macro property parameter (viscosity or modulus), subscript 0, t and infinity means time zero, time t and the end of reaction. Eq. (1) is accurate only when the relative conversion is a linear function of viscosity or modulus, which is not satisfied under most conditions. The other thing about Eq. (1) is that it implies a 100% relative conversion, which is doubtable especially for reactions in polymeric systems.

In this paper, the coupling reaction of polyethylene initiated by peroxide was investigated. A combined analysis based on the results of ESR, chemical titration and rheology can show clearly the kinetics of such reaction under simple shear flow.

2. Experimental section

2.1. Materials

Linear low density polyethylene (LLDPE), grade

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Nomenclature

D	polydispersity ratio of LLDPE ($=M_w/M_n$)
f	coupling efficiency of DCP
g	gel content
I	ESR spectral intensity at experiment temperature, 77 K
I_0	ESR spectral intensity at reference temperature, 293 K
k	front factor in η–M_w correlation
m_I	mass of DCP ($=0.2$ g in this paper)
m_p	mass of LLDPE ($=100$ g in this paper)
M_c	critical molecular weight
M_I	molecular weight of DCP ($=270$ g/mol)
M_n	number average molecular weight
M_w	weight average molecular weight
n	index in η–M_w correlation
N_s	concentration of $Na_2S_2O_3$ solution
$[P^{\bullet}]$	instant radical concentration (mol/l)
t	reaction time
t_{pre}	pre-time, the time used in preparation for reaction ($=180$ s in this paper)
T	experiment temperature of ESR, 77 K
T_0	reference temperature of ESR, 293 K
T_r	whole reaction time
V_s	volume of $Na_2S_2O_3$ solution used for titration
x	amount of DCP involved in coupling reaction
X	macro property related with conversion
β_{actual}	actual conversion calculated by our method
$\beta_{half\ spin}$	percent of DCP in macroradical form ($=$half the spin number of radicals)
β_{ideal}	absolute conversion got by ESR and titration
β_{rel}	relative conversion calculated by traditional equation
β_{res}	percent of residual DCP got by titration
$\beta_{res,cal}$	percent of residual DCP got by calculation
$\dot{r}$	steady shear rate
η	steady shear viscosity

Subscript of D and η

0	time zero, that is reaction start
t	time t
∞	reaction end

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/cm^3 (20 °C), was obtained from ExxonMobil Chemical, USA. Dicumyl peroxide (DCP, molecular weight=270 g/mol) and xylene (a mixture of *o*-, *m*- and *p*-xylene whose boiling point is about 140 °C and density 0.87 g/cm^3 at 20 °C) are chemical pure and purchased from Shanghai Chemicals Factory, People's Republic of China. The decomposition rate constant of DCP, k_d, is 1.53×10^{-4} and 1.37×10^{-3} s^{-1} at 130 and 150 °C, respectively, provided by the suppler. The half-life time is 4530 and 533 s, correspondingly.

2.2. Sample preparation

LLDPE and DCP (weight percentage, 0.2%) were mixed in a torque rheometer (Haake Rheocord90, Germany) at 130 °C with the rotor speed 60 round/min. The torque decreased after the input peak and leveled off in 180 s. The samples were taken out after 200 s and compressed into sheet (thickness ≈ 1 mm) at 130 °C under 1.0 MPa. The sheet was cut into round discs with the diameter of 25 mm for rheological measurements. Mixing LLDPE with DCP at 130 °C can reduce the possibility of decomposition of DCP due to the long half-life time at the temperature.

2.3. Coupling reaction

Reaction was carried out on a rotational rheometer (MCR300, Paar Physica, Germany) under nitrogen atmosphere with a cone and plate geometry. The diameter of the lower plate was 25 mm, and the cone angle of upper cone was 3°. The disc was put on the lower plate, which was preheated to 150 °C. Then the sample and plates were heated. After the sample was softening, the upper cone was lowered very slowly to the desired position. The small pressure imposed by the upper cone on the sample relaxed very quickly, and was believed to have no influence on the reactions. All those adjustments were finished in 3 min, which was called pre-time (t_{pre}). Then a specific shear rate (0.4 s^{-1}) was exerted on the sample. We set this moment as time zero, and recorded shear viscosity as a function of time (Fig. 1).

