# Kinetics Study on Melt Grafting Copolymerization of LLDPE with Acid Monomers Using Reactive Extrusion Method

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**ABSTRACT:** Graft copolymerization in the molten state is of fundamental importance as a probe of chemical modification and reactive compatibilization. However, few grafting kinetics studies on reactive extrusion were carried out for the difficulties as expected. In this work, the macromolecular peroxide-induced grafting of acrylic acid and methyl methacrylate onto linear low density polyethylene by reactive extrusion was chosen as the model system for the kinetics study; the samples were taken out from the barrel at five ports along screw axis and analyzed by FTIR, $^1$H NMR, and ESR. For the first time, the time-evolution of reaction rate, the reaction order, and the activation energy of graft copolymerization and homopolymerization in the twin screw extruder were directly obtained. On the basis of these results, the general reaction mechanism was tentatively proposed. It was demonstrated that an amount of chain propagation free radicals could keep alive for several minutes even the peroxides completely decomposed and the addition of monomer to polymeric radicals was the rate-controlled step for the graft copolymerization. The results presented here revealed that the relative importance of graft copolymerization compared with homopolymerization mainly depended on the monomer solubility and reactivity, while the process parameters such as reaction temperature also influenced the reaction tendency. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 4301–4312, 2006

**Key words:** electron beam irradiation; graft copolymerization; kinetics; reactive extrusion

## INTRODUCTION

The functionalization of polyethylene (PE) through grafting unsaturated monomers such as maleic anhydride (MAH), acrylic acid (AA), and its derivatives, in the presence of organic peroxide as an initiator, has received much attention over the past decades. Functionalized PE has been prepared successfully by using solution,[1] melt,[2–4] and solid state routes.[5] Properties such as adhesion, environmental stress cracking resistance, thermo-oxidative stability, ion-exchange capacity, etc., may be notably improved by such modifications. Functionalized PE are also widely recognized as novel, potential additives to improve the compatibilizing influence in binary or multicomponent polymer blends, and they are finding increasing use in reactive blending.[2,6]

Most of the studies carried out in the melt so far have focused on the influence of reaction parameters, the degree of functionalization and optimal properties achieved,[3,7–9] and on the determination of the nature of grafted unit.[10] Melt processing of PE is often accompanied by side reactions such as crosslinking of PE and homopolymerization of graft monomer and many efforts have been made to enhance degree of grafting and reduce the side reactions.[3,7,8] Grafting MAH onto PE molecular chains was initially studied by Gaylord and Mehta.[7] They proposed that the presence of nitrogen-, phosphorous-, and sulfur-containing organic electron donors would help to prevent crosslinking of PE and homopolymerization of MAH. Previous work in our laboratory[8] also showed that *p*-benzoquinone, triphenyl phosphate, and tetrachloromethane were good inhibitors for crosslinking of LDPE. Recent work made by Pesneau et al.[9] who studied grafting glycidyl methacrylate onto linear low density polyethylene (LLDPE) reported that the high graft degree (GD) could be obtained by a proper selection of the feed composition and process parameters.

Little work has been done on the grafting copolymerization kinetics in the melt state. The conditions for melt grafting copolymerization usually involve relatively high temperature and viscosity, the former has proved to influence rate constants for various initia-

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tion and propagation reactions while the latter has distinctive effect on the rate of initiation and termination since the melt grating copolymerization is typical diffusion-controlled processes.[3] These complications render systematic studies on melt free-radical grafting difficult, especially for the system whose grafting monomer can homopolymerize under the typical grafting conditions. To obtain a better understanding of the true intrinsic chemical kinetics of graft and homopolymerization, Wong Shing et al. studied the kinetics on grafting of 2-(dimethylamino) ethyl methacrylate to model hydrocarbons and LLDPE in the temperature range from 130 to 170°C.[11,12] They separated the overall rate of loss of monomer into parts, one due to grafting and the other due to the formation of homopolymer. Their reports showed that both grafting and homopolymerization were a half order dependence on initiator concentration at 130–160°C, with a constant activation energy of 120 ± 10 kJ $\text{mol}^{-1}$ for production of the grafted product onto model hydrocarbons, and the order with respect to monomer was ~0.66 for the grafting process but varied from 1.4 to 2 for the homopolymerization at 150°C. The authors attributed these results to the different reaction pathway for graft copolymerization and homopolymerization.[12] They also pointed that the conclusions obtained from model compounds would apply to LLDPE melt grafting reaction. Since graft copolymerization and homopolymerization are occurring simultaneously, each can influence the other, particularly through the occurrence of cross-termination reactions, and it is thus an oversimplification to treat the two processes separately.[12] However, the analysis leads to clear understandings for grafting and homopolymerization during functionalization. Ghosh et al. studied graft copolymerization of low density PE with AA, ethyl acrylate, and butyl acrylate initiated by dicumyl peroxide (DCP) using differential scanning calorimetry (DSC) under the dynamic condition. They reported that, for each monomer system, the overall reaction (including grafting and homopolymerization) was first order with respect to monomer concentration and the observed activation energy lied in the range of 150–170 kJ $\text{mol}^{-1}$.[13] There was disagreement between these two studies concerning the reaction order with respect to monomer concentration and reaction mechanism involved in the grafting process. Thus, the detailed knowledge of reaction kinetics in the melt can be useful to understand completely the overall reactions, which take place during the functionalization. Moreover, an insight into the reaction mechanism and kinetics would help to devise process conditions so as to minimize the side reactions while at the same time maximizing the graft degree (GD) to achieve optimal product properties.

The aim of the present work is to study the reaction kinetics including graft copolymerization and homopolymerization in the melt. For this purpose, the grafting of AA and methyl methacrylate (MMA) onto preirradiated LLDPE by reactive extrusion is chosen as the model system. AA and MMA are chosen for they are well documented in the literature[8,14] and the difference in reactivity and solubility in melt LLDPE.[15] To determine the evolution of the graft copolymerization and homopolymerization, a special twin-screw extruder is adopted to satisfy sampling at specified reaction time and to control reaction parameters. The reaction rate for the graft copolymerization and homopolymerization and their evolution with time and temperature are systematically studied. The effects of monomer solubility, reactivity, and reaction temperature are discussed to interpret the aforementioned results. The reaction activation and the order of reaction rate with respect to irradiation dose and monomer concentration are also studied. On the basis of the experimental results, the possible mechanism of graft copolymerization and homopolymerization are tentatively proposed.

## EXPERIMENTAL

### Materials

LLDPE (DFDA-7042) with butene content of 6 ± 0.5 wt % was provided by Jilin Chemical (People's Republic of China). Its melt flow rate is 1.02 g/10 min (ASTM D 1238), with the weight–average molecular weight ($\overline{M}_w$) of $1.17 \times 10^5$ and polydispersity ($\overline{M}_w/\overline{M}_n$) of 3.44.

