

The Reaction Mechanism of Diethyl-2,3-dicyano-2,3-di(*p,m*-dimethoxyphenyl) Succinate with Styrene

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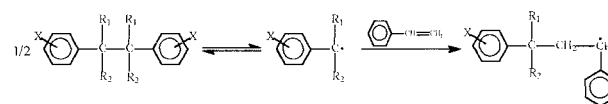
ABSTRACT: The radical polymerization of styrene (ST) can be initiated by diethyl-2,3-dicyano-2,3-di(dimethoxyphenyl) succinate (ECPS). The reaction mechanism has been studied by means of UV, H¹-NMR, product analysis, gel permeation chromatography, electronic spin resonance (ESR), and the conversion of monomer via time. These experimental results indicate that ECPS probably takes the place of complex with ST, and the complex interaction between ECPS and ST can take advantage of the dissociation of the C—C bond. The complex interaction and thermal effect are the important factors causing the dissociation of C—C bond. © 1999 John Wiley & Sons, Inc. *J Appl Polym Sci* 74: 1140–1145, 1999

Key words: diethyl-2,3-dicyano-2,3-di(dimethoxyphenyl) succinate; styrene; polymerization; mechanism

INTRODUCTION

It is well known that substituted dibenzyls can initiate the free-radical polymerization of vinyl monomers because of the thermal scission of the C—C bond,^{1–10} and the increase in the speed of the scission with rising polymerization temperature usually results in a decrease in the average molecular weight of polymer.¹¹ In previous studies on the reaction mechanism of the C—C bond initiators of dibenzyl type, people mainly depended on measuring electronic spin resonance (ESR) spectra of the reactive intermediates, carbon radicals,^{12–14} or on product distribution,⁸ and

have not undertaken the detailed and comprehensive investigation on the reaction mechanism. The mechanism is generally interpreted as



The purpose of the present work is to expand the investigation of this kind of polymerization reaction and, particularly, to examine the behavior of diethyl-2,3-dicyano-2,3-di(*p,m*-dimethoxyphenyl) succinate (ECPS) in the polymerization reaction system before the scission of C—C bond.

EXPERIMENTAL

Materials

Commercial styrene (ST) (Shanghai Third Chemicals, Shanghai, China) was washed with aqueous

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NaOH to remove inhibitor, dried over CaCl_2 , and distilled under reduced pressure. Commercial acrylonitrile (AN) (Shanghai Third Chemicals, Shanghai, China) was passed through a silica gel column and then distilled. Commercial methyl methacrylate (MMA) (Shanghai Third Chemicals, Shanghai, China) was distilled under reduced pressure. Commercial chloroform (Xi'an Chemicals, Xian, China) was kept in 0.4-nm molecular sieve for 24 h to remove any trace water and then distilled. Diethyl-2,3-dicyano-2,3-di(*X*-phenyl) succinate ($X = p,m\text{-OCH}_3, p\text{-OCH}_3, \text{ and } p\text{-CH}_3$) were synthesized according to the method described by De Jonge.¹² Their structure has been determined by means of $\text{H}^1\text{-NMR}$, IR, mass spectroscopy (MS), elemental analyses, and X-ray diffraction experiment.^{9,15,16} Those compounds were purified by recrystallization in methanol before use. Commercial benzoyl peroxide (BPO) and azobisisobutyronitrile (AIBN) were purified by recrystallization before use.

UV Spectra

A chloroform solution of 0.0092M diethyl-2,3-dicyano-2,3-di(*X*-phenyl) succinate ($X = p,m\text{-OCH}_3, p\text{-CH}_3, \text{ and } \text{H}$) and 0.4570M ST was sealed in a 1-cm quartz cell that was kept at constant temperature ($20 \pm 0.5^\circ\text{C}$). The absorption spectra were recorded using a Jasco Uvidec-505 UV/VIS digital spectrometer in the wavelength region of 340–400 nm at intervals of 15 min. The measurement of the complex constant was described in ref. 21.

Monomer Polymerization

(a) The solution of initiator and monomer was accurately made [initiator (ECPS, BPO, and AIBN): ST = 1 : 400 mol/mol and ECPS : AN = 1 : 800 mol/mol]. The solution was transferred into a glass tube of 5-mm diameter and after sealing, was placed in a thermostat at the assigned temperature (temperature error, $\pm 0.5^\circ\text{C}$) and reacted about 72 h (conversion, $>99\%$). The unreacted monomer in polymer was removed in vacuum.

(b) The concentration of ECPS in monomers (ST, AN, and MMA) is the same as that in experiment a. Those solutions were sealed in glass tubes and allowed to react at room temperature. On the other hand, we also performed a similar experiment on the mixed solutions of ST and AN as well as ST and MMA (ECPS : monomer = 1 : 400 mol/mol). We found that only ST and a mixed solution of ST and AN or MMA were initiated by

ECPS to polymerize, and AN or MMA were not done. After reacting for 6 days at room temperature, the products were dissolved to toluene or dimethyl formamide, and then precipitated in methanol. The precipitated polymers were dried in a drying box under reduced pressure. The conversion ratio (%) is: 46% (ST), 82% (ST and AN), and 38% (ST and MMA), respectively.

(c) The concentration of ECPS in ST is same as that in experiment a. In this experiment, we carried out the comparative test at the room temperature ($20 \pm 2^\circ\text{C}$). The solution was placed in two glass tubes; one glass tube was wrapped in a black cloth and the other was not.

(d) The concentration of ECPS in ST is the same as in experiment a. The solutions were placed in the