The shear viscosity increased with the time, which revealed the existence of chemical reactions. The reaction

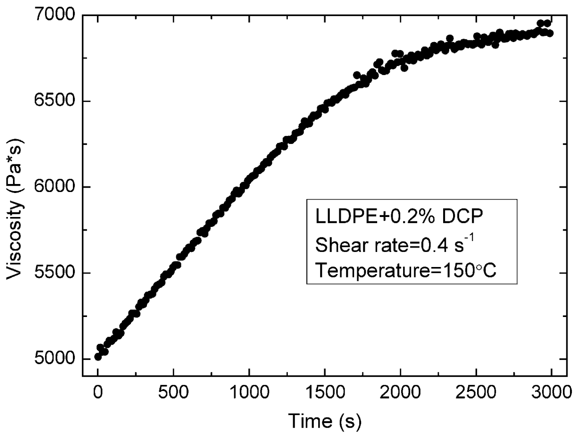

Fig. 1. Shear viscosity as a function of reaction time.

time, T_r, is taken as the point that the viscosity stop rising. In our experiment $T_r = 2500$ s. In order to assure the completion of reaction, after T_r, shear flows in the opposite direction were applied for a long enough time and no evident changes in viscosity were observed.

2.4. Gel content characterization

After all the tests on rheometer, the sample was taken off for gel content tests. The gel content was measured using Soxhlet extraction cycle for 24 h with xylene as the solvent at 140 °C. The gel content g was obtained by:

$$g = \frac{\text{the mass after extraction}}{\text{the mass before extraction}} \qquad (2)$$

The values of g of original and reacted LLDPE samples are all zero, which meant that no gel (networks) but only extended chains were formed in the reaction. In our experiment, 0.2% DCP is not enough for LLDPE ($M_n \approx 20{,}000$) to form gel, which was consistent with early experiment with low dose of DCP [7]. So, we use coupling reaction instead of crosslinking reaction to avoid confusion.

2.5. Measurement of DCP conversion

The coupling reaction showed good reproducibility judged by the viscosity–time curves. We repeated it and stopped the reaction at different time, and dropped the sample immediately into liquid nitrogen (77 K). One part of the sample was used for ESR characterization and the other part was used for chemical analysis.

Generally, the reaction and conversion of DCP can be represented as:

$$\mathrm{DCP} \rightarrow 2\mathrm{R} \rightarrow 2\mathrm{P}^{\cdot} \rightarrow \mathrm{P}-\mathrm{P} \qquad (3)$$

First, DCP is decomposed into the primary radicals ($R = C_6H_5(CH_3)_2CO^{\cdot}$), which is very active. They absorb hydrogen and convert to macroradicals ($P^{\cdot}$) immediately. Previous works showed that primary radicals cannot be detected by ESR [11]. The macroradicals can then couple with each other to increase the molecular weight.

Considering the conservation of DCP quantity, at a given time, the quantity of original DCP (known when preparing the sample) is the sum of three parts:

(1) half the quantity of macroradicals which can be detected by ESR (Section 2.5.1);
(2) the residual DCP which can be determined by chemical titrated (Section 2.5.2);
(3) and the quantity that have reacted.

If the side reactions such as disproportionation are ignored, the ideal conversion of original DCP is:

$$\text{Conversion of DCP } (\beta_{\text{ideal}}) = \frac{\text{Original DCP} - \text{Residual DCP} - \text{Half the spin number of macroradicals}}{\text{Original DCP}} = 1 - \beta_{\text{res}} - \beta_{\text{half spin}} \qquad (4)$$

2.5.1. ESR

ESR test was carried out on JM-FE3A (JEOL). The operation parameters were: Microwave frequency, 5 GHz; Microwave power, 1 mW; modulation frequency, 100 kHz; modulation width, 0.1 mT; sweep time, 60 s. A typical ESR spectrum of polyethylene macroradicals was shown in Fig. 2. Hyper structures [7,8] were not observed due to the low concentration of macroradicals and the sensitivity of instrument. The quantity of macroradicals was obtained by double integration of the curve in Fig. 2 and compared with a standard sample of 2,2,6,6-tetramethyl-1-piperidinyloxy radical (TEMPO, C_9H_8NO, Beijing Odyssey Chemical Industry Co. Ltd). TEMPO is a stable radical at room temperature, whose free radical concentration is 3.78×10^{18} spin/mg. At 77 K, the ESR spectral intensity of TEMPO is too strong to measure. So we used the following equation [7] to calculate the intensity at 77 K:

$$I = I_0 \exp\left(\frac{T_0}{T} - 1\right) \qquad (5)$$

where I is the ESR spectral intensity at T ($T = 77$ K in this paper) and I_0 is that measured at T_0 ($T_0 = 293$ K in this paper).

