

EPR/rheometric studies on radical kinetics in melt polyolefin elastomer initiated by dicumyl peroxides

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Received 27 November 2006; received in revised form 20 March 2007; accepted 22 March 2007

Available online 27 March 2007

Abstract

Peroxide-initiated reaction of poly(ethylene-*co*- α -butene) (EB), a kind of polyolefin elastomer (POE), was studied at elevated temperatures using an on-line electron paramagnetic resonance (EPR) spectrometer and was also evaluated by monitoring the viscosity of the reaction system on a rotational rheometer. It is clear that the reaction process experiences the free radical mechanisms. According to the EPR spectra, notable changes in signal hyperfine structure, the intensity and lifetime of the radical were recognized. Different from the case of PE and PP modified by peroxide, there is a new type of EPR signal, which is assisted to the tertiary alkyl radicals. And it is verified that the primary alkyl radicals are first produced at elevated temperatures. A rheokinetic analysis was made by EPR and rheology. The kinetic coefficients of coupling and disproportionating reactions were not fixed, but the functions of the reacting time or the system viscosity. Accordingly, the kinetics is substantially controlled by diffusion of the polymer chains and a formula reflecting this kind of effect of the viscosity on termination rate coefficients is founded.

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Keywords: POE; EPR; Rheokinetics

1. Introduction

The metallocene-based polyolefin elastomer (POE), produced by copolymerization of ethylene with α -olefin such as butene-1, hexene-1, octene-1 or 4-methyl pentene-1, has received much attention because of its homogeneous distribution of short chain branched (SCB) and narrow range of molecular weight [1]. This kind of new material has been already used to replace the conventional polyethylene for industrial applications, especially in the field of wire and cable coating. Crosslinking of POE by thermochemical reactions using peroxides is commercially the economical way to improve the dimensional stability and strength, and such chemical modification is also interesting from a technological point of view due to the unique uniform distribution of SCB.

It is well known that the crosslinking reaction of polyolefin is implemented via radical reactions. So the modern electron paramagnetic resonance (EPR) technique has provided a unique and powerful tool to establish reaction kinetics and further elucidate the radical mechanisms. Recently, the online EPR studies have been carried out successfully for the peroxide-initiated radical reactions in melt polyethylene (PE), polypropylene (PP), ethylene–propylene copolymer and ethylene–propylene–diene copolymer (EPDM) [2–9]. Anyway, there lacks the EPR study for the melt POE system.

EPR is widely used to detect transient radical species and monitor the changes of radical concentration with reaction time. For a given reactive system at a specified temperature, the kinetic parameters are kept constant for most reactions between inorganic or organic small molecules, which are independent of the reactants concentration, the flow field and the system viscosity. However, the fluctuations of rate constants can be observed as the system or environment changes. This phenomenon is more evident if the reactants become macromolecules, where reaction process is diffusion controlled due

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to the high viscosity of polymer. To correlate the rheological properties with the reaction kinetics and analyze their interdependences, the concept of rheokinetics was proposed by Cherkinskii [10] and developed by Malkin [11,12] and other authors [13–17].

In this present paper, ethylene- α -butene copolymer (EB) was chosen as the reaction matrix and we have used online EPR technique to evaluate the reaction process in EB/DCP system. Since POE owns branched chains, it maybe degraded by β -scission just like PP. According to our previous study on the reaction of POE with DCP under shear flow field [18], there is one critical value of strain rate below which only the coupling reaction occurs, and the POE chains are able to degrade just when exceeding this threshold. So in the present work, the degradation can be excluded due to the reaction condition of quiescent state. After proposing a tentative mechanism for the crosslinking reaction, the kinetics was studied quantitatively by correlating the EPR data with the rheological responses for the first time.

2. Experimental

2.1. Materials

Ethylene- α -butene copolymer (EB) grade Tafmer A-4085, with the butene content of 13.3 mol% (determined from ^1H NMR analysis), melt flow index of 3.6 g/10 min (190 °C, 2.16 kg), and density of 0.885 g/cm³ (20 °C), was obtained from Mitsui Chemicals, Japan. Its number average molecular weight (M_n) and distribution (M_w/M_n) are 55.4 kg/mol and 2.3, respectively. Dicumyl peroxide (DCP, chemical pure), acetone (chemical pure) and xylene (a mixture of *o*-, *m*- and *p*-xylene whose boiling point is around 140 °C and density 0.87 g/cm³ at 20 °C), purchased from Shanghai Chemicals Factory, PR China, were used after recrystallization or distillation. The decomposition rate constant of DCP provided by the supplier is as follows:

$$K_d (\text{s}^{-1}) = 2.124 \times 10^{16} \exp(-155.46 \times 10^3/RT) \quad (1)$$

where R is the gas constant and T is the absolute temperature, respectively.

2.2. Sample preparation and rheological measurements

Pellets of EB were impregnated in acetone solution of DCP over 12 h at room temperature. They were premixed in a torque rheometer (Haake Rheocord90, Germany) at 90 °C with the rotor speed of 60 rpm for 8 min after evaporation to remove the solvent at a reduced pressure. Then an EB sample well mixed with DCP at a concentration of 0.148 mol/kg was obtained. It was molded into rods with diameter of 3 mm for EPR detections and discs (diameter ≈ 25 mm and thickness ≈ 1 mm) for rheological measurements at 90 °C. Even though the half-time of DCP at 90 °C is as long as 208.5 h, it is still possible to have a small amount of reaction during the preparation. However, such small amount of reaction

will not affect our experimental results. So we can pay little attention to this reasonably.

The rheological evaluation was based on a rotating rheometer (Gemini 200HR, Bohlin Instruments, UK) with parallel plate geometry of 25 mm in diameter and carried out in steady mode with a gap of 1 mm between two parallel plates. Shear rates were applied as low as 10^{-4} , 5×10^{-4} and 10^{-3} s^{-1} to ensure the quiescent state for comparison to the reaction process on EPR.