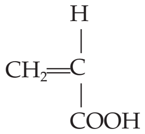
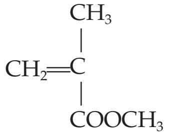
LLDPE was irradiated by the electron beam (EB) in the air at about 25°C, with the electron energy of 2.5–3 MeV, dose rate of 1.1 kGy $\text{s}^{-1}$ and total dose in the range of 15–45 kGy. The peroxides (POOH and POOP) generated after irradiation.[16]

AA and MMA were supplied by Tian Jin Institute of Chemical Reagents (People's Republic of China). They were distilled under reduced pressure before use. Acetone, xylene, and *n*-heptane were reagent grade and used without any further purification. The physical properties of monomer and LLDPE are tabulated in Table I.

### Determination of peroxides density and decomposition rate constants

The concentration of POOH was determined by Iodimetric analysis.[17,18] This method was based on the oxidation of sodium iodide by peroxides in the presence of ferric chloride. About 50 mg powder of irradiated LLDPE with an average diameter of about 50 μm was swollen in 2 mL xylene in the 25 mL ampoule for 2 days, then isopropyl alcohol (12 mL), 0.8 mL of 0.123 m*M* $\text{Fecl}_3$ in acetic acid, and 0.4 mL of 1.33*M* NaI in isopropyl alcohol were added to the ampoules. After degassing with nitrogen bubbling for 10 min and

**TABLE I**
**Physical Character and Solubility Parameter of Monomer and LLDPE**

| Monomer | Chemical structure | Molecular weight ($M_w$) | Density (g cm$^{-3}$) (20°C) | Melt point (°C) | Boiling point (°C) | Solubility parameter (MPa$^{1/2}$) |
|---|---|---|---|---|---|---|
| AA |  $\mathrm{CH_2{=}C(H)COOH}$ | 72.06 | 1.051 | 13 | 139 | 24.6 |
| MMA |  $\mathrm{CH_2{=}C(CH_3)COOCH_3}$ | 100.12 | 0.936 | −48 | 100 | 18.0 |
| Polyethylene | | $1.17 \times 10^5$ | 0.92 | | | 16.5 |

sealing, the ampoules were heated at 60°C for 30 min and then 2 mL water was added to stop the redox reaction. POOH rapidly react with iodide ion at room temperature, whereas dialkyl peroxides (POOP) were unreactive even with $Fe^{3+}$ catalysis or elevated temperature.[18] The concentration of POOH was calculated from the optical density of the solution at 360 nm.[17]

About 2 g powder of irradiated LLDPE was treated by iodide ion according to the aforementioned procedure , then the treated powder was filtered by vacuum and washed with isopropyl alcohol for 5 times and dried to the constant weight in a vacuum oven at 60°C. From now on, these dried samples were called treated LLDPE. The concentration of POOP was determined by a Perkin–Elmer DSC-7 DSC measurement. The sample was encapsulated in a hermetically sealed pan of the DSC instrument and heated from 20 to 250°C at a rate of 5 K/min under a cover of flowing nitrogen gas at a flow rate of 80 mL min$^{-1}$ The concentration of POOP was determined by using the following procedure: The LLDPE and DCP were mixed homogenously in the minimiller with the known DCP concentration, $C_D$ (mol g$^{-1}$). Then the enthalpy change of mixture, $\Delta H_M$ (J g$^{-1}$), and that of neat LLDPE, $\Delta H_N$, were obtained by DSC experiments, thus the referential enthalpy change $\Delta H_R$ (J mol$^{-1}$) was calculated by the ratio of enthalpy change difference between the mixture and neat LLDPE to the DCP concentration.

$$\Delta H_R = (\Delta H_M - \Delta H_N)/C_D \qquad (1)$$

Similarly, the enthalpy difference $\Delta H_{T,N}$ ($\Delta H_T - \Delta H_N$) between treated LLDPE and the neat LLDPE were obtained by DSC. To avoid the influence of branch, the program that the samples were fixed at 80°C for 2 h was added to the whole program. Thus, the concentration of POOP can be obtained by the ratio of $\Delta H_{T,N}$ to $\Delta H_R$.

$$C_{\mathrm{POOP}} = (\Delta H_T - \Delta H_N)/\Delta H_R \qquad (2)$$

The irradiated LLDPE and treated LLDPE were annealed for various times at temperature range from 100 to 200°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 $k_{d,\mathrm{POOH}}$ and $k_{d,\mathrm{POOP}}$, and the value of $k_{d,\mathrm{POOH}}$ was in good agreement with that obtained by God'dberg et al.[19] and the value of $k_{d,\mathrm{POOP}}$ was slightly higher than that of diheptylperoxide[20] at each temperature. The concentration and half-time of the peroxides at each temperature are listed in Table II.

**TABLE II**
**The Concentration and Half-Time of Peroxides**

| | Dose (kGy) | Concentration ($10^{-6}$ molg$^{-1}$) | Half-time (s) 100°C | 170°C | 180°C | 190°C | 200°C | 210°C |
|---|---|---|---|---|---|---|---|---|
| POOH | 15 | 1.40 | 100,236 | 135.3 | 62.2 | 29.6 | 14.5 | 7.32 |
| | 30 | 1.75 | | | | | | |
| | 45 | 2.05 | | | | | | |
| POOP | 15 | 5.07 | 286,320 | 154.8 | 63.9 | 27.4 | 12.2 | 5.59 |
| | 30 | 6.86 | | | | | | |
| | 45 | 8.95 | | | | | | |