During the course of transferring the sample from rheometer to liquid nitrogen and reserving the sample in low temperature, the decomposition of DCP is very slow, but the coupling reaction of radicals is still in process at a comparatively faster speed. So $\beta_{\text{half spin}}$ was a little smaller than it should be.

2.5.2. Chemical titration

The other part of sample was dissolved in xylene with strong agitation (slightly heating, lower than 70 °C). Methanol was added to deposit the polyethylene, which was filtered. The filtrate (DCP solution) was condensed by solvent evaporation. Then sufficient acetic acid (methanol solution) and excess potassium iodide (pre-solved in

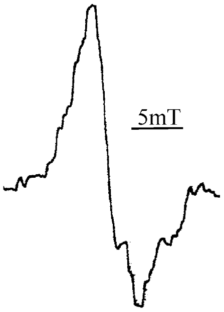

Fig. 2. ESR spectrum of polyethylene macroradical at 77 K.

methanol) was added into the condensed solution to reduce the DCP, as shown in Eq. (6).

$$\text{RO–OR} + 2\text{H}^+ + 3\text{I}^- = 2\text{ROH} + \text{I}_3^- \quad (6)$$

Then the liberated I_3^- was titrated by $Na_2S_2O_3$ (methanol solution) with the starch indicator (water solution):

$$2\text{S}_2\text{O}_3^{2-} + \text{I}_3^- = \text{S}_4\text{O}_6^{2-} + 3\text{I}^- \quad (7)$$

Water is insoluble with xylene. We can see that blue color in water part, and red color in xylene. The titration was carried under heating and stirring, and ended at the point when both the blue color and the red color disappear.

The residual DCP content was calculated by:

$$\beta_{\text{res}} = \frac{N_S V_S M_I}{2m_I} \quad (8)$$

where N_S is the concentration of $Na_2S_2O_3$ (mol/cm^3), V_S is the volume of $Na_2S_2O_3$ solution (cm^3), M_I is the molecular weight of DCP, and m_I is the mass of original DCP.

The residual DCP could also be calculated by the decomposition rate and time. But in the pre-time (Section 2.2) and the adjustment time (Section 2.3), the temperature were not a constant, which brought difficulties for calculation. For the sake of simplifying, we took the temperature as 150 °C for calculation.

$$\beta_{\text{res,cal}} = \exp(-k_d(t + t_{\text{pre}})) \quad (9)$$

where $k_d = 1.37 \times 10^{-3}\ \text{s}^{-1}$ at 150 °C, and $t_{\text{pre}} = 180$ s.

3. Calculation of DCP conversion

3.1. Measurement of polydispersity ratio

To calculate the chemical conversion in the reactions, the most straightforward approach is to know the evolution of molecular weight and its distribution. The molecular weight distribution (MWD) of original LLDPE and completely reacted samples were measured by GPC (GPC2000, Waters, USA; solvent, 1,2,4-trichlorobenzene), and shown in Fig. 3. The shapes of the two curves are both single-peak. The curve of reacted sample shifted to higher molecular weight direction, which confirmed the occurrence of chain extension reaction. The polydispersity ratio (the ratio between M_w and M_n), can be calculated from GPC results. The polydispersity ratio of original (D_0) and fully reacted (D_∞) sample is 2.10 and 2.23, respectively. The polydispersity ratios increased after reactions [4].

To explore the change style of D_t, at different reaction times, samples after ESR measurement were also used for GPC measurement. Typical results of D_t are shown in Fig. 4. A linear increase of D_t can be recognized and the results will be used in the following analysis.

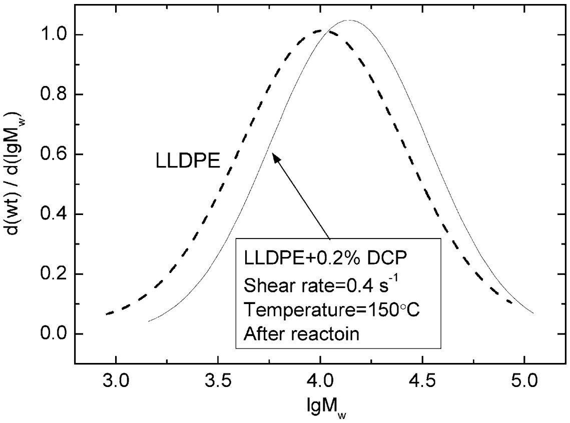

Fig. 3. Molecular distribution of original LLDPE and reacted LLDPE measured by GPC.