2.3. EPR detection

The rod sample was inserted into an EPR glass with internal diameter of 3 mm, which was sealed after degassing by nitrogen. Once the temperature in EPR cavity reached the set value, the sample tube was inserted into the cavity. After the sample was heated up and the temperature was stable, 30 s usually, EPR spectrum was recorded at each time interval on a Bruker EMX-8 spectrometer (Bruker BioSpin Corp., Germany). EPR working conditions were as follows: X-band; 100 kHz modulation; microwave frequency, 9.597 GHz; microwave power, 19.92 mW; modulation amplitude, 2.0 G; time constant, 163.84 ms; sweep width, 150G; scan time, 83.89 s. And the spectral simulations were undertaken by employing Bruker's WIN-EPR *simfonia* Version 1.2.

For each crosslinking experiment, the radical concentration at each time interval was calculated from the double integration of EPR signal (intensity vs. magnetic field). The well-resolved 3-line EPR spectrum of 4-hydroxy-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO, Aldrich, 98%) radical, which is stable at room temperature, is generally agreed to provide an excellent calibration standard for the absolute radical concentration. EPR spectra of precisely known amount of TEMPO dispersed in EB without peroxides were measured at 25 °C. Taking into account the elevated testing temperature, we corrected the radical concentration by the following equation [3]:

$$\text{Int} = \text{Int}_0 \exp\left(1 - \frac{T_0}{T}\right) \quad (2)$$

where Int is the corrected EPR signal intensity at high temperature T , and Int₀ is the intensity at T_0 ($T_0 = 298$ K in our experiments).

2.4. Product treatment and characterization

After EPR and rheological measurements, the fully reacted samples were treated for further determination of gel content and FTIR characterization. Each reacted sample was cut into small pieces and extracted in a fabric bag with an excess volume of xylene employing Soxhlet extractor for 24 h at about 120 °C. Then the extracted fabric bags were vacuum-dried to a constant weight. According to the weight of the insoluble portion, the gel content of the modified EB sample ($x\%$) can be determined as follows:

$$x\% = \frac{m_2}{m_1} \times 100\% \quad (3)$$

where m_1 is the weight of the modified EB sample before the xylene extraction and m_2 is the one after xylene extraction. There is no gel in the EB sample modified on rheometer and the gel content of fully reacted EB sample on EPR device is about 81.4%. On the other hand, the resulting solution containing the soluble portion was dropped slowly down into acetone, followed by the filtration of polymer precipitates to remove the residue of initiators. Then the peroxide-modified EB was washed with acetone three times and dried in a vacuum oven at 50 °C for 48 h.

The resulting polymer was compressed into films (thickness \approx 50 μm) at 90 °C under 12 MPa for FTIR characterization. The FTIR spectra were recorded by a Paragon 1000 FTIR spectrometer (Perkin–Elmer, Inc., USA).

3. Results and discussion

3.1. EPR evaluation

Fig. 1 shows the whole evolution of the EPR spectra recorded in the reaction process of EB with DCP (initial concentration 0.148 mol/kg) at 150 °C. The appearance of four different types of radicals in different stages of the reaction and their intensity changes with reaction time were nicely monitored. The intensity of total radicals first increased, followed by a decrease process. In the beginning (after 120 s), a 10-line (doublet and pentet) EPR signal with hyperfine splitting constants 20.56G (one α -H) and 23.87G (four β -H) appeared as the predominant component. This type of radical was surely resulted in H-abstraction by cumyloxy radical (RO^\bullet) from the backbone methylene of EB, as the same in the case of the modification of PE with peroxide [3,5,9]. Simultaneously, one may

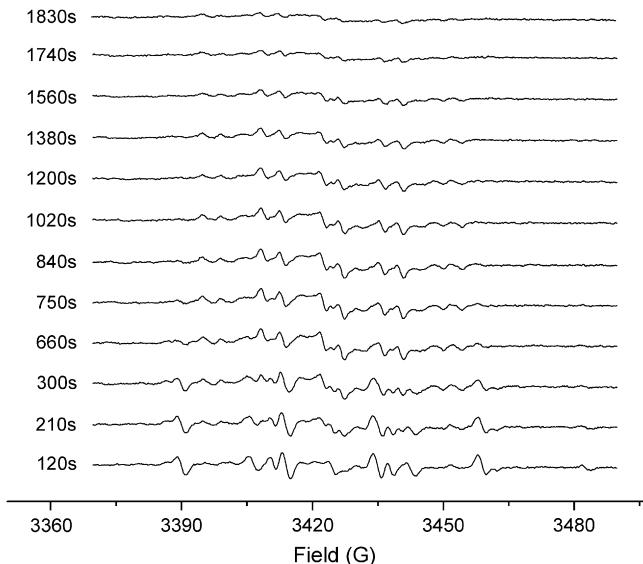
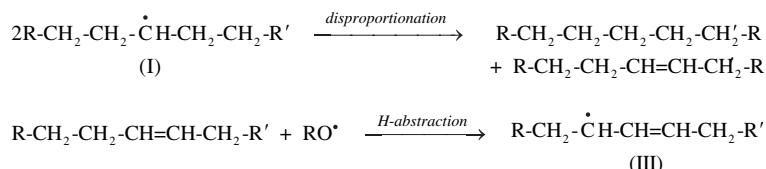


Fig. 1. Successive EPR spectra recorded in DCP initiated crosslinking reaction of EB at 150 °C.

As time went by, the heptet of tertiary radicals still existed, but a gradual transition of the 10-line component to a 14-line new species occurred. This phenomenon appeared since 210 s and came to 840 s when the 14-line signal became dominant (Fig. 1). During this transition period, three types of different radicals coexisted and their EPR signals appeared simultaneously and overlapped each other, though they own different easy of formation and lifetimes. The 14-line signal is typical of allyl-type radical with splitting constants 13.31G due to six equivalent protons (two α -H and four β -H) and 4.24G due to one β' -H as interpreted in Fig. 3 and Scheme 1. These kind of allyl radicals might be created by following subsequent radical steps:



find another weak heptet signal accompanying the 10-line one. The characteristic splitting constant 18.02G corresponds to the six nearly equivalent β -H atoms of the tertiary carbon radical, which did not arise during the modifications of PE and PP. Though the factor of C–H bond dissociation energy favors tertiary carbon as site for H-abstraction, the big steric hindrance around tertiary carbon and the much higher number of backbone methylene units worked together to result in the signal of secondary carbon radical (I) was the major component and it of tertiary carbon radical (II) was the minor component in EPR spectra. The simulated EPR spectra of (I), (II) and (I) + (II), as shown in Fig. 2, are well coincided with the recorded ones.