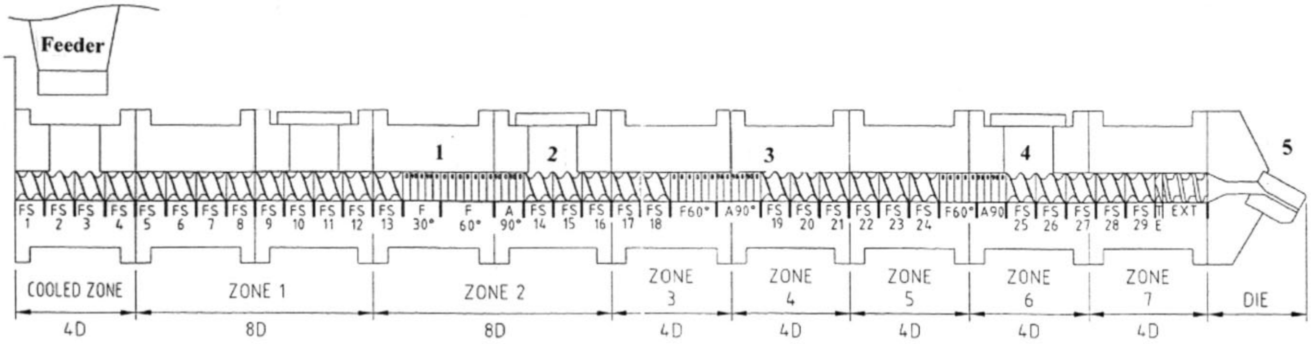


**Figure 1** Screw profile of the corotating twin-screw extruder and sampling ports (shown in number).

### Twin-screw extruder system

Graft reactions of LLDPE with AA and MMA were carried out in a Rheomex PTW24/40p modular twin-screw extruder (RC500P Germany), shown in Figure 1. The diameter of two screws is 24 mm and the ratio of length to diameter ($L/D$) is 40. The maximum torque is 180 N m. The barrel of the extruder is divided into 7 segments and each segment is heated independently, the fluctuation of process temperature is within ±0.1°C, the set temperature at each segment and the exit die are listed in Table III. When the twin screw extruder reached the preset temperature, the premixed monomer and LLDPE were fed into the hopper using metering feeder. To keep the polymer-melt temperature with the preset temperature, the experiments were performed at relative low screw speed (50 rpm) and feed speed (3.13 kg $h^{-1}$). After the extruder was in a steady state, samples were taken rapidly (less than 5 s) from 5 locations along the screw axis (shown in Fig. 1) with a special nylon tool and immediately quenched in liquid nitrogen to stop any further reaction. The samples remained in liquid nitrogen until they were measured by electron spin resonance (ESR), then they were reserved in silicagel desiccator at room temperature for 48 h before purification. The initial melt time of polymer was generally accepted as the origin of reaction $T_{\mathrm{Im}}$,[21] and the melt process of polymer was determined by the change of pellet size.[22] In this work, the change of pellet size was directly observed along the screw after splitting the barrel. The mean residence time of reaction medium corresponding to each port $T_{\mathrm{re}}$ was accurately measured according to the procedure suggested by Chen et al.[23] and the reaction time at each sample port $T_r$ was determined by eq. (3):

$$T_r = T_{\mathrm{re}} - T_{\mathrm{lm}} \tag{3}$$

$T_r$, $T_{\mathrm{re}}$, and $T_{\mathrm{Im}}$ at each port are summarized in Table III.

### Separation of grafted LLDPE copolymer

About 2 g of raw sample was dissolved in 100 mL boiling *n*-heptane, and then the solution was poured into in 400 mL acetone with stirring to precipitate the grafted LLDPE. The precipitate was filtered by vacuum and washed with acetone for five times, then dried to the constant weight in a vacuum oven at 60°C. The unreacted monomer and homopolymer formed during reactive extrusion remained in the mother liquor, and the homopolymer was recovered by removing the mixture of acetone and *n*-heptane under 0.02 MPa in the vacuum oven.

### FTIR and $^1$H NMR analysis

The formation of LLDPE-*g*-AA and MMA was confirmed by using FTIR and $^1$H NMR. A BIO-RAD FTS-135 IR spectrometer was adopted. Its resolution is 4 $cm^{-1}$ and the scan number is 5. Samples were prepared by solution casting method on NaCl plate. The film thickness is about 0.10 mm.

The $^1$H NMR spectrum of the sample was recorded on a Bruker AV400 with $C_6D_4Cl_2$ as a solvent. The best experiment conditions were as follows: SWH, 4194.6 Hz; relaxation time, 8.00 s; 90° pulse (P1), 6.8 $\mu$s.

### ESR analysis

The concentrations of the radical species in the systems of grafting AA and MMA onto LLDPE were determined by ESR spectroscopy with a Bruker ESP 300 spectrometer at −196°C. The samples were cut into strips and introduced in 3-mm diameter ESR tubes that were purged with Ar and sealed. During each measurement, several spectra were recorded and the concentration of free radicals was obtained from the individual ESR spectra by double integration. To deduce absolute free-radical concentrations, ESR spectra of precisely known amounts of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPOL) dispersed in LLDPE were measured at −196°C before each mea-

**TABLE III**
**Temperature Profile and Mean Residence Time, Initial Melt Time, and Reaction Time at Each Sampling Port**

| $T$ (°C) | Temperature profile (°C) | Sampling port[a] | Mean residence time (s) | Initial melt time (s) | Reaction time (s) |
|---|---|---|---|---|---|
| 170 | 160/170/170/170/170/170/170/170 | 1 | 18 | 20 | – |
| | | 2 | 68 | | 48 |
| | | 3 | 92 | | 72 |
| | | 4 | 133 | | 113 |
| | | 5 | 204 | | 184 |
| 180 | 170/180/180/180/180/180/180/180 | 1 | 18 | 18 | – |
| | | 2 | 68 | | 50 |
| | | 3 | 92 | | 74 |
| | | 4 | 133 | | 115 |
| | | 5 | 204 | | 186 |
| 190 | 180/190/190/190/190/190/190/190 | 1 | 18 | 14 | 4 |
| | | 2 | 68 | | 54 |
| | | 3 | 92 | | 78 |
| | | 4 | 133 | | 119 |
| | | 5 | 204 | | 190 |
| 200 | 190/200/200/200/200/200/200/200 | 1 | 18 | 14 | 4 |
| | | 2 | 68 | | 54 |
| | | 3 | 92 | | 78 |
| | | 4 | 133 | | 119 |
| | | 5 | 204 | | 190 |
| 210 | 200/210/210/210/210/210/210/210 | 1 | 18 | 12 | 6 |
| | | 2 | 68 | | 56 |
| | | 3 | 92 | | 80 |
| | | 4 | 133 | | 121 |
| | | 5 | 204 | | 192 |

[a] The Feed Speed is 3.13 kg h$^{-1}$ and the screw speed is 50 rpm.

surement.[24] The best conditions were as follows: microwave frequency, 9.2 GHz; modulation frequency, 1 00 kHz; modulation amplitude, 10 G; time constant, 30 ms; sweep time, 2 min; power, 1 mW; receiver gain, 3 × 10$^5$; and scan number, 5.

### Determination of GD and mass of homopolymer

The GD and mass of homopolymer (MH) are defined as follows:

$$\mathrm{GD\ (wt\%)} = \frac{m_g}{M} \times 100 \tag{4}$$

$$\mathrm{MH\ (wt\%)} = \frac{m_h}{M} \times 100 \tag{5}$$

where $M$, $m_g$, and $m_h$ are the mass of polymer matrix, grafted monomer, and homopolymer of monomer, respectively.

The GD and MH were determined by the FTIR spectra.[8] The calibration equations were obtained by using following procedure: A series of blends of LLDPE/PAA and LLDPE/PMMA with different composition were prepared using solution casting method. FTIR spectrometer were adopted to analyze the blend films to get the optical density ratios of the carbonyl band of PAA (or PMMA) and the methyl rocking band due to butene units in LLDPE. By comparing the absorbency of the carbonyl band to the methyl rocking band with the same ratio obtained for mixtures of LLDPE/homopolymer of known composition,[25] the calibration curves to determine monomer content in LLDPE could be obtained and shown as follows:

$$M_{c,\mathrm{AA}}\ (\mathrm{wt\%}) = 1.77 A_{1716}/A_{1379} \tag{6}$$

$$M_{c,\mathrm{MMA}}\ (\mathrm{wt\%}) = 1.70 A_{1732}/A_{1379} \tag{7}$$

where $M_{c,i}$ denotes the content of $i$ monomer, $A_{1716}$, $A_{1732}$, and $A_{1379}$ are absorbent peak area of carbonyl of graft AA, MMA, and methyl of LLDPE, respectively.