3.2. Determination of parameters in $\eta \sim M_w$ correlation

When M_w exceed the critical molecular weight, M_c (for PE, $M_c \approx 4000$), under a given shear rate, a common recognized formula stands:

$$\eta = kM_w^n \quad (10)$$

where η is the steady shear viscosity, k is a constant that is determined only by the type of polymer and temperature, and n ranges from 3.5 to 1 as the shear rate changes from near-zero to infinity, which was experimental shown by Schreiber et al. [12] for linear polyethylene and theoretically proven by Vinogradov and Malkin [13].

To convert the time-dependent viscosity to the absolute conversion of DCP, it is necessary to know k and n under different shear rate. Original polyethylene was dissolved in xylene at about 130 °C and then was separated into five fractions by dropping into the mixture of acetone/methanol ($v/v = 8/2$). For every fraction, the MWD were measured by GPC. The distribution curves' shapes are similar (single peak), though their positions and sizes differ. The M_w can be calculated from MWD curves and the shear viscosity was

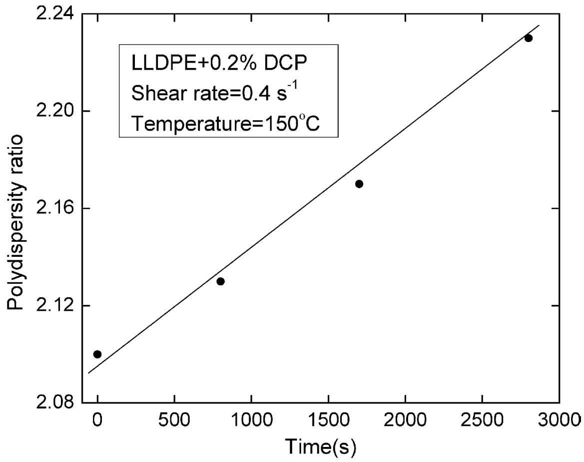

Fig. 4. GPC measurement of polydispersity ratio at different reaction time.

measured by rotating rheometer. Fig. 5 shows the correlation between η and M_w. Calculated by Eq. (10), we got: $n=2.65$ and $lgk=-8.5$.

3.3. Calculation of conversion

When ignoring the influence of unreacted DCP on the system viscosity, Eq. (10) is a good approximation. Although Eq. (10) is generally valid for linear chain polymers, it still can be used here for LLDPE with a very small amount of long chain extension. At time t, we have

$$\eta_t = kM_{wt}^n \tag{11}$$

The subscript t represents time. Considering:

$$D_t = \frac{M_{wt}}{M_{nt}} \tag{12}$$

We have

$$\eta_t = k(D_t M_{nt})^n \tag{13}$$

Let m_p be the mass of LLDPE, x be the amount of DCP contributing to coupling reaction, m_p/M_{n0} is the mole number of original LLDPE molecular, and $((m_p/M_{n0})-x)$ is the mole number of LLDPE molecular at time t, because one DCP combines two LLDPE chains, resulting in reducing one LLDPE chain. So

$$M_{nt} = \frac{m_p}{(m_p/M_{n0}) - x} \tag{14}$$

Combine Eqs. (13) and (14), we have

$$\eta_t = k\left(\frac{D_t m_p}{(m_p/M_{n0}) - x}\right)^n \tag{15}$$

The amount of DCP contributing to coupling reaction can be solved from Eq. (15):

$$x = \frac{m_p}{M_{n0}} - \frac{m_p}{M_{nt}} = \frac{m_p}{M_{n0}} - \frac{m_p}{\sqrt[n]{\eta_t/k}/D_t}$$

$$= m_p\left(\frac{D_0}{\sqrt[n]{\eta_0/k}} - \frac{D_t}{\sqrt[n]{\eta_t/k}}\right) \tag{16}$$

where $\eta_0=4600$ Pa s is the steady shear viscosity of original LLDPE at $\dot{r}=0.4\ \mathrm{s}^{-1}$. In Fig. 4, we confirmed the linear change of D_t, so

$$D_t = D_0 + \frac{D_\infty - D_0}{T_r} t \tag{17}$$

Substituting Eq. (17) into Eq. (16), we have

$$x = m_p\left(\frac{D_0}{\sqrt[n]{\eta_0/k}} - \frac{D_0 + (D_\infty - D_0)t/T_r}{\sqrt[n]{\eta_t/k}}\right) \tag{18}$$

