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Graft chain propagation rate coefficients of acrylic acid in melt graft copolymerization with linear low density polyethylene

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Abstract

Graft chain propagation rate coefficients ($k_{p,g}$) for grafting AA onto linear low density polyethylene (LLDPE) in the melt in ESR tubes have been measured via Fourier transform infrared (FTIR) spectroscopy and electron spin resonance (ESR) spectroscopy in the temperature range from 130 to 170 °C. To exclude the effect of homopolymerization on the grafting, the LLDPE was pre-irradiated in the air by electron beam to generate the peroxides and then treated with iodide solution to eliminating one kind of peroxides, hydroperoxide. The monomer conversion is determined by FTIR and the chain propagation free-radical concentration is deduced from the double integration of the well-resolved ESR spectra, consisting nine lines in the melt. The temperature dependence of $k_{p,g}$ is expressed:

$$\ln\left[\frac{k_{p,g}}{\mathrm{g\ mol^{-1}\ s^{-1}}}\right] = (26.2 \pm 0.22) - (3876.9 \pm 92.8)\left(\frac{T}{K}\right)^{-1}.$$

The magnitude of $k_{p,g}$ from FTIR and ESR analysis is in good agreement with the theoretical data deduced from ethylene-AA copolymerization, suggesting this method could reliably and directly provide the propagation rate coefficient. The comparison of $k_{p,g}$ with the data extrapolated from solution polymerization at modest temperature indicates that the extrapolated data might not be entirely fitting to discuss the kinetics behavior in the melt.

Keywords: Graft copolymerization; Chain propagation rate coefficient; ESR

1. Introduction

In recent years, there has been a great practical interest in the grafting of vinyl monomers to polyefins [1]. This grafting can be performed in an inert solvent but the preferred method is the direct grafting of monomer to molten polyolefin in the presence of a free radical initiator [2,3]. Although the success has the industrial process gained [1], surprisingly little is understood about detailed grafting kinetics at high temperature and in high viscosity systems, and up to now, the understanding of melt grafting comes mainly from studies carried out at modest temperatures (<100 °C) and pressure, no kinetics data directly obtained from the melt grating reactions are published [2,3]. Thus, it is worthwhile measuring the rate coefficients, especially the graft chain propagation rate coefficient ($k_{p,g}$), to gain the further understand for the graft kinetics in the melt.

In general, the free radical facilitated grafting copolymerization mechanism involves Eqs. (1)–(6), where $I^{\cdot}$ is the primary radical, P–H is the polyolefin backbone and M is the monomer [3]. Eqs. (5) and (6) describe the steps of chain propagation for grafting and homopolymerization, respectively.

$$I_2 \rightarrow 2I^{\cdot} \quad (1)$$

$$I^{\cdot} + P\text{–}H \rightarrow P^{\cdot} + IH \quad (2)$$

$$P^{\cdot} + M \rightarrow PM^{\cdot} \quad (3)$$

$$I^{\cdot} + M \rightarrow IM^{\cdot} \quad (4)$$

$$\Sigma PM_i^{\cdot} + M \rightarrow \Sigma PM_{i+1}^{\cdot} \quad (5)$$

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$$\Sigma\mathrm{I}-\mathrm{M}_i^{\cdot}+\mathrm{M}\rightarrow\Sigma\mathrm{IM}_{i+1}^{\cdot} \quad (6)$$

A kinetic treatment [4] with the reaction rate has shown that the rate of the monomer depletion is expressed by Eq. (7).

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t}=k_{\mathrm{p}}[\mathrm{M}]\left(\Sigma\left[\mathrm{P}-\mathrm{M}_i^{\cdot}\right]+\Sigma\left[\mathrm{I}-\mathrm{M}_i^{\cdot}\right]\right) \quad (7)$$

where k_{p} is the chain propagation rate coefficient. In the melt grafting system where the phase separation may occur, the chain propagation rate coefficient for homopolymerization may be different from that for grafting [5]. Therefore, it is reasonable to substitute Eq. (7) with Eq. (8).

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t}=k_{\mathrm{p,g}}\Sigma\left[\mathrm{P}-\mathrm{M}_i^{\cdot}\right][\mathrm{M}]+k_{\mathrm{p,h}}\Sigma\left[\mathrm{I}-\mathrm{M}_i^{\cdot}\right][\mathrm{M}] \quad (8)$$

where $k_{\mathrm{p,g}}$ and $k_{\mathrm{p,h}}$ are chain propagation rate coefficients for grafting and homopolymerization, respectively. Since, grafting and homopolymerization are occurring simultaneously, each can influence the other, especially through the occurrence of cross-termination reactions, it is difficult to treat these two processes separately [3]. Thus, it is anticipated that step (4) and (6) could be eliminated from the grafting mechanism if we want to investigate the graft chain propagation reaction in detail. Then, the Eq. (8) can be simply expressed by Eq. (9)

$$-\frac{\mathrm{d}[\mathrm{M}]}{\mathrm{d}t}=k_{\mathrm{p,g}}\Sigma\left[\mathrm{P}-\mathrm{M}_i^{\cdot}\right][\mathrm{M}] \quad (9)$$

If the concentration of chain propagation free radical is constant, we can obtain the integrated expression for graft rate, (Eq. (10))

$$\ln\left(\frac{c_{\mathrm{M},1}}{c_{\mathrm{M},2}}\right)=k_{\mathrm{p,g}}C_{\mathrm{R}}(t_2-t_1) \quad (10)$$

here, C_{R} is used to denote the $\Sigma[\mathrm{P}-\mathrm{M}_i^{\cdot}]$ for simplification and $c_{\mathrm{M},1}$, $c_{\mathrm{M},2}$ are monomer concentrations at reaction time t_1 and t_2, respectively.