The coarse and purified samples of each reaction system were dissolved in $n$-heptane in a concentration of 2% and filmed on the NaCl plate, respectively. With the FTIR measurement, the content of converted monomers ($m_g + m_h$), $M_{c,\mathrm{coase}}$ (%), in coarse film and grafted monomers ($m_g$), $M_{c,\mathrm{graft}}$ (%) in purified film can be obtained. Thus, GD and MH are determined by following equations:

$$\mathrm{GD\ (wt\%)} = M_{c,\mathrm{graft}}\ (\%) \tag{8}$$

$$\mathrm{MH\ (wt\%)} = M_{c,\mathrm{coase}}\ (\%) - M_{c,\mathrm{graft}}\ (\%) \tag{9}$$

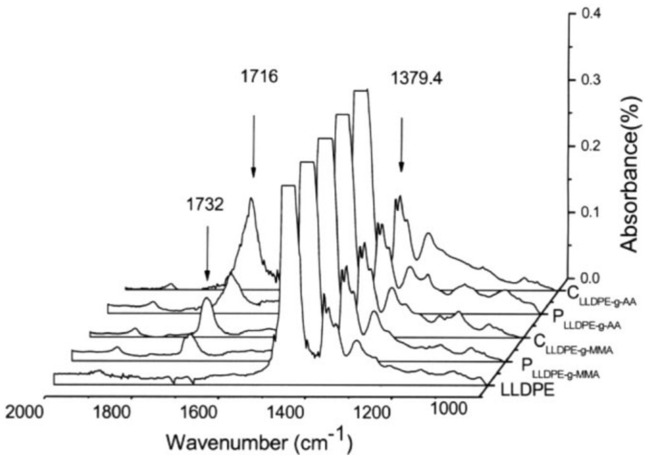


**Figure 2** FTIR spectra of LLDPE, coarse, and purified LLDPE-*g*-AA and LLDPE-*g*-MMA.

## RESULTS

### Evidence for graft copolymerization and homopolymerization

Figure 2 shows representative IR spectra of LLDPE, coarse, and purified LLDPE-*g*-AA and LLDPE-*g*-MMA. To compare the characteristic peak intensity of the coarse and purified samples, the absorbance peaks were normalized with the intensity of the methyl band of LLDPE at 1379 cm$^{-1}$. The new peaks at 1716 and 1732 cm$^{-1}$ in the purified sample that have been attributed to carbonyl group ($C{=}O$) stretch vibration of grafted AA and grafted MMA were qualitative evidence of grafting in the melt.[8,26] The peak area of the coarse sample was higher than that of purified sample for each graft system, indicating that the homopolymerization has occurred during grafting process.

Figure 3 shows the $^1$H NMR spectra of LLDPE, purified LLDPE-*g*-AA, and LLDPE-*g*-MMA. For unmodified LLDPE, the functional groups —$CH_3$ (δ: 1.2–1.4 ppm), —$CH_2$— (δ: 1.0–1.6 ppm), —CH— (δ: 0.8–1.0 ppm) can be observed. The $^1$H NMR spectrum of LLDPE-*g*-AA shows new peaks at 2.0–2.4 ppm in addition to the original —$CH_3$ and —$CH_2$— peaks of the unmodified LLDPE. The appearance of peaks is due to AA grafted onto the main or branch chain of LLDPE skeleton.[26] The resonance of the α-methylene —$CH_2$(OOH) protons is not observed, suggesting that the chain transfer reaction is not dominant termination mode. By comparing the integral of the resonance of the α-methine —CH(OOH)— protons at 2.35 ppm with that of the methylene —$CH_2$— protons at 1.0–1.6 ppm, the average number of AA units per $10^4$ carbon backbone is estimated to be 1.7, which is consistent with the results obtained by FTIR. For LLDPE-*g*-MMA, the new peaks at 3.64 ppm and about 2.30 ppm