Let M_I be the molecular weight of DCP, m_I be the mass of DCP, the actual conversion of DCP β_{actual} at time t can be,

$$\beta_{actual} = \frac{xM_I}{m_I}$$

$$= \frac{m_p M_I}{m_I}\left(\frac{D_0}{\sqrt[n]{\eta_0/k}} - \frac{D_0 + ((D_\infty - D_0)t/T)}{\sqrt[n]{\eta_t/k}}\right) \tag{19}$$

The absolute chemical conversion can be readily calculated from Eq. (19). In this method, no presumption on final conversion had been made.

4. Results and analysis

β_{res} and $\beta_{half\ spin}$ are shown in Fig. 6. The calculated residual of DCP ($\beta_{res,cal}$) is also plotted in Fig. 6. It is seen that β_{res} got by chemical titration is a little higher than calculated value ($\beta_{res,cal}$). This is due to the variant temperature during the pre-time and the adjustment time before rheological test. $\beta_{half\ spin}$ represents the total macroradicals in the sample at a specific time. It starts to increase at the beginning of test, reach a peak at certain time and then decrease with time. This trend is similar with some

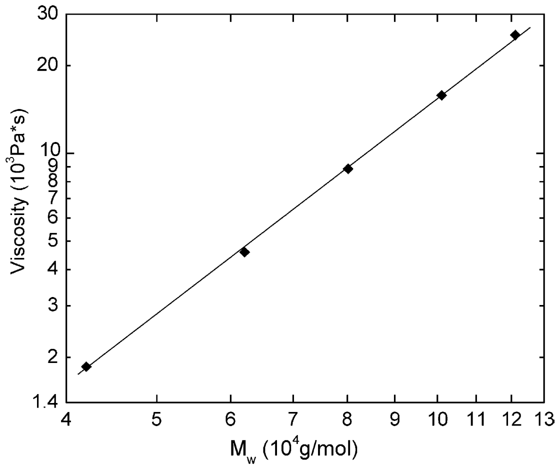

Fig. 5. Correlation of viscosity and M_w under shear rate 0.4 s^{-1}.

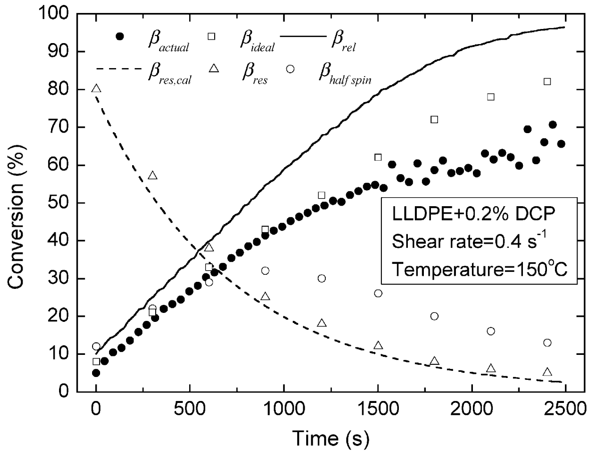

Fig. 6. Conversions of DCP as a function of time.

previous studies under static conditions [7,8]. It should be noticed that the macroradicals measured in this work comprise all possible macroradicals, such as alkyl radicals and allyl radicals. The difference between these radicals is not considered in this work due to the low concentration of macroradicals.

Referring Eq. (1) and using the data in Fig. 1, $\beta_{\rm rel}$ can be calculated by:

$$\beta_{\rm rel} = \frac{\eta_t - \eta_0}{\eta_\infty - \eta_0} \tag{20}$$

$\beta_{\rm ideal}$ and $\beta_{\rm actual}$, together with $\beta_{\rm rel}$ are plotted in Fig. 6 for comparison. $\beta_{\rm rel}$ is relative conversion which implies the final conversion to be 100%. This cannot, at least not always can, be reached. It is not strictly related to any evolution of the microstructure or chemical reaction kinetics. Therefore, it is not surprising to see that $\beta_{\rm rel}$ is completely different from $\beta_{\rm ideal}$ and $\beta_{\rm actual}$ at all times.