It had been reported that there were two kinds of polymeric peroxides, namely, hydroperoxide (POOH) and dialky peroxides (POOP) generating on the PE backbone when the PE was irradiated in the air, and if the pre- irradiated LLDPE was mixed with graft monomer and heated, the POOP could effectively initiate the grafting while the POOH led to the homopolymerization to some extent [6]. On the other hand, the pioneering works by Silbert showed that POOH rapidly reacted with iodide ion at room temperature whereas dialkyl peroxides were unreactive without perchloric acid and Fe^{3+} as the catalysts [7]. Thus, it is promising to eliminate the POOH and the subsequent homopolymerization using conventional iodide assay to study the chain propagation rate coefficient for grafting in detail.

Electron spin resonance (ESR) spectroscopy can theoretically provide direct information on the structures [8], dynamics [9], and environment [10,11] of free radical species. This technique has been applied by several authors to the determination of the k_{p} in free radical polymerization [12,13]. In this work, the data $k_{\mathrm{p,g}}$ was measured by direct determination of the concentration of the propagating free radicals, C_{R}, via ESR accompanied by measurement of the overall graft copolymerization rate with FTIR. Calculation of $k_{\mathrm{p,g}}$ proceeds via Eqs. (9) and (10).

The aim of this study is to determine: (a) the graft chain rate coefficient in the melt and (b) whether the data extrapolated from the solution polymerization at modest temperature are fitting in the melt or not. For these purposes, the grafting acrylic acid (AA) onto LLDPE was chosen as model system. AA was chosen because of well-document k_{p} data [14–16] and the relatively high graft degree [17]. All the graft copolymerizations were performed in the ESR tubes.

2. Experimental section

2.1. Materials

LLDPE(DFDA-7042) with butene content of 6 ± 0.5 wt% was provided by Jilin Chemical Corp. (China). Its melt flow rate (MFR) is 1.02 g/10 min (ASTM D 1238), with the weight-average molecular weight ($\bar{M}_{\mathrm{w}}$) of 1.17×10^5 and polydispersity ($\bar{M}_{\mathrm{w}}/\bar{M}_{\mathrm{n}}$) of 3.44.

AA, supplied by Tian Jin Institute of Chemical Reagents (China), was distilled before using. Acetone, xylene, isopropyl alcohol and *n*-heptane were reagent grade and used without any further purification. $FeCl_3$ and NaI were purchased from Shang Hai Shenglong Chemicals Co., Ltd (China) and Zhe Jiang HaiChuan Chemicals Co., Ltd (China), respectively.

2.2. Treatment of LLDPE

LLDPE was pre-irradiated by the electron beam (EB) in the air at about 25 °C, with the electron energy of 2.5–3 MeV, dose rate of 1.1 kGy/s and total dose of 15 and 30 kGy, respectively. Both POOP and POOH generated on the LLDPE backbone [6]. The iodide-treatment reaction was carried out in a 1000-ml, three-necked flask equipped with a condenser, a stirrer, and a gas inlet. In a typical reaction, about 2 g irradiated LLDPE was swollen in 80 ml xylene with the constant stirring under N_2. After 7-day swell, isopropyl alcohol (480 ml), 32 ml of 0.123 mM $FeCl_3$ in acetic acid and 16 ml of 1.33 M NaI in isopropyl alcohol were added to the reaction flask and the vessel was put in the oil bath. The flask was heated at 60 °C for about 2 h. To track the extent of reaction, every 20 min, the samples were taken out from the mixture for UV characterization with UV-2450 UV–visible spectrophotometer, and the absorbance at 360 nm was used as the standard [18]. Each time, 2 ml of reaction mixture was diluted by two-fold volume of isopropyl alcohol. Here, time zero was defined as the time when the NaI was fed into the flask. About 80 ml of water was added to stop the redox reaction after POOH was completely reacted. Then the treated LLDPE was filtered by vacuum and washed with isopropyl alcohol for five times and then dried to the constant weight in a vacuum oven at 60 °C. Hereafter, the LLDPE irradiated by electron beam in the air and the irradiated LLDPE treated by iodide ion are referred to as LLDPE(R), and LLDPE(T), respectively.

The concentration of POOP and half-time of POOP decomposition were measured by DSC. The detailed procedure to measure the POOP density and half-time of POOP decomposition has been described on another publication [19], and here, it was only briefly stated. The LLDPE and dicumyl peroxide (DCP) were mixed homogenously in the mini-miller with the known DCP concentration, C_D (mol g^{-1}). Then the enthalpy change of mixture, ΔH_M (J g^{-1}) and that of neat LLDPE, ΔH_N were obtained by DSC experiments, and the referential enthalpy change ΔH_R (J mol^{-1}) was calculated by the ratio of enthalpy change difference between the mixture and neat LLDPE to the DCP concentration.

$$\Delta H_R = \frac{\Delta H_M - \Delta H_N}{C_D} \tag{11}$$

Similarly, the enthalpy difference $\Delta H_{T,N}$ ($\Delta H_T - \Delta H_N$) between LLDPE(T) and the neat LLDPE were obtained by DSC. And the concentration of POOP was calculated by the ratio of $\Delta H_{T,N}$ to ΔH_R.

$$C_{POOP} = \frac{\Delta H_T - \Delta H_N}{\Delta H_R} \tag{12}$$

A series of LLDPE(T) were annealed for various times at temperature range from 100 to 170 °C, respectively. The first half of the decomposition curve was used to calculate the rate constant assuming the first-order kinetics. A least-squares fit of the data provided the rate constant of $k_{d,POOP}$, the values of $k_{d,POOP}$ were slightly higher than those of di-heptylperoxide [20] at each temperature. The concentration and half-time of the peroxides at each temperature are listed in Table 1.