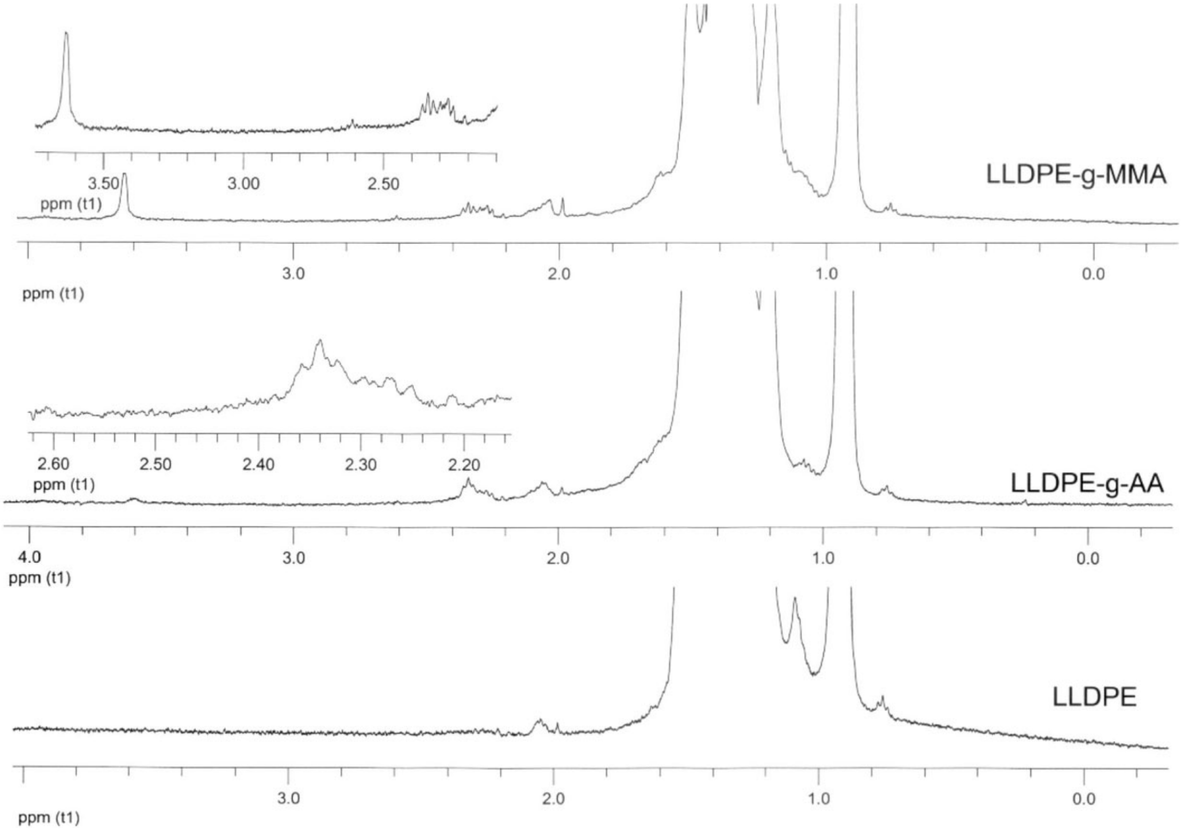


**Figure 3** The $^1$H NMR spectra of LLDPE, purified LLDPE-*g*-AA, and LLDPE-*g*-MMA.

**TABLE IV**
**The Experimental Conditions and Kinetic Data for Grafting AA onto LLDPE**

| Runs | T (°C) | Irradiation dose (kGy) | Monomer concentration ($10^{-4}$ mol g$^{-1}$) | Reaction rate ($10^{-4}$ mol g$^{-1}$ s$^{-1}$) $R_g$ | $R_h$ | Final product (%) GD | MH |
|---|---|---|---|---|---|---|---|
| A | 170 | 15 | 7.5 | 0.62 | 0.10 | 0.65 | 0.22 |
| | 180 | 15 | 7.5 | 1.36 | 0.23 | 0.83 | 0.35 |
| | 190 | 15 | 7.5 | 2.91 | 0.48 | 1.10 | 0.48 |
| | 200 | 15 | 7.5 | 6.01 | 0.99 | 1.31 | 0.66 |
| | 210 | 15 | 7.5 | 12.0 | 1.95 | 1.58 | 0.93 |
| B | 190 | 15 | 7.5 | 2.91 | 0.48 | 1.11 | 0.48 |
| | 190 | 30 | 7.5 | 3.96 | 0.66 | 1.18 | 0.57 |
| | 190 | 45 | 7.5 | 5.39 | 0.89 | 1.26 | 0.61 |
| C | 190 | 15 | 1.5 | 0.68 | 0.18 | 0.41 | 0.18 |
| | 190 | 15 | 2.0 | 1.17 | 0.22 | 0.49 | 0.23 |
| | 190 | 15 | 2.5 | 1.50 | 0.34 | 0.52 | 0.30 |
| | 190 | 15 | 3.0 | 1.80 | 0.37 | 0.59 | 0.33 |
| | 190 | 15 | 3.5 | 2.53 | 0.43 | 0.63 | 0.38 |

were observed. The new peaks at 3.64 ppm has been assigned to the H of the ester group ($OCH_3$),[27] and the peaks about 2.30 ppm is attributed to the proton of $\alpha$-methine —($CH_3$)CH(COOH), which indicates that the graft chain is terminated by chain transfer.[11,12] By comparing the integral of the resonance of the —$OCH_3$ protons with that of the $\alpha$-methine protons, the length of grafted chain is estimated to be 1. The average number of MMA units per $10^4$ carbon backbone is obtained to be 1 by comparing the integral of the resonance of the —$OCH_3$ protons with that of the methylene —$CH_2$— protons, and this result is in agreement with that obtained by FTIR. These features suggest that LLDPE-*g*-AA and LLDPE-*g*-MMA are formed by adopting the method of the reactive grafting processing.

## Kinetics studies of AA grafting onto LLDPE

Rates of grafting reaction and homopolymerization for AA were determined in the temperature range 170–210°C. The monomer concentration varied from 0.15 to 1.12 mmol g$^{-1}$ and irradiation dose ranged from 15 to 45 kGy. A typical set of experimental data for a high monomer concentration (0.72 mmol g$^{-1}$) and a low irradiation dose (15 kGy) in the 170–210°C temperature range is tabulated in A series of Table IV and the time-evolution of GD and MH is shown in Figure 4. It is clear from Figure 4 that the GD increased linearly with the reaction time over the first 75% or so of reaction and the MH increased in proportion with the reaction time about 80% of homopolymerization, then the reaction rate increased gradually. The data in A series of Table IV show that the rate of graft copolymerization and homopolymerization increases with increasing temperature and the rate of graft copolymerization is higher than that of homopolymerization. The activation energy estimated from these data is 132 kJ mol$^{-1}$ for graft copolymerization and 130 kJ mol$^{-1}$ for polymerization of AA, which are in agreement with the result of 120 kJ mol$^{-1}$ observed by Wong Shing et al.[12] and 150–170 kJ mol$^{-1}$ observed by Ghosh et al.[13] and are of the right magnitude for a chain reaction in which the initiation reaction has an activation energy of about 160 kJ mol$^{-1}$.[28]

To achieve the reaction order of reaction rate with respect to monomer concentration and irradiation dose, the dependence of initial reaction rate on the feed monomer and irradiation dose is investigated.[14] And the initial rates of graft copolymerization and homopolymerization were obtained from the slopes of the curves in the linear portion of the reaction.[29] The feed monomer and irradiation dose were used because the time-evolution concentration of monomer

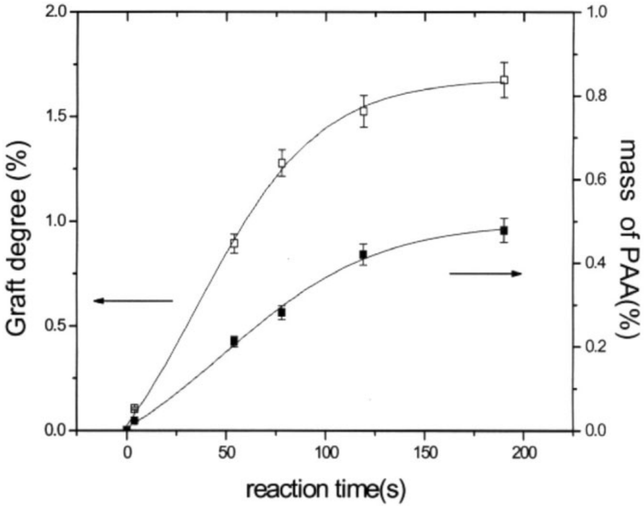


**Figure 4** The time evolution of GD and MH for grafting of AA to LLDPE. Irradiation dose is 15 kGy, the monomer concentration is 0.75 mmol g$^{-1}$, and the reaction temperature is 190°C.

**TABLE V**
**The Experimental Conditions and Kinetic Data for Grafting MMA onto LLDPE**

| Runs | $T$ (°C) | Irradiation dose (kGy) | Monomer concentration ($10^{-4}$ mol g$^{-1}$) | Reaction rate ($10^{-5}$ mol g$^{-1}$ s$^{-1}$) |  | Final product (%) |  |
|---|---|---|---|---|---|---|---|
|  |  |  |  | $R_g$ | $R_h$ | GD | MH |
| A | 170 | 15 | 6.0 | 3.70 | 1.01 | 0.49 | 0.19 |
|  | 180 | 15 | 6.0 | 8.81 | 2.20 | 0.52 | 0.34 |
|  | 190 | 15 | 6.0 | 20.0 | 4.70 | 0.67 | 0.52 |
|  | 200 | 15 | 6.0 | 44.1 | 4.02 | 0.79 | 0.34 |
|  | 210 | 15 | 6.0 | 93.9 | 3.22 | 0.83 | 0.32 |
| B | 180 | 15 | 6.0 | 8.81 | 2.20 | 0.52 | 0.34 |
|  | 180 | 30 | 6.0 | 17.58 | 4.11 | 0.60 | 0.38 |
|  | 180 | 45 | 6.0 | 26.30 | 6.52 | 0.68 | 0.40 |
| C | 180 | 15 | 1.5 | 1.14 | 0.57 | 0.12 | 0.08 |
|  | 180 | 15 | 2.0 | 1.98 | 0.77 | 0.19 | 0.14 |
|  | 180 | 15 | 2.5 | 2.53 | 1.01 | 0.24 | 0.17 |
|  | 180 | 15 | 3.0 | 3.35 | 1.16 | 0.30 | 0.19 |
|  | 180 | 15 | 3.5 | 4.15 | 1.36 | 0.34 | 0.21 |