This mechanism has been also confirmed by Yamazaki and Seguchi [3] and Zhou and Zhu [5] in their study on chemical crosslinking of polyethylene. The simulations of (III), (II) + (III) and (I) + (II) + (III) are well coincident with the experimental results (Figs. 3 and 4). Compared with the alkyl radicals, (I) and (II), the further stronger EPR intensity of allyl radical (III) in the later period of reaction is attributed to its longer lifetime derived from the lone electron's spin delocalization (Scheme 1). Finally, all radicals gradually diminished via bimolecular termination of chain radicals including recombination and disproportionation.

At the temperatures of 140, 160 and 170 °C, the generation and termination of radicals were also observed. The shape of

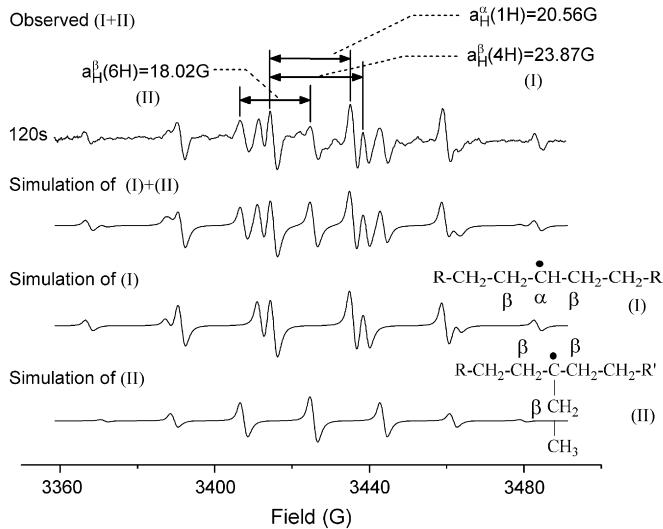


Fig. 2. Observed and simulated EPR spectra of alkyl radicals (I) + (II) at 120 s in DCP initiated crosslinking reaction of EB at 150 °C.

the spectrum does not vary significantly, but the evolution in the radical intensity clearly changed with the temperature. The concentration changes of radicals with reaction time at different temperatures were shown in Figs. 5 and 6. Both the time for the 14-line signal to arise and the time required to finish the whole process were ahead as the temperature increased.

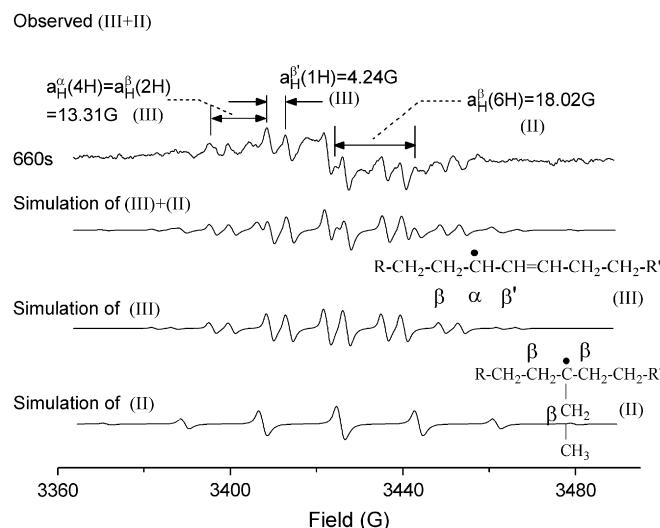
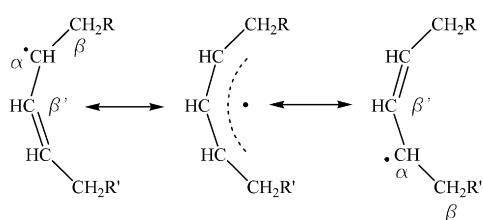


Fig. 3. Observed and simulated EPR spectra of tertiary alkyl radicals (II) and allyl radicals (III) at 660 s in DCP initiated crosslinking reaction of EB at 150 °C.



Scheme 1. The electron's delocalization in allyl radical (III).

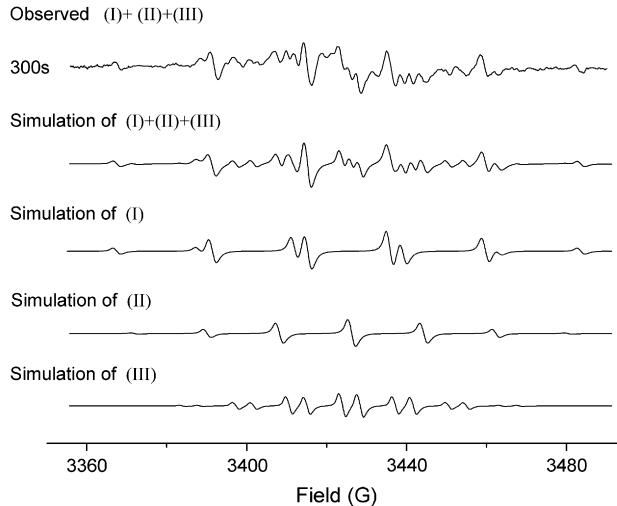


Fig. 4. Observed and simulated EPR spectra of alkyl radicals (I) + (II) and allyl radicals (III) at 300 s in DCP initiated crosslinking reaction of EB at 150 °C.