2.3. ESR measurement

All the experiments were performed in the ESR tubes at temperature range from 130 to 170 °C. The LLDPE(T) with two irradiation dose (15 and 30 kGy) was premixed with AA in a feed concentration of 2 wt% in the mini-muller, respectively. As shown in Table 1, the life-time of the peroxide becomes short with the increasing temperature; to make sure that the life-time of polymer peroxides is sufficient long enough to test all experiments, the test time for each experiment is shorter than the half-time of peroxides decomposition at corresponding temperature. About 50 mg mixtures were introduced into a 0.5-cm (o.d.) ESR quartz tube in an argon atmosphere and sealed. When the ESR cavity reached preset temperature, the quartz tube was set in the cavity and the ESR spectra began to be recorded. ESR spectra were recorded on a JES-FE3AX spectrometer operating in the x-band at a 100-kHz modulation field and a microwave power of 1 mW. Temperature was controlled by a JES-UCT-2AX variable-temperature adapter. The spectra were recorded over a magnetic field range of 50 mT with a time constant of 0.03 s. Total sweep time (to measure one ESR spectrum) varied between 0.5 and 4 min, depending on the reaction conditions.

During each grafting, several spectra were recorded at specific time. To deduce absolute free-radical concentrations at high temperature, ESR spectra of precisely known amounts of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxyl (TEMPOL) dispersed in LLDPE were measured at 25 °C [12], then the ESR spectral intensity was corrected to the high temperature with Eq. (13) [21]:

$$I = I_0 \exp\left(T_1\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) \tag{13}$$

where I_0 is the ESR spectral intensity at T_1 (T_1 = 25 °C in this case) and I is the corrected intensity at high temperature T_2 (up to 170 °C).

2.4. FTIR measurement

The graft rates r_0 were derived from a series of graft copolymerization runs under the same conditions as performed in ESR measurements. At preselected time t, the grafting was stopped by quenching the ESR tube in the liquid nitrogen for 10 min, and the quenched samples were annealed for 24 h in the air before purification. Then, about 50 mg quenched sample was dissolved in 10 ml of boiling *n*-heptane for 30 min, and 40 ml acetone was poured into the solution with stirring to precipitate the grafted LLDPE. The precipitate was filtered by vacuum and washed with acetone for five times, then dried to constant weight in a vacuum oven at 60 °C for FTIR measurement.

A BIO-RAD FTS-135 IR spectrometer was adopted to measure the graft degree (GD). Its resolution is 4 cm^{-1} and the scan number 5. The purified sample was dissolved in *n*-heptane in a concentration of 5% and cast on the NaCl plate with the film thickness of about 0.10 mm. The GD was defined as follows [22]:

$$GD(\%) = \frac{[M]_g}{M_{PE}} 100 \tag{14}$$

where M_{PE} and $[M]_g$ were the weight of LLDPE(T) and grafted monomer, respectively. The calibration equation (Eq. (15)) reported in our previous work [19] was used for the quantitative measurement of grafted AA onto LLDPE(T).

Table 1
The Concentration of POOP and half-time of POOP Decomposition

Dose (kGy)	Concentration (10^6 mol g^{-1})	Half-time (s)					
15	5.07	100 °C	130 °C	140 °C	150 °C	160 °C	170 °C
30	6.86	286,320	8277.8	2848.0	1030.5	390.8	154.8

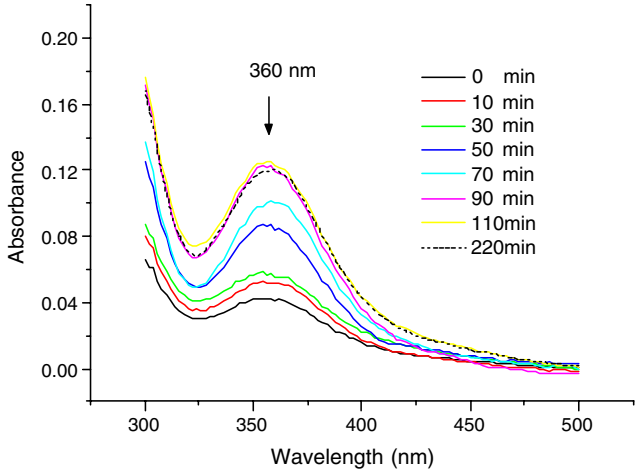

Fig. 1. Time-evolution UV spectra of I_3^- at 360 nm during iodide redox reaction. The LLDPE was irradiated by electron beam with the total dose 15 kGy. Here, time zero was defined as the time when the NaI was fed into the flask.

$$GD(\%) = \frac{1.77A_{1713}}{A_{1379}} \quad (15)$$

where A_{1713} and A_{1379} were the carbonyl absorption band area of grafted AA and methyl absorption band area of LLDPE, respectively. Calibration equation was obtained by comparing the ratio of the absorption band area at 1713 cm^{-1} to that at 1379 cm^{-1} with the same ratio obtained for mixtures of LLDPE/PAA of known composition [19].