and initiator at reaction site could not be accurately measured for the heterogeneous system with high viscosity. It should be pointed out that the effective concentrations of monomer and initiator participating in the reaction are not the feed concentrations in the melt state, while the effective concentrations should go linearly with the feed concentrations under certain conditions.[21,28] In the experiment, the reaction rate changed distinctly with initiator concentration (irradiation dose from 15 to 45 kGy) when the monomer concentration is stationary, and with the feed monomer concentration (in the range of 0.15–0.84 mmol g$^{-1}$) when the irradiation dose is steady. Thus, the experiments with three irradiation doses (15–45 kGy) and excess monomer concentration (0.72 mmol g$^{-1}$) and those with five monomer concentrations (from 0.15 to 0.35 mmol g$^{-1}$) and irradiation dose 15 kGy were performed at 190°C, respectively. We assume that the ratio of effective monomer concentration to feed monomer concentration is constant when the monomer concentration is in the range from 0.15 to 0.35 mmol g$^{-1}$. The experiment results are tabulated in B and C series of Table IV. The order of graft reaction with respect to irradiation dose is about 0.55, and the order of homopolymerization to irradiation dose is also nearly 0.55, a result typical of chain reactions in which radicals disappear in pairs.[28] The order of graft reaction with respect to AA concentration is estimated to be 1.46, one possible explanation is that the addition of graft monomer to polymeric radicals is a slow step.[12] The order of homopolymerization to AA concentration is 1.08, the same result with the normal free-radical polymerization.[28]

## Kinetics studies of MMA grafting into LLDPE

The graft copolymerizations of MMA onto LLDPE were performed in the temperature range 170–210°C. The monomer concentration varied from 0.15 to 0.80 mmol g$^{-1}$ and irradiation dose ranged from 15 to 45 kGy. The typical set of experimental data for a high monomer concentration (0.60 mmol g$^{-1}$) and a low irradiation dose (15 kGy) in the temperature from 170 to 210°C is summarized in A series of Table V and the time-evolution of GD and MH is shown in Figure 5. Similar to AA, the graft copolymerization and homopolymerization of MMA exhibit two regimes, the linear and flat stage. The rate of graft copolymerization is higher than that of homopolymerization, and the reaction rate is lower than that in AA graft copolymerization. The rate of graft copolymerization increased with increasing temperature, but the homopolymerization rate increased with temperature until 190°C, and then decreased with further increasing reaction temperature, which indicated that the ceiling temperature for MMA polymerization under present conditions should be in the region of 190°C. The acti-

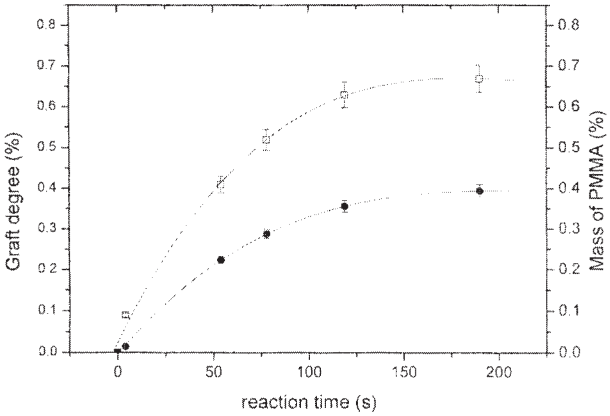


**Figure 5** Time evolution of GD and MH for grafting of MMA into LLDPE. Irradiation dose is 15 kGy, the monomer concentration is 0.60 mmol g$^{-1}$ and the reaction temperature is 180°C.

vation energy of 144 kJ $mol^{-1}$ is calculated for the graft copolymerization (170°C $\leq T \leq$ 210°C) and 130 kJ $mol^{-1}$ for polymerization of MMA (170°C $\leq T \leq$ 190°C). These results are slightly higher than those for AA grafting system, which may in part due to the steric hindrance effect on monomer reactivity.[28]

To obtain the reaction order with respect to the concentration of monomer and irradiation dose, the experiments with three irradiation doses (15–45 kGy) and excess monomer concentration (0.60 mmol $g^{-1}$) and those with five monomer concentrations (from 0.15 to 0.35 mmol $g^{-1}$) and irradiation dose 15 kGy were performed at 180°C, respectively, in which the difference of reaction rate can be distinctly observed. The series of B and C in Table V summarize the results of the aforementioned experiments. The order of graft copolymerization with respect to the irradiation dose is estimated to be 0.99, and the order of homopolymerization to irradiation dose about 0.98, which is consistent with the chain transfer termination mechanism.[30] The order of graft copolymerization with respect to MMA concentration is estimated to be 1.49, and the order of homopolymerization to MMA concentration is nearly 1, the similar results with those of AA.

### The concentration of propagation free radicals

In the experiment, two kinds of ESR spectra were observed, one was a large singlet ($g \approx 2.0298$) covering several hundred gauss (G) line width, the other was a multiple-line spectrum ($g \approx 2.004$ for LLDPE/AA system and $g \approx 2.0035$ for LLDPE/MMA system) with the thin line width (several G). Singlet signal have been observed previously in air-irradiated PE and have been assigned to either peroxy[31] or polyenyl radicals.[30] For the high temperature, we believe the singlet we observe results from the peroxy radical mostly. The thin multiple-line has been assigned to chain propagation free radicals, PM·. It should be pointed that the alkyl free radicals that showed six-line spectra with several G[32] might overlap the spectra of propagation free radicals. To separate these two spectra, the blank experiments performed at 190°C were made. Under the same experiment conditions as that of graft copolymerization, the irradiated LLDPE without blending with monomer was feed into the twin-screw extruder, sampled, and then analyzed by ESR. No six-line spectrum was observed, indicating that the multiline spectra were only attributed to the spectra of chain propagation free radicals. As the reaction progress was one of focuses of this study, more attention was paid to the propagating free radicals. Experimental ESR spectra of the propagation radicals corresponding to LLDPE/AA and LLDPE/MMA systems at reaction temperature 190°C are shown in Figure 6. Propagation free radical of AA exhibits the 9-line ESR signals, which are observed in acrylate polymerization at high monomer conversion.[33] The ESR spectrum of MMA is similar to that of AA, but it is not as obvious as AA. The time evolution of concentration of propagation free radical [$M_i$·] is shown in Figure 7. Figure 7 shows that the concentration of propagation free radical reaches the maximum within 10 s and then it decreases, but the concentration can be detected at 190 s, namely, the fifth sample port.