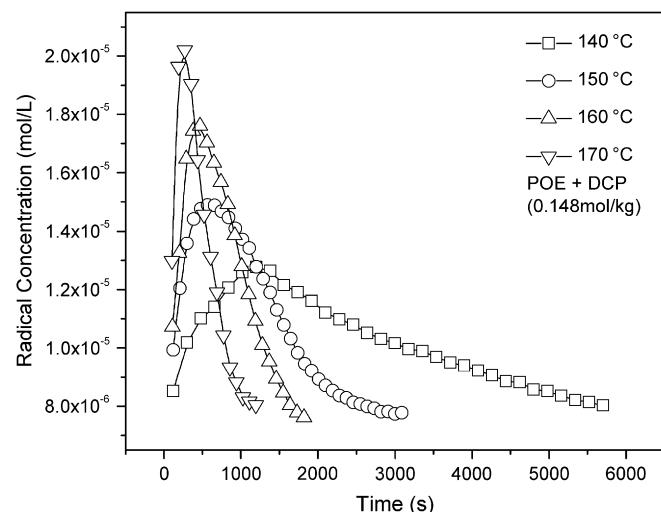


Fig. 5. Profiles of total radical concentration vs. reaction time in DCP initiated crosslinking reaction of EB at 140, 150, 160 and 170 °C.

It is remarkable that a different pattern of 9-line (triplet and triplet) signal appeared in the early period in the case at 140 °C, which was not observed at higher temperatures, although the intensity of it is not very strong. This 9-line EPR signal is attributed to the primary alkyl radicals produced in hydrogen abstraction by RO^\cdot from the methyl groups at branched chain ends. The characteristic hyperfine splitting constants are 1.89G (two α -H) and 8.60G (two β -H). According to the EPR spectrum recorded at 120 s (Fig. 7), the 10-line and 7-line EPR signals were not present at that moment, which proves the foremost hydrogen abstraction should come from the methyl groups. Statistically there are about 16 methylene units between two branch points in EB chains and the mean distance can be calculated by

$$\bar{R} = \langle R^2 \rangle^{1/2} = \sqrt{nb} = \sqrt{16+2} \times 0.1553 \approx 0.659 \text{ nm} \quad (4)$$

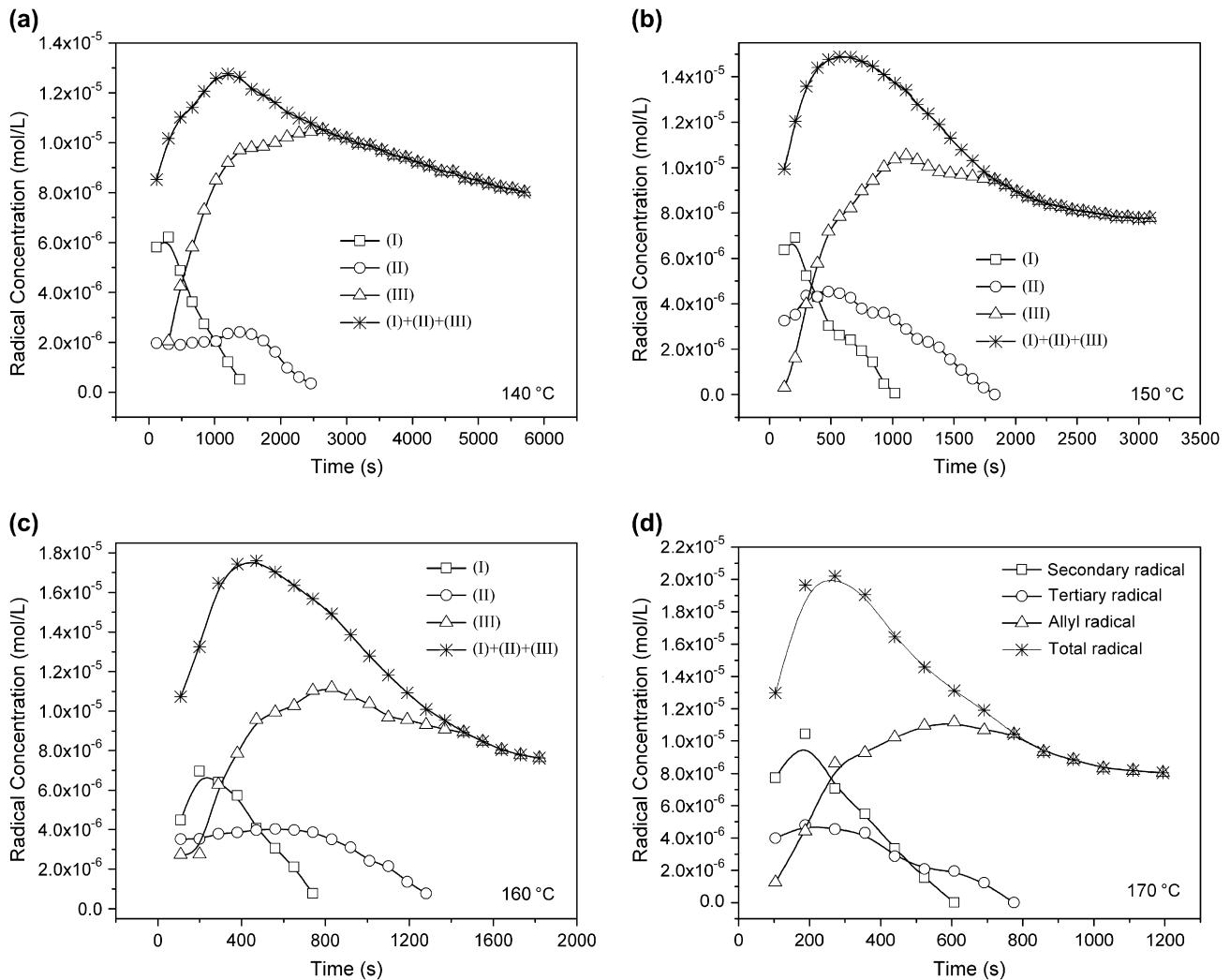


Fig. 6. The concentration changes of various radicals with reaction time in DCP initiated crosslinking reaction of EB at (a) 140 °C, (b) 150 °C, (c) 160 °C and (d) 170 °C.