3. Results and discussions

3.1. Hydroperoxide and homopolymerization elimination

The POOH elimination was expressed by Eqs. (16) and (17) [23],

$$2POOH + 2I^{-1} \xrightarrow{Fe^{3+}} 2PO^{\cdot} + I_2 + 2OH^- \quad (16)$$

$$I^- + I_2 \rightleftharpoons I_3^- \quad (17)$$

UV–vis absorption spectroscopy was used to track and identify the reaction extent. The time-evolution UV spectra of I_3^- at 360 nm are plotted in Fig. 1, here, the time zero is defined as the time when NaI is fed into the flask. As shown in Fig. 1, the intensity of absorbency increases with time, and reaches the maximum at 90 min, then the intensity does not change anymore, indicating that the POOH has been completely eliminated.

To determine whether the poly(acrylic acid)(PAA) exists or not in the product of LLDPE(T)-*g*-AA, the graft products were analyzed by scanning electron microscopy (SEM) and extracted by methanol at 40 °C. For comparison, the graft products of LLDPE(R)-*g*-AA was also obtained under the same experimental conditions. These experiments were performed at 170 °C, with the feed monomer concentration of 2 wt%. Fig. 2 presents SEM images of LLDPE(R)-*g*-AA and LLDPE(T)-*g*-AA demonstrating that the PAA existing in LLDPE(R)-*g*-AA (white spots in Fig. 2(a)) can not be seen in LLDPE(T)-*g*-AA (Fig. 2(b)) at this magnification scale. The LLDPE(T)-*g*-AA was also extracted in methanol at 40 °C for 1 month then analyzed by FTIR. The FT-IR spectrum showed no characteristic peaks of PAA in methanol, indicating that no PAA existing in the product of LLDPE(T)-*g*-AA since methanol is a good solvent for PAA [24,25]. Both the results show that the PAA is not generated during grafting of AA onto LLDPE(T). Our results contrast with the works of Kim et al., who reported that PAA was easily produced once AA was copolymerized on pre-made polyolefin [24,25]. Considering the difference in the experiment conditions, we believe that this difference is not unreasonable: (i) the initiator inducing to polymerize of AA is eliminated in our experiments, (ii) the typical temperature for thermally initiated polymerization of AA is 250 °C [26], while our experiments are performed at relatively low temperature (from 130 to 170 °C), so the possibility of thermally initiated AA polymerization is decreased at this temperature range [26], and (iii) the low feed concentration of AA (2 wt%) should be associated with a very small amount of PAA even if PAA has been produced, and it has been confirmed by the observation that the very small quantity of PAA existed in the graft product, LLDPE(R)-*g*-AA.

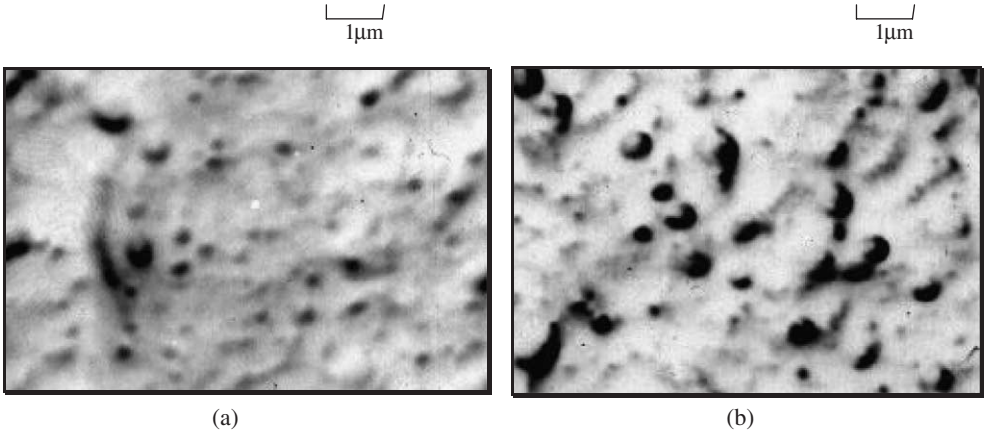

Fig. 2. Scanning electron micrographs of LLDPE-*g*-AA. (a) LLDPE(R)-*g*-AA, without eliminating POOH. (b) LLDPE(T)-*g*-AA eliminating POOH. Here, dispersed domains consisting of PAA homopolymers are clearly visible as white spots in (a), but in a small quantity; these are seldom seen in (b).

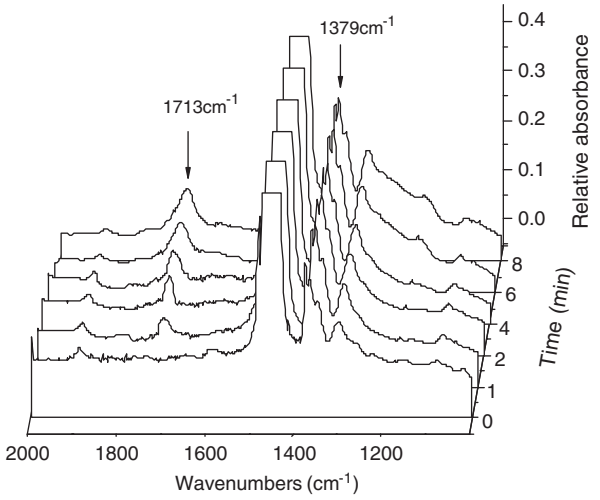

Fig. 3. The time evolution of the >C=O FTIR absorption peak during grafting AA onto LLDPE(T) at 150 °C. The feed monomer concentration is 2 wt%, and the initial concentration of POOP ($C_{POOP,0}$) is 5.07×10^{-6} mol g^{-1}.