## DISCUSSION

### Time evolution of reaction

The time evolution of reactions including grafting and homopolymerization exhibits two regimes, linear stage and flat stage. This behavior is mainly controlled by the monomer solubility in polymer melt and diffusion of reactive species.[4] In this work, the initiators (POOP+POOH) are introduced into the LLDPE by EB irradiation in the air, the mixture of initiator, and polymer is in the molecular scale. Thus, the monomer solubility in the melt polymer plays a pivot role for the reaction. For AA and MMA, the monomers are partly miscible with the polymer and prefer to form "aggregates" near the end sites of the polymer chains.[34] The quasi-interface between melt LLDPE and monomer is readily formed. Graft copolymerization is believed to occur at the quasi-interface in the polymeric phase, and homopolymerization will take place both in the polymeric phase and in the aggregates.[3] Before the

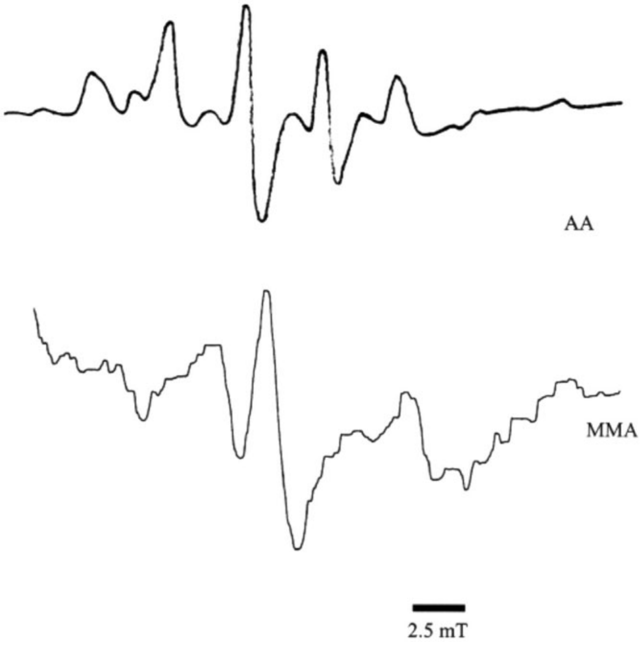


**Figure 6** ESR spectra of the propagating free radicals during grafting AA onto LLDPE and MAA onto LLDPE at 190°C. Samples are quenched in liquid nitrogen and measured at −196°C.

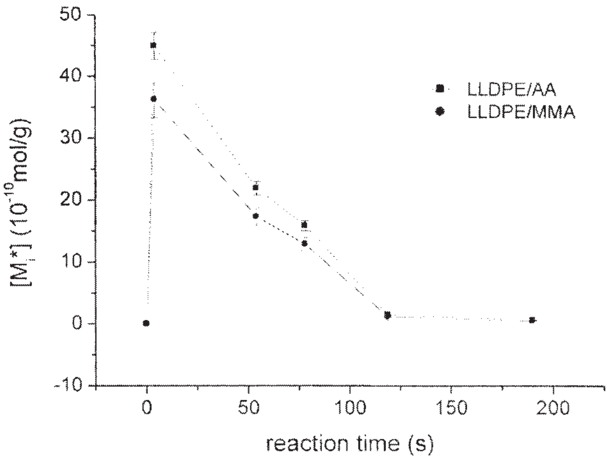


**Figure 7** Time evolution of the concentration of propagation free radicals at reaction temperature 190°C.

reaction occurs, the monomer aggregates will diffuse to the polymer matrix, which would result in a certain concentration of monomer residence in the interface. Therefore, the concentration of the thermodecomposed macromolecular peroxides and monomer were high enough to support graft reaction at the initial stage, and the GD grew linearly with reaction time. Because of high viscosity of polymer melt, the mobility of monomer is seriously retarded, and when the rate of disappearance of monomer in the interfacial region exceeds the diffusive flux of monomer, the graft reaction becomes diffusion-controlled and it exhibits the flat at second stage. As shown in Table II, the concentration of peroxides rapidly increases at high temperature, while the reaction rate is nearly not changed during the stage I, indicating that there must be an amount of free radicals alive in the melt after complete decomposition of peroxides.[35] This assumption was confirmed by propagation free radical measurement. Figure 7 showed that the concentration of chain propagation free radical only slightly changed at the stage I (from $4 \times 10^{-9}$ to $2{\times}10^{-9}$ mol $g^{-1}$), while the concentration dropped abruptly at the stage II (from $10^{-9}$ to $10^{-11}$ mol $g^{-1}$). Thus, it is reasonable to associate the decreasing rate with the fall in concentration of reaction species. Moreover, the change of free radical concentration in the melt also provides the clue to explain the mismatch between the half-life time of peroxides (a few seconds) and the reaction time scale (several minutes).[21] At high reaction temperature, the peroxides decompose fast and form the alkoxy radicals, which may abstract the hydrogen from the polymer substrate to generate secondary radicals.[36] These secondary radicals are reactive for the monomer addition. However, the two-molecular termination is difficult for the high viscosity in the melt, especially for the low monomer concentration. Thus, the chain propagation free radicals will survive for several minutes and the concentration of chain propagation free radicals remains high enough to continue the reaction. So it is only for the decreased monomer concentration at reaction sites that the reaction rate becomes slow, while the reaction will not stop.

The homopolymerization also undergoes the same process with that of graft copolymerization. Since the homopolymerization takes place between free radical (HO·) and monomer, it is expected that the reaction extent of homopolymer at initial stage is higher than that of graft reaction. This conclusion was confirmed by the experiment results. For example, the homopolymerization reached 80% or so of final products and graft reaction reached about 75% of final products. Obviously, high solubility of monomer with LLDPE will favor the graft reaction. That the rates of graft reaction and homopolymerization of AA are higher than those of MMA can be explained by the fact that the reactivity and diffusion coefficient of AA are higher than those of MMA.[15] The lower activation energy of AA polymerization (130 kJ $mol^{-1}$) than that of MMA (135 kJ $mol^{-1}$) is also due to the different reactivity of AA and MMA.

### The graft copolymerization and homopolymerization

As shown in Tables IV and V, AA and MMA readily homopolymerize under the conditions generally employed in grafting system. The relative importance of grafting and homopolymerization will be determined by the inherent reactivity of free radicals and monomer combination and monomer distribution.[3] At present system, there are mainly two kinds of initiating free radicals, namely, p and HO. It has been demonstrated that the small radicals adding to double bonds are 1–3 orders of magnitude faster than high-polymeric radicals,[37,38] and the diffusion coefficient of small radicals are several orders faster than high-polymeric radicals,[39] and so addition of HO to vinyl monomers will be much faster than P·. Furthermore, the monomer aggregating in the polymer melt is susceptible to homopolymerization, which makes the monomer polymerization readily occurred with initiation by HO·. However, in the experiment, the rate of graft copolymerization was always faster than that of homopolymerization. One possible explanation is that the higher the concentration of p, the greater reactivity of the free radical HO is offset by the high concentration of p. In addition, it seems that the thermoinitiated polymerization should make a minor contribution to the total homopolymer yields.