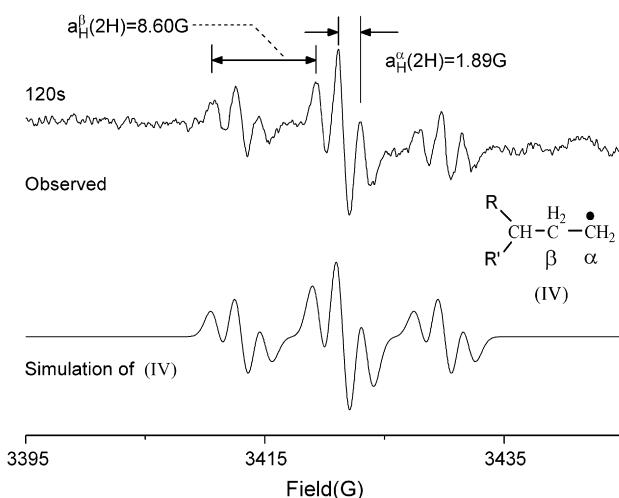
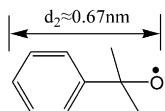


Fig. 7. Observed and simulated EPR spectra of primary alkyl radical (IV) at 120 s in DCP initiated crosslinking reaction of EB at 140 °C.

where n and b are the number and length of the C–C bonds, respectively. Thus, the branched chain ends could be attacked first by very bulky cumyloxy radicals ($\text{Me}_2\text{phCO}\cdot$) (Scheme 2). Although C–H bond dissociation energy increases in the order of $(\text{RR}'\text{C–H}, 376.6 \text{ kJ/mol}) < (\text{RR}'\text{CH–H}, 393.3 \text{ kJ/mol}) < (\text{RCH}_2\text{–H}, 405.8 \text{ kJ/mol})$, at higher temperatures the hydrogen abstraction from various types of C–H bonds becomes faster but less discriminated kinetically. Therefore the primary alkyl radicals were generated reasonably in the beginning with much higher methyl concentrations than in the case of PE.

The strong signal of 10-line then appeared around 320 s and made the shape of the 9-line EPR spectrum unclear (Fig. 8), as a result of which only an envelope line could be observed. However, the rather quick disappearance of the primary radicals evidently reflected the higher reactivity in rapid inter- or intra-molecular hydrogen transfer from the methylene and methenyl groups. It is considered that the primary alkyl radicals were also produced in the cases at 150, 160 and 170 °C, but they were not able to be captured by EPR machine.



Scheme 2. The size of cumyloxy radical $\text{Me}_2\text{phCO}^\cdot$ generated in thermal decomposition of DCP.

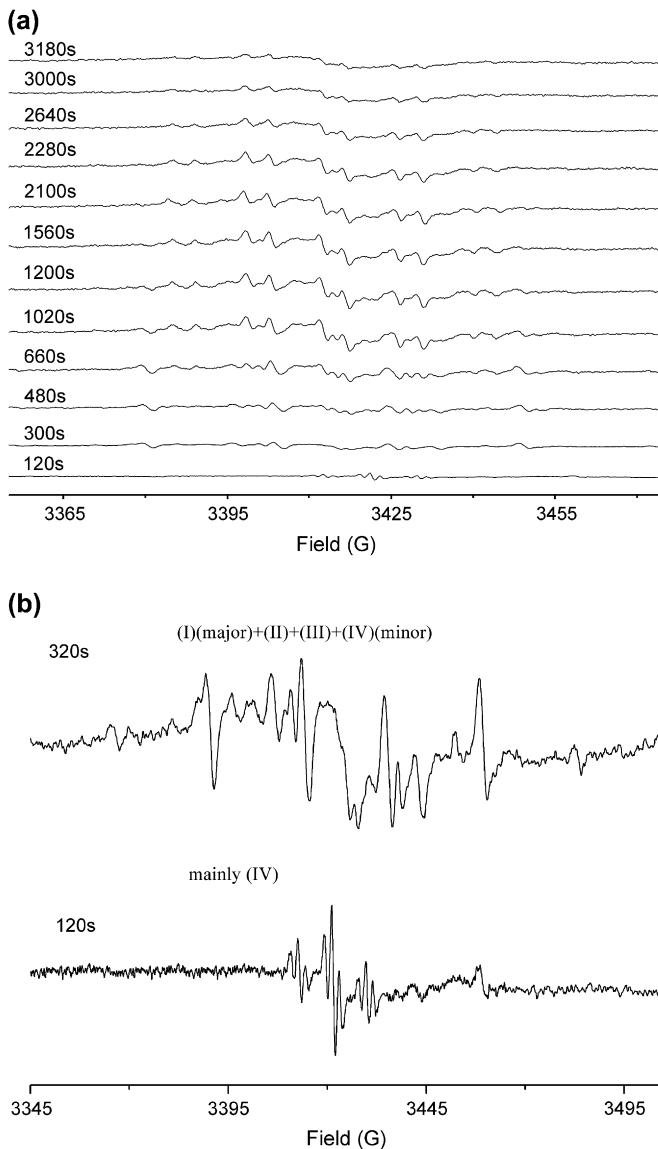


Fig. 8. (a) Successive EPR spectra and (b) the first two EPR spectra at 120 and 320 s recorded in DCP initiated crosslinking reaction of EB at 140 °C.

Based on the above analysis, a tentative mechanism of the whole process could be proposed:

(i) Initiation:



where I and RO^\cdot denote the initiators and the alkoxy radicals, respectively.

(ii) Hydrogen abstraction:



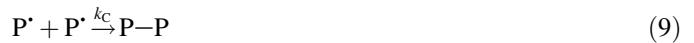
where P^\cdot denotes all the alkyl macromolecular radicals and P_\equiv^\cdot denotes the allyl ones.

(iii) Termination by disproportionating:



where P_2^\cdot represents the secondary alkyl macromolecular radicals.

(iv) Termination by coupling:



(v) Chain transfer:



The parameters on the arrows are the corresponding rate coefficients, and the rate coefficients of the coupling reactions are treated here without any differences in step (iv).