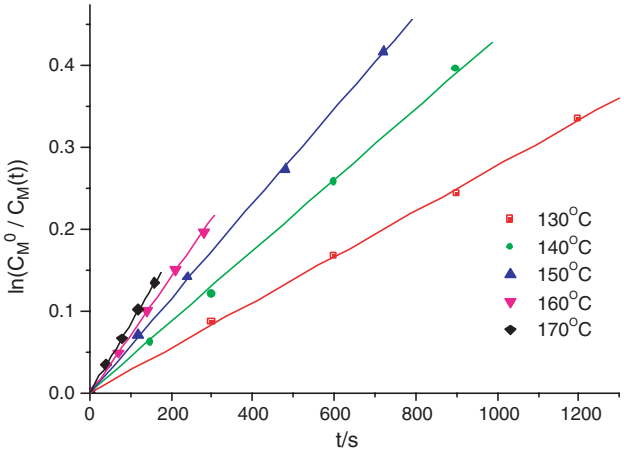

Fig. 4. Plots of relative monomer concentration vs reaction time for the reaction of AA grafting onto LLDPE(T) at temperature range from 130 to 170 °C. The feed monomer concentration is 2 wt%, and the $C_{POOP,0}$ is 5.07×10^{-6} mol g^{-1}. Here, C_M^0 is the effective monomer concentration (0.7 wt%) at time zero.

3.2. Determination of graft chain propagation rate coefficient

The time-evolution of FTIR spectra of LLDPE(T)-*g*-AA are shown in Fig. 3, Here, the FTIR spectra are normalized with absorption band area at ca. 1379 cm^{-1}, which is the $-CH_3$ absorption peak of LLDPE(T). The new absorption peak at about 1713 cm^{-1} is the carbonyl group (>C=O) stretch vibration of grafted AA [17,19], and the absorption band area at ca. 1713 cm^{-1} increases with reaction time indicating AA is being grafted onto LLDPE(T) continuously. Assuming that the grafting is the only depletion of the monomer, the rate of monomer consumption can be measured from the increment of monomer that has been grafted onto LLDPE(T), and thus, the monomer conversion is obtained.

As AA is partially miscible with the LLDPE [27], the AA monomer prefers to form 'aggregates' to reside near the end sites of the polymer chains [28]. The interface between melt LLDPE and AA is readily formed and the graft copolymerization is believed to occur at the interface [19]. Only the monomers that is resident the interface or capable of reaching the interface by diffusion could react. Therefore, the effective concentration of monomer that has participated in the graft copolymerization has to be defined. The effective concentration of monomer is determined by the independent graft copolymerization runs using the same mixture as that in the corresponding ESR study. The experiments were performed in ESR quartz tubes at 170, 180, 190 °C for 60 min with the oil bath heating and the GD of final products were 0.69, 0.70 and 0.70%, respectively, the results that almost the same GD of grafted products was obtained for these experiments are not unexpected since the experiments performed on ESR tubes are static and the grafting rate and grafting products are mainly determined by the distribution of reaction species and the concentration of reaction species at the reaction site [29]. Thus, the effective concentration of monomer in the grafting system is defined as the concentration of finally converted monomer. In Fig. 4, the conversion data obtained from FTIR analysis in terms of the natural logarithm of inverse relative monomer concentration, $c_M^0/c_M^{(t)}$, vs t are plotted. Here, c_M^0 refers to the effective concentration of monomer at reaction site at time zero (0.70 wt%), and the time zero in the melt grafting is defined as the time when the peroxides begin to decompose [19,30]. As shown in Fig. 4, the data points from each experiment nicely fit a straight line. According to Eq. (10), the slope of the individual lines may be identified with the product term $k_{p,g}c_R$, thus the values of $k_{p,g}c_R$ are obtained and summarized in the Table 2. The linear dependences suggest that c_R remains approximately constant during each polymerization (at least within the conversion range under investigation), which is confirmed by the direct measurement of c_R.

The another piece of experimental information for $k_{p,g}$ determination is c_R measured by ESR. An experiment ESR spectrum of the propagation free-radical recorded during the melt grafting is shown in Fig. 5. The graft copolymerization was run at 130 °C and the initial POOP concentration of 5.07×10^{-6} mol g^{-1}. The ESR spectrum was measured between $t=0$ and $t=1200$ s, and the monomer conversion during the scanning of this particular ESR spectrum increased from 0 to 28.5% taking effective concentration of monomer as reference. Similar with the ESR spectrum of acrylate polymerization at high monomer conversion, the ESR signal of AA propagating free-radical exhibits the 9-line spectrum, and the 9-line spectrum is attributed to an enhanced hindrance in the mobility of the propagating free radical in the melt [13]. Our experiments reveal that the shape of the spectrum does not vary significantly with the temperature, thus, the shape of the ESR signal may be considered immaterial with respect to the quantitative analysis of C_R.