One of the important factor influences the graft copolymerization is the ceiling temperature of monomer, at which the rates of depropagation and propagation are equal. The ceiling temperature for methacrylate esters is ~200°C at 1*M* monomer concentration,[4] which should have impact effect on grafting of MMA with LLDPE. Because the monomer involved in polymerization and grafting is the same, the ceiling temperature for graft is expected to be equal to that for polymerization. However, at present system, while the homopolymerization rate and MH decreased beyond the reaction temperature 190°C, the graft rate and GD continued to increase with the increasing temperature. The same tendency was also observed by other researchers,[12,40] which can be explained as follows: as the propagation rate constant for very small radicals is a function of a molecular size, the oligomerization may occur over ceiling temperature even when high polymer formation is forbidden.[11,41]In the experiment, the graft chain length is much shorted than that of homopolymer chain in the melt.[11] Thus, when the depropagation occurs in the long chains of homopolymer above ceiling temperature, the short grafted chain may be little influenced. Besides, the monomer reactivity and the decomposition rate of peroxides are increased with increasing reaction temperature, which would lead to more monomers participating into the graft reaction and result in high graft rate and final GD.

### Reaction mechanism

The mechanism for melt graft copolymerization initiated by macromolecular peroxides could be tentatively postulated as follows:

Peroxides formation

$$P + O_2 \xrightarrow{\text{irradiation}} \mathrm{POOP} + \mathrm{POOH} \quad (10)$$

Thermal decomposition of peroxides

$$\mathrm{POOP} \rightarrow 2\mathrm{PO}\cdot \quad (11)$$

$$\mathrm{POOH} \rightarrow \mathrm{PO}\cdot + \mathrm{HO}\cdot \quad (12)$$

Graft reaction initiation

$$\mathrm{PO}\cdot + \mathrm{P} \rightarrow \mathrm{POH} + \mathrm{P}\cdot \quad (13)$$

$$\mathrm{P}\cdot + M \rightarrow \mathrm{P}M_i\cdot \quad (14)$$

Homopolymerization initiation

$$\mathrm{HO}\cdot + M \rightarrow \mathrm{HOM}\cdot \quad (15)$$

Graft chain propagation

$$\Sigma\mathrm{P}M_i\cdot + M \rightarrow \Sigma\mathrm{P}M_{i+1}\cdot \quad (16)$$

Homopolymer chain propagation

$$\Sigma\mathrm{HO} - M_i\cdot + M \rightarrow \Sigma\mathrm{HO}M_{i-1}\cdot \quad (17)$$

Graft chain transfer to P

$$\Sigma\mathrm{P}M_i\cdot + \mathrm{P} \rightarrow \mathrm{P}\cdot\mathrm{P}M_i \quad (18)$$

Homopolymer chain transfer to P

$$\Sigma\mathrm{HO} - M_i\cdot + \mathrm{P} \rightarrow \mathrm{P}\cdot + \mathrm{HO}M_i \quad (19)$$

Graft chain termination

$$\Sigma\mathrm{P}M_i\cdot + \Sigma\mathrm{P}M_j\cdot \rightarrow \mathrm{P}M_{i+j} \quad (20)$$

$$\Sigma\mathrm{P}M_i\cdot + \Sigma\mathrm{P}M_j\cdot \rightarrow \mathrm{P}M_i + \mathrm{P}M_j \quad (21)$$

$$\Sigma\mathrm{P}M_i\cdot + \Sigma\mathrm{HO} - M_j\cdot \rightarrow \mathrm{PO}M_{i+j}\mathrm{OH} \quad (22)$$

$$\Sigma\mathrm{P}M_i\cdot + \Sigma\mathrm{HO} - M_j\cdot \rightarrow \mathrm{P}M_i + \mathrm{HO}M_j \quad (23)$$

Homopolymer chain termination

$$\Sigma\mathrm{HO} - M_i\cdot + \Sigma\mathrm{HO} - M_j\cdot \rightarrow \mathrm{HO}M_{i+j} \quad (24)$$

$$\Sigma\mathrm{HO} - M_i\cdot + \Sigma\mathrm{HO} - M_j\cdot \rightarrow \mathrm{HO}M_i + \mathrm{HO}M_j \quad (25)$$

$$\Sigma\mathrm{HO} - M_i\cdot + \Sigma\mathrm{P}M_j\cdot \rightarrow \mathrm{P}M_{i+j}\mathrm{OH} \quad (26)$$

$$\Sigma\mathrm{HO} - M_i\cdot + \Sigma\mathrm{P}M_i\cdot \rightarrow \mathrm{HO}M_i + \mathrm{P}M_j \quad (27)$$

where $P$ denotes LLDPE and $M$ denotes AA, MMA; $P\cdot$ is secondary polymeric radical; $\Sigma\mathrm{HO} - M_i$ are free radicals formed by grafting monomers and $\Sigma PM_i\cdot$ are grafted polymeric radicals. Since there are two kinds of polymeric radicals, $p$ and $pM_i$, in the reaction system, couple reactions should exist, and the couple reaction will lead to low graft degree because the reaction reduces the concentration of macro radicals that would react with the new monomers. Moreover, the couple reactions will cause the crosslink of product to some extent. Solubility tests indicated that no crosslinking was present in the samples as evidenced by complete dissolution. Therefore, it can be assumed that the crosslink density is lower than critical density at which the gel could be formed.[42] It seems that for AA, two free radical termination is dominant, while for MMA, the chain transfer termination is dominant[11,12]; for both monomers, the adding monomer to polymeric radicals is a slow step for the graft copolymerization with the high viscosity.[40]

## CONCLUSIONS

The kinetics study on melt grafting AA and MMA onto LLDPE by using reactive extrusion method was carried out. The experiment showed that the reaction process was mainly controlled by the monomer solubility in polymer melt and diffusion of reacting species. The rate of graft reaction and homopolymerization, and the final products of AA were higher than that of MMA, which can be explained by the fact that the reactivity and diffusion coefficient of AA are higher than that of MMA. The rate of graft copolymerization was always faster than that homopolymerization for the high concentration of P•. It was demonstrated that an amount of chain propagation free radicals could keep alive for several minutes even the peroxides completely decomposed.

For the graft reaction of AA with LLDPE, the order with respect to irradiation dose is about 0.55, monomer concentration is 1.46, and the activation energy is 132 kJ $mol^{-1}$; for homopolymerization, the order with respect to irradiation dose is 0.51, monomer concentration is 1.08, and activation energy is 130 kJ $mol^{-1}$. For the graft reaction of MMA with LLDPE, the order with respect to irradiation dose is 0.99, monomer concentration is 1.49, and activation energy is 144 kJ $mol^{-1}$; for homopolymerization, the order with respect to irradiation dose is about 0.98, monomer concentration is about 1, and activation energy is 135 kJ $mol^{-1}$ in the range from 170 to 190°C. These results indicate that the adding monomer to polymeric radicals is a slow step for the graft copolymerization with the high viscosity.

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