$\beta_{\rm actual}$ is an actual conversion of DCP, which only takes the DCP contributing to coupling reaction into consideration, and ignores other side reactions. $\beta_{\rm ideal}$ is an ideal one, which accounts for all possible reactions of macroradicals. Actually, the disappearing radicals might couple, disproportionate, and react with impurities; the primary radicals might recombinate with macroradicals [14]. Therefore, $\beta_{\rm ideal}$ should be larger than $\beta_{\rm actual}$ to some extent, and this is clearly shown in Fig. 6.

In the end stage, $\beta_{\rm actual}$ increases very slowly, which is consistent with the slowly increasing viscosity in Fig. 1. That means the coupling reactions are nearly completed, but the side reactions are still in process, which consume macroradicals and do not contribute to the increase of the molecular weight or viscosity. This is also reflected by the increasing difference between $\beta_{\rm actual}$ and $\beta_{\rm ideal}$ in this stage. $\beta_{\rm actual}$ and $\beta_{\rm ideal}$ are both below 100% at the final stage, which is rational.

DCP coupling efficiency can by defined as the ratio between the DCP contributing to coupling reaction and that decompositing to radicals, that is

$$f = \frac{\beta_{\rm actual}}{\beta_{\rm ideal}} \tag{21}$$

The coupling efficiency of DCP and $\beta_{\rm half\ spin}$ as a function of time is plotted in Fig. 7. The efficiency is found to be about 90% at the beginning, and increases to a maximum about 95% and then decrease to about 65%. The final efficiency of DCP in our experiments is consistent with some previous studies [15,16]. The decrease of the efficiency in the late stage is probably due to the cage effect caused by the high viscosity [17].

From $\beta_{\rm half\ spin}$ and the original DCP concentration, the instant radical concentration can be calculated. Furthermore, a linear relationship between the coupling efficiency and radical concentration is found and shown in Fig. 8. When radical concentration is higher, the radicals have more possibility to meet each other and couple, which increase coupling efficiency. The contacting possibility of radicals is proportional to their concentration, resulting in the above linear relation. This trend is similar to previous work [18].

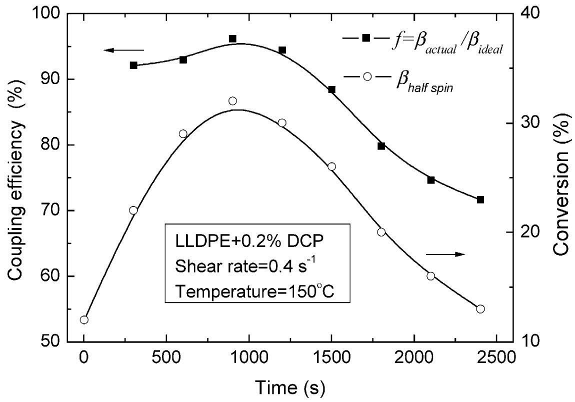

Fig. 7. Coupling efficiency of DCP and $\beta_{\rm half\ spin}$ as a function of time.

5. Conclusions

Coupling reaction of LLDPE/low dose of DCP under simple shear flow was carried out on a rotating rheometer. The ideal conversion of DCP ($\beta_{\rm ideal}$) was measured by ESR and chemical titration, and compared with relatively conversion ($\beta_{\rm rel}$) and absolutely actual conversion ($\beta_{\rm actual}$) obtained by a rheological method. The evolution of the coupling efficiency of DCP during reactions can be obtained from $\beta_{\rm ideal}$ and $\beta_{\rm actual}$. The efficiency was found to increase at the beginning and decrease after a maximum in the end stage. At the same time, a linear relation between the coupling efficiency of DCP and radical concentration was found.

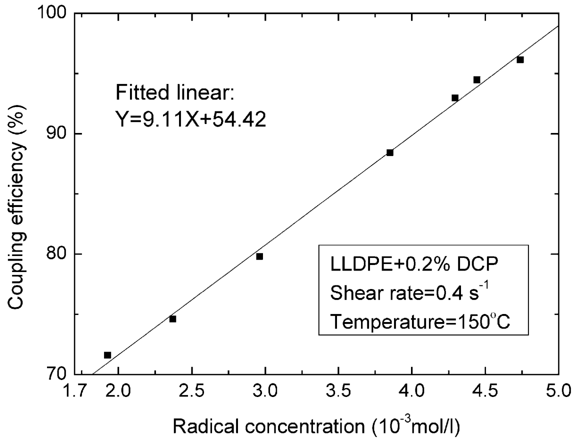

Fig. 8. Correlation between coupling efficiency of DCP and radical concentration.

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