The well-resolved 3-line ESR spectrum of TEMPOL is generally agreed to provide an excellent calibration standard for quantitative determination of C_R [12]. The TEMPOL reference signal was measured at 25 °C in the same ESR tube and ESR cavity as was used in graft copolymerization, then the

Table 2
Main parameters obtained in this work

T (°C)	Dose (kGy)	c_{POOP} (mol g$^{-1}\times10^{-6}$)	$k_{p,g}\langle C_R\rangle$ (s$^{-1}\times10^{-4}$)	$\langle C_R\rangle$ (mol g$^{-1}\times10^{-11}$)	$k_{p,g}$ (g mol^{-1} s$^{-1}\times10^{7}$)
130	15	5.07	2.79	1.65	1.70
130	30	6.86	3.39	1.97	1.72
140	15	5.07	4.32	1.95	2.22
140	30	6.86	4.91	2.24	2.19
150	15	5.07	5.8	2.09	2.78
150	30	6.86	6.96	2.46	2.83
160	15	5.07	7.24	2.16	3.35
170	15	5.07	9.41	2.31	4.07

The feed monomer concentration is 2 wt%, the effective concentration of monomer is 0.7 wt%.

spectral intensity at high temperature is corrected by Eq. (13). Therefore, the value for C_R in grafting is found, by direct ratioing of the sample and the corrected reference (TEMPOL) ESR signals after double integration. Values of c_R, during graft copolymerization at 130 °C and at an initial POOP concentration ($C_{POOP,0}$) of 5.07×10^{-6} mol g^{-1} and at 150 °C and $C_{POOP,0}=6.86\times10^{-6}$ mol g^{-1} are plotted vs reaction time in Fig. 6.

Fig. 6 shows that there is a weak tendency that c_R increases with t increasing. However, the change in c_R during single graft copolymerization occurs within the limits of experimental accuracy for c_R determination. Thus for each experiment at constant temperature and identical concentration of POOP, an arithmetic mean value, $\langle c_R\rangle$, is derived from individual ESR measurements of c_R. These mean values for the two experiments are plotted as dashed lines in Fig. 6. The finding that the c_R keeps approximately constant during each experiment could be explained as follows: (i) the consumption of POOP during the conversion range covered in the experiments is small (shown in Table 1), (ii) the termination of free radicals is slow in the melt [2] and (iii) the concentration of reaction species is high enough to sustain the reaction at an initial stage [31]. The $\langle c_R\rangle$ data for the entire set of graft copolymerization carried out in the present investigation are summarized in the Table 2. As expected, the value of $\langle c_R\rangle$ increases with the increasing temperature and concentration of POOP.

With $k_{p,g}\langle c_R\rangle$ and $\langle c_R\rangle$, the value $k_{p,g}$ is easily calculated and listed in Table 2. The straight line is obtained when the data of

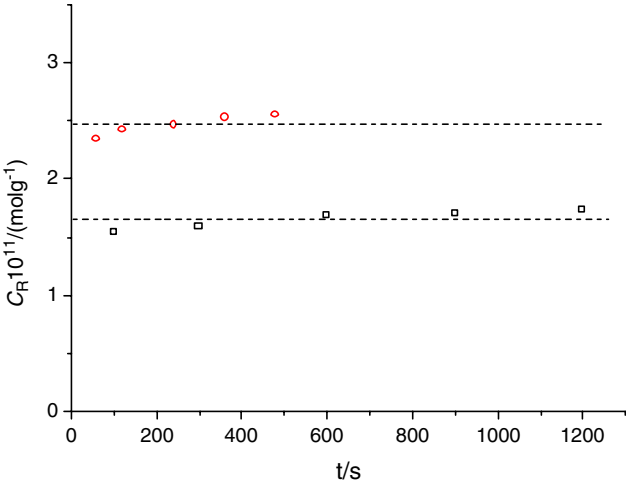

Fig. 6. Free-radical concentration, C_R, plotted vs reaction time, t, for grafting AA onto LLDPE(T) at $C_{POOP,0}=6.86\times10^{-6}$ mol g^{-1} and 150 °C (open circles) and at $C_{POOP,0}=5.07\times10^{-6}$ mol g^{-1} and 130 °C (open squares). The dashed lines indicate the arithmetic mean values of free-radical concentrations, $\langle C_R\rangle$, for each polymerization experiment. The feed monomer concentration is 2 wt% and effective monomer concentration is 0.7 wt%.

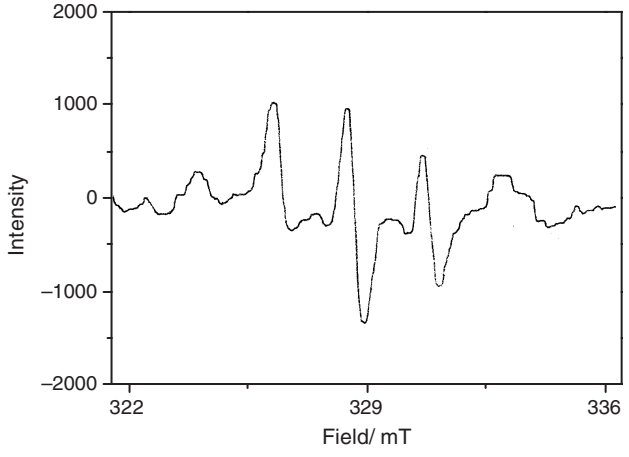

Fig. 5. ESR spectra of the propagation free radicals in grafting AA onto LLDPE(T) at 130 °C. The feed monomer concentration is 2 wt%, the effective monomer concentration is 0.7 wt% and $C_{POOP,0}$ is 5.07×10^{-6} mol g^{-1}.