3.2. Rheological measurements and FTIR characterization

The viscosity (η) evolution in the reaction of EB initiated by DCP was performed for about 1300 s at 150 °C. It should be the short reaction time that resulted in no gel creation. As shown in Fig. 9, the developments of system viscosity were independent of the shear rates that indicated that the case under such weak shear flow was nearly in quiescent state. Thus, the degradation can be excluded due to the reaction condition of quiescent state [18] and the reaction process carried out on rheometer is reasonably the same as it on EPR device. Obviously, the monotonous increase of η during the given reaction time should be the result of the coupling reactions of two macromolecular radicals that lead to an increase in the molecular weight of the system. Because it is not very probable for the reactive site to be near the end of the polymer chain, the product should own long chain branched (LCB), mostly in the topological structure of four-arm star, but the length of arm can be different from one another due to the random position of the reactive site on the polymer chain.

FTIR characterization of the reaction product has been carried out to confirm whether oxidation occurred or not during the EPR detection. By comparing the FTIR spectra of the

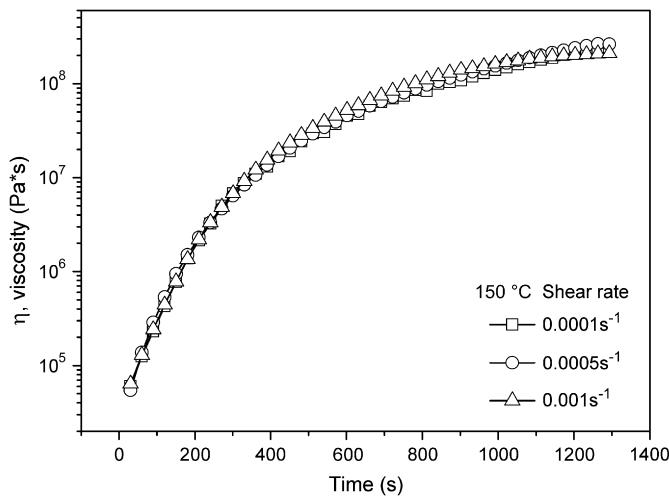


Fig. 9. The viscosity evolution in DCP initiated crosslinking of EB at 150 °C.

modified and original EB, as shown in Fig. 10, it can clearly be seen that no new absorption attributable to the carbonyl groups is observed. It is possible that the number of the carbonyl groups was may be too low to be detected, even if there has been oxidation in the reaction. So the effect of oxidation can be excluded. On the other hand, the band present at 965 cm⁻¹ in Fig. 10(b) is due to in-chain unsaturated structures that are the characteristic winding vibrations of *trans*-vinylidene bonds. This is well consistent with the appearance of absorption band at 1690 cm⁻¹, corresponding to the stretching vibration of the C=C double bonds. The presence of this new structure should be ascribed to the disproportionating termination of two secondary alkyl radicals, which accorded well with the results of EPR experiments mentioned above.

3.3. Kinetic analysis

The estimation of the kinetics during this course of modification can be carried out through the radical concentration

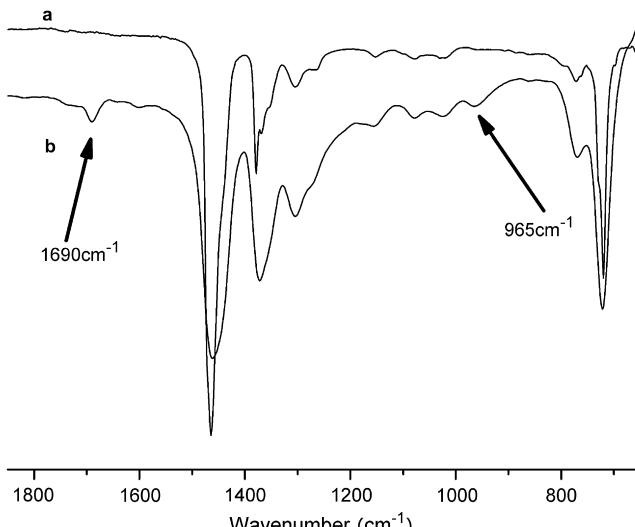


Fig. 10. FTIR spectra: (a) the original and (b) the modified EB.

profiles shown in Fig. 6. The kinetic rate coefficients of the termination reactions can be determined from several fundamental formulae as follows, which can be used to describe the whole reaction process:

$$-\frac{d[I]}{dt} = k_d[I] \quad (13)$$

$$-\frac{d[RO^\cdot]}{dt} = k_a[RO^\cdot][P-H] + k'_a[RO^\cdot][P_-H] - 2fk_d[I] = 0 \quad (14)$$

$$\begin{aligned} -\frac{d[P^\cdot]}{dt} = & k_D[P_2^\cdot]^2 + k_C([P^\cdot]^2 + [P^\cdot][P_-^\cdot]) \\ & + k_{tr}[P^\cdot][P_-H] - k_a[RO^\cdot][P-H] \end{aligned} \quad (15)$$

$$\begin{aligned} -\frac{d[P_-^\cdot]}{dt} = & k_C([P_-^\cdot]^2 + [P^\cdot][P_-^\cdot]) - k_{tr}[P^\cdot][P_-H] \\ & - k'_a[RO^\cdot][P_-H] \end{aligned} \quad (16)$$

where $[I]$ is the concentration of initiators at time t , $[P^\cdot]$, $[P_2^\cdot]$ and $[P_-^\cdot]$ are the concentration of total, secondary alkyl and allyl radicals at time t , correspondingly. Considering the hyperfine structure of the allyl radical signal kept in the shape of 14-line during the course that the radical intensity decayed, here it can be assumed that the disproportionation reaction should not occur between two allyl-type radicals.