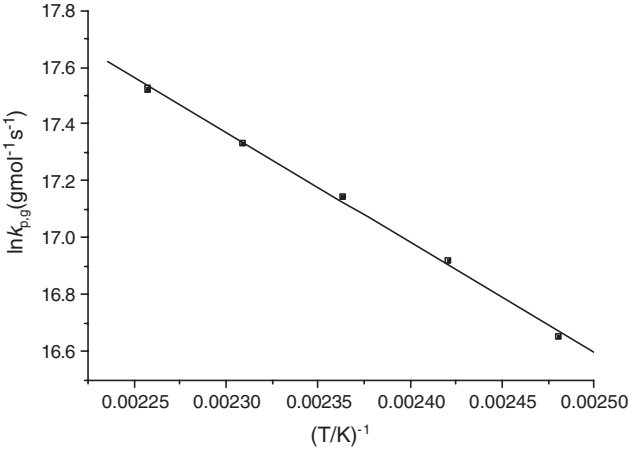

Fig. 7. Arrhenius plots of ln $k_{p,g}$ vs T^{-1} for grafting AA onto LLDPE(T). The feed monomer concentration is 2 wt%, the effective monomer concentration is 0.7 wt%, and the $C_{POOP,0}$ is 5.07×10^{-6} mol g^{-1}.

Table 3
Comparison between the measured $k_{p,g}$, A, E_a with data extrapolated from the solution polymerization

k_p (g mol^{-1} s$^{-1}\times10^7$)	T (°C)					E_a (kJ mol^{-1})	A (g mol^{-1} s$^{-1}\times10^9$)
	130	140	150	160	170		
$k_{p,g}$[a]	1.70	2.20	2.77	3.34	4.07	32.2	2391
$k_{p,extra}$[b]	16.7	18.2	19.8	21.5	23.2	12.0	6.34

[a] The feed monomer concentration is 2 wt%, the effective concentration of monomer is 0.7 wt%, and $C_{POOP,0}=5.07\times10^{-6}$ mol g^{-1}.
[b] The data were extrapolated from aqueous solution polymerization. The concentration of AA in solution is 40 wt% and temperature between 2.6 and 28.5 °C[16].

$k_{p,g}$ are plotted with T^{-1} (K^{-1}) in Fig. 7, and linear regression yields the Arrhenius expression in Eq. (18):

$$\ln\left[\frac{k_{p,g}}{\text{g mol}^{-1}\ \text{s}^{-1}}\right] = (26.2\pm0.22)-(3876.9\pm92.8)\left(\frac{T}{K}\right)^{-1} \quad (18)$$

The calculated frequency factor A is 2.39×10^{11} g mol^{-1} s^{-1} and activation energy E_A 32.2 kJ mol^{-1}.

The rate coefficient for the melt grafting reaction between macromolecular radicals, P$^{\cdot}$, and vinyl monomer AA could be estimated from the copolymerization of ethylene-AA [3] by using the Eq. (19)

$$k'_{p,g} = \frac{k_{p,e}}{r} \quad (19)$$

where $k_{p,e}$ and r are propagation rate coefficient for ethylene polymerization at high temperature and the reactivity ratio for ethylene-AA copolymenzation, respectively. The pressure, temperature and viscosity dependence $k_{p,e}$ had, been reported with the following expressions [15,32]:

$$k_{p,e}(T,P,\eta) = \frac{k^0_{p,e}}{1+\frac{k^0_{p,e}}{1.13\times10^{10}}\eta_r} \quad (20)$$

$$k^0_{p,e}(\text{l mol}^{-1}\ \text{s}^{-1}) = 1.88\times10^7\exp\left(\frac{-4126+0.33(\text{bar})}{T(\text{K})}\right) \quad (21)$$

where $k^0_{p,e}$, η_r, P and T are $k_{p,e}$ value at zero conversion, relative bulk viscosity, pressure and temperature, respectively. The parameters, P, 51 bar [15], η_r, 1×10^6 (obtained from the experiment [32]) and r, 0.015 [27] are used to calculate the theoretical value, $k'_{p,g}$, which is expressed in Arrhenius equation (Eq. (22))

$$\ln\left[\frac{k'_{p,g}}{\text{g mol}^{-1}\ \text{s}^{-1}}\right] = (26.5\pm0.06)-(3724.5\pm24.2)\left(\frac{T}{\text{K}}\right)^{-1} \quad (22)$$

Here, the frequency factor A is 3.23×10^{11} g mol^{-1} s^{-1} and activation energy E_A is 31.0 kJ mol^{-1}. It is evident that the values of $k_{p,g}$ are satisfactorily in agreement with those of $k'_{p,g}$, indicating that the technology combining ESR and FTIR can reliably measure the chain propagation rate coefficient in the melt.

Since, the values of $k_{p,h}$ and $k_{p,g}$ are the same ($=k_p$) in the solution graft copolymerization [5], it is interesting to examine if the propagation rate coefficient (k_p) of AA obtained from the solution polymerization at low temperature are fitting for $k_{p,g}$ in the melt. The data, k_p of AA in aqueous solution at concentration of 40 wt% and temperature between 2.6 and 28.5 °C [16] are extrapolated to 130–170 °C, and compared with $k_{p,g}$ in Table 3. Table 3 shows that the extrapolated data are 1 order of magnitude larger than the measured data, $k_{p,g}$, which indicates that it may be not entirely justified to use the data extrapolated from the solution polymerization at modest temperature to interpret the kinetics behavior in the melt. One possible reason may be the different viscosity of the reaction medium. The viscosity of a free radical grafting system in the melt can be several orders of magnitude (10^2–10^5 Pa s) higher than that in solution, and the high viscosity would impart more effects to the individual reaction step involved in grafting [3]. Besides, the possible presence of kinetics excluded volume effect, attributed to the polymeric molecular coil, acting as physical barrier, would prevent collisions from occurring between monomer and polymeric radicals [33] and thus decrease the $k_{p,g}$ value in the melt. Furthermore, the influence of solvent on the chain propagation rate coefficient is also a possible reason [14,16]. The apparent solution k_p may be different from $k_{p,g}$ in cases of polar intersegmental interactions. It has been reported that, because of hydrogen bonding between the monomers and between the solvent and carboxyl groups in the polar solvents, the acid exhibited an associated structure forming oligmeric associates and monomer–solvent association complexes [14,16], which would be result in higher reaction rate than that in the melt.

4. Conclusions

By combination ESR and FTIR measurement, we directly obtain the graft chain propagation rate coefficient, $k_{p,g}$ in the melt and expressed in Arrhenius equation

$$\ln\left[\frac{k_{p,g}}{\text{g mol}^{-1}\ \text{s}^{-1}}\right] = (26.2\pm0.22)-(3876.9\pm92.8)\left(\frac{T}{\text{K}}\right)^{-1}$$

here, the frequency factor A is calculated to be 2.39×10^{11} g mol^{-1} s^{-1} and activation energy E_A 32.2 kJ mol^{-1}. The magnitude of $k_{p,g}$ is in good agreement with the theoretical data deduced from ethylene-AA copolymerization, indicating

that the technology combining ESR and FTIR can reliably measure the chain propagation rate coefficient in the melt. The comparisons between the measured data, $k_{p,g}$ and those data, k_p, extrapolated from solution polymerization show that using the extrapolated data to discuss the kinetics behavior in the melt state might not be entirely justified.

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References

[1] Xanthos M. Reactive extrusion. New York: Oxford University Press; 1992 [chapter 1].
[2] Moad G. Prog Polym Sci 1999;24:81–142.
[3] Russell KE. Prog Polym Sci 2002;27:1007–38.
[4] Cha J, White JL. Polym Eng Sci 2001;41:1238–50.
[5] Huang N-J, Sundberg DC. J Polym Sci, Polym Chem 1995;33:2533–49.
[6] Guimon C. Radiat Phys Chem 1979;14:841–6.
[7] Silbert LS. Analyst 1992;117:745–9.
[8] Molochnikov LS, Kovalyova EG, Zagorodni AA, Muhammed M, Sultanov M, Efendiev AA. Polymer 2003;44:4805–15.
[9] Woliska-Grabczyk A. Polymer 2004;45:4391–402.
[10] Ulin J, Andreis M, Veksli Z, Gallot Y. Polymer 2003;44:7875–81.
[11] Culin J, Smit I, Andreis M, Veksli Z, Anzlovar A, Zigon M. Polymer 2005;46:89–99.
[12] Tonge MP, Kajiwara A, Kamachi M, Gilbert RG. Polymer 1998;39: 2305–13.
[13] Buback M, Kowollik C, Kajiwara A, Kamachi M. Macromolecules 1998; 31:7208–12.
[14] Kuchta F-DA, Van Herk AM, German AL. Macromolecules 2000;33: 3641–9.
[15] Beuermann S, Buback M. Prog Polym Sci 2002;27:191–254.
[16] Laci'k I, Beuermann S, Buback M. Macromolecules 2001;34:6224–8.
[17] Yang J, Yao Z, Shi D, Huang H, Wang Y, Yin J. J Appl Polym Sci 2001; 79:535–43.
[18] Kulik EA, Ivanchenko MI, Kato K, Sano S, Ikada Y. J Polym Sci, Polym Chem 1995;33:323–30.
[19] Shi Q, Zhu LC, Cai CL, Yin JH, Costa G. J Appl Polym Sci; in press.
[20] Sahetchian KA, Rigny R, Blin N, Heiss A. J Chem Soc, Faraday Trans 1987;83:2035–43.
[21] Yamazaki T, Seguchi T. J Polym Sci Polym Chem 1997;35:279–84.
[22] Oliphant KE, Russell KE, Baker WE. Polymer 1995;36:1597–603.
[23] Mair MD, Graupner A. J Anal Chem 1964;36:194–204.
[24] Kim S, Kim JK, Park CE. Polymer 1997;38:1809–15.
[25] Kim JK, Yi DK, Jeon HK, Park CE. Polymer 1999;40:2737–43.
[26] Spychaj T, Hamielec AE. J Appl Polym Sci 1991;42:2111–9.
[27] Brandrup J, Immergut EH, Grulke EA.. 4th ed Polymer handbook, vol. II. New York: Willey; 1999 p. 282.
[28] Nath SK, De Pablo JJ. J Phy Chem, B 1999;103:3539–44.
[29] Prut EV, Zelenetskii AN. Russ Chem Rev 2001;70:65–79.
[30] Cartier H, Hu GH. J Polym Sci, Part A: Polym Chem 1998;36:1053–63.
[31] Kitaeva NK, Zamyslov RA, Dyakova MG, Shevlyakova NV, Tverskoi VA, Dobrov IV. Vysokomolekulyarnye Soedineniya Krarkie Soobshcheniya 1990;32:746–9.
[32] Buback M, Schweer J. Z Phys Chem NF 1989;161:153–65.
[33] Ferrari DF, Baker WE. J Polym Sci, Part A: Polym Chem 1998;36: 1573–82.