By solving Eq. (13), we obtain:

$$[I] = [I]_0 \exp(-k_d t) \quad (17)$$

where $[I]_0$ is the original concentration of initiator with the value of 0.131 mol/L. Because the rate constant, k_a , which is in the order of 10^6 – 10^7 L/mol s [19], is so high that the reaction of hydrogen abstraction is very fast in this predominantly hydrogen medium. That means the cumyloxy radicals turn to macromolecular ones immediately when they are produced from thermal decomposition of peroxides, as a result of which Eq. (14) can be considered to be zero. Here the efficiency of initiator, f , is taken as 0.5 [2,20]. On the other hand, about 25–30% of the originally added DCP escaped from the samples during the evaporation of acetone and drying of the samples after impregnation [21], the value of f should be modified to around 0.35.

From Eqs. (14)–(16), the concentration of all radicals $[R_1^\cdot]$ ($[R_1^\cdot] = [P^\cdot] + [P_-^\cdot]$) meets the equation expressed as

$$-\frac{d[R_1^\cdot]}{dt} = k_D[P_2^\cdot]^2 + k_C[R_1^\cdot]^2 - 2fk_d[I] \quad (18)$$

It has been well established that the rate coefficient of termination reaction satisfies the Arrhenius equation:

$$k_C = A \exp\left(-\frac{E_{aC}}{RT}\right) \quad (19)$$

$$k_D = A \exp\left(-\frac{E_{aD}}{RT}\right) \quad (20)$$

where A and E_a are the collision frequency and activation energy for the termination reaction, respectively. Since termination reactions are both in the mode of double radicals, no matter the coupling or disproportionating termination, the effect of the evolution of system viscosity on the value of A is approximately identical which is different from the case of the small molecules due to the high entanglement of polymers. Accordingly, the ratio of k_C and k_D should keep constant induced by the difference in the activation energies of these two reactions, which can be considered the same as in the case of the small molecules. The ratio, Q , is defined as

$$Q = \frac{k_D}{k_C} = \exp\left(\frac{E_{aC} - E_{aD}}{RT}\right) \quad (21)$$

Considering $E_{aC} < E_{aD}$, the value of Q should be smaller than one.

By inserting Eq. (21) in Eq. (18), the rate coefficient of recombination can be obtained:

$$k_C = \frac{2fk_d[I]_0 \exp(-k_d t) - \frac{d[R_1^*]}{dt}}{Q[P_2^*]^2 + [R_1^*]^2} \quad (22)$$

So it is sufficient to investigate the kinetic process only using k_C in the following section. When $[P_2^*] = 0$, there would be no disproportionating reactions, and k_C can be rewritten as

$$k_C = \frac{2fk_d[I]_0 \exp(-k_d t) - \frac{d[R_1^*]}{dt}}{[R_1^*]^2} \quad (23)$$

which can be also applied when all the alkyl radicals disappeared ($[R_1^*] = [P_2^*]$).

So the evolution of the rate coefficients of termination reactions during the whole modification can be calculated by Eqs. (21)–(23), which are shown in Fig. 11 for the case of $Q = 0.5$. Further, Fig. 12 exemplifies that the value of Q does not affect the curve of the rate coefficients of termination reactions very much when Q is smaller than one due to the dominant value of $[R_1^*]$ compared with $[P_2^*]$ as shown in Fig. 6, which illustrates that the thermodynamics is the minor factor. On the other hand, the fact that k_C decreased with time accounted for the dramatic increase of the system viscosity that resulted in the poorer mobility of macromolecules and lower probability of collision between two reactive sites. So in diffusion-controlled reaction, the system viscosity plays an important role on the kinetics. When the gels were yielded, the macromolecular radicals were trapped in them due to the constraints imposed by the three-dimensional network structure and the lifetime of them became longer.

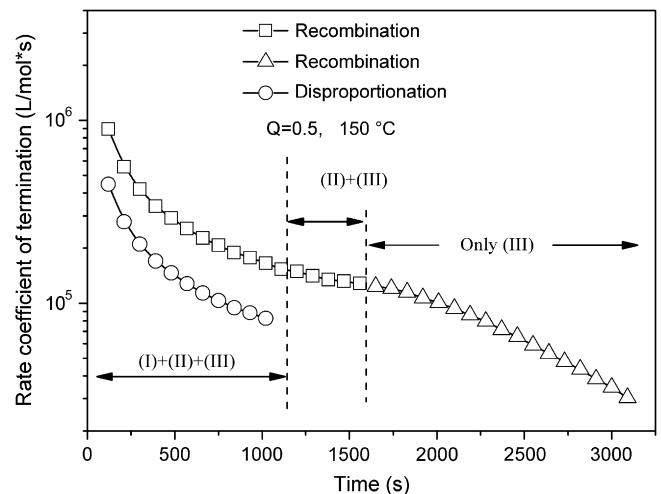


Fig. 11. The evaluation of the rate coefficients of termination steps ($Q = 0.5$) at 150 °C.

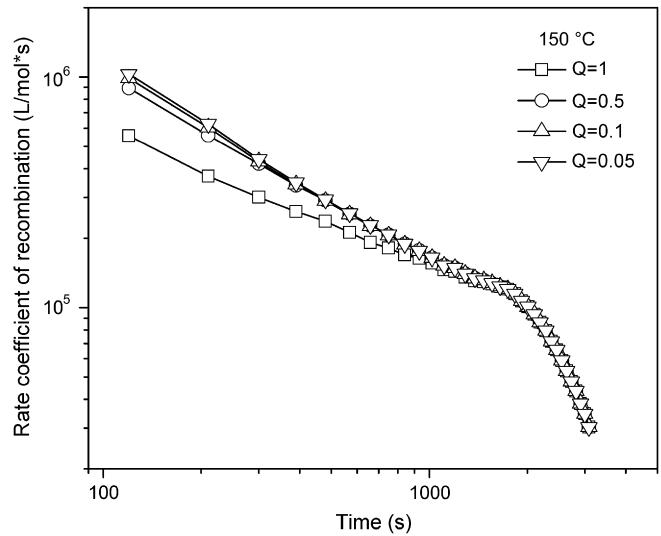


Fig. 12. The comparison of the rate coefficients of recombination for different values of Q at 150 °C.

3.4. Rheokinetics

Because the reaction on rheometer can be treated as in quiescent state, it is convenient for us to correlate the viscosity, η , with the rate coefficients of termination steps. Since there was no gel in the sample during the early short period (1300 s), the reaction system is homogeneous. Here only the rate coefficient of recombination works and the relation between k_C and η is obtained as shown in Fig. 13. The remarkably dramatic decrease of k_C also revealed that mobility of polymer chains became poorer and poorer as system viscosity increased and the kinetics is substantially controlled by diffusion of the polymer chains. The quantitative relation can be described by the following formula:

$$k_C = 5.629 \times 10^7 \eta^{-0.31} \quad (24)$$

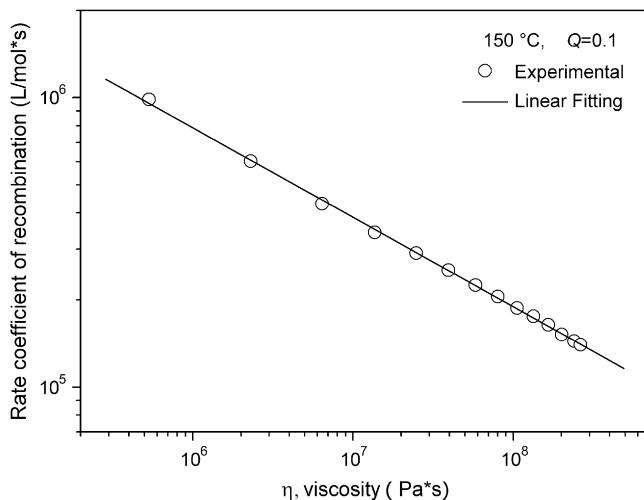


Fig. 13. The changes of rate coefficients of recombination ($Q=0.5$) with viscosity in DCP initiated crosslinking reaction of EB at 150 °C.

The value of index in Eq. (24) represents the sensitivity of k_C to the system viscosity.

Theoretical frameworks have been developed to handle the diffusion-controlled reactions involving active groups attached to polymers by many researchers, especially de Gennes [22], who made important conceptual advances. According to de Gennes' investigation which is based on the reptation model, the coupling rate k satisfies

$$k = \alpha_1 D_0 R_g \quad (25)$$

where D_0 is the center-of-mass diffusivity, R_g is the chain radius of gyration. For linear chains, $D_0 \sim M^{-2}$, $R_g \sim M^{1/2}$, which gives $k \sim M^{-1.5}$. During the start of reaction, it has $\eta \sim M^{3.4}$, which results in $k \sim \eta^{-0.44}$. However, such scaling relationship has never been observed. One of the reasons is that Eq. (25) is obtained for coupling rate at sufficient long time when the viscosity dependence $\eta \sim M^{3.4}$ is not accurate any more.

The situation in our case is not exactly the same as de Gennes' assumption. The result of coupling is probably to produce branched chains, and the material becomes a mixture of linear and branched chains during the early period of reaction. Although de Gennes had argued that branching affect a little on the kinetics, our results show different scaling relationship, which is induced by the branched chains and change of viscosity. We have $k \sim t^{-m}$ and $\eta \sim t^n$, which gives $k \sim \eta^{-m/n}$. The approximate single scale, -0.31 , between k and η is induced by fixed value of m and n , and only can be applied during the first 1300 s in our case. Suppose that (1) there is no gel formation, (2) product is a blend of linear and four-arm star chains, (3) power-law mixing rule, (4) only one kind of macromolecular radical is considered and (5) $m=0.3$, the calculated result is shown in Fig. 14, where three stages are usually observed:

- (1) the initial stage: the induction period due to the decomposition of DCP, which is usually ignored;
- (2) the middle stage: there is a scaling relationship between the rate coefficient of recombination and viscosity;

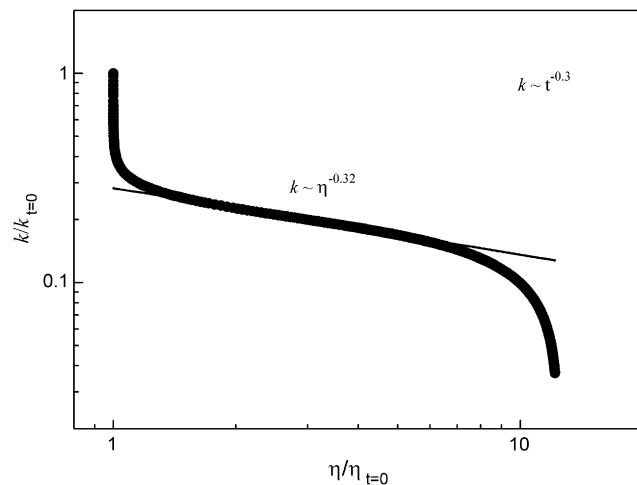


Fig. 14. The calculated evaluation of rate coefficients of recombination with viscosity based on several assumptions.

(3) the late stage: the reaction approaches to the end. k decreases with time as assumed, while the viscosity reaches constant.

In our experiments, one scaling is found between k and viscosity, which is only possible when the viscosity keeps increasing even in the late stage. This can be ascribed to the crosslinking due to the large amount of initiators.

4. Conclusions

In the modification of EB with DCP at different temperatures (140–170 °C), EPR detections were carried out to monitor the structures and concentrations of the macromolecular radicals. It is clear that the primary alkyl radicals are first produced at elevated temperatures which can be reasonably explained by steric effect. The allyl radicals produced by disproportionation are more stable because an unpaired electron is delocalized in the allylic form. Different from the case of PE and PP modified by peroxide, there is a new type of EPR signal which is assisted to the tertiary alkyl radicals. The termination rate coefficients (k_C and k_D) are determined by EPR data and their decrease with time or system viscosity is remarkably dramatic. Accordingly, a formula (Eq. (24)) reflecting the effect of the viscosity on termination rate coefficients is founded, and the kinetics is substantially controlled by diffusion of the polymer chains.

Acknowledgements

The authors thank financial support for this work from the National Science Foundation of China (Nos. 50390090 and 20574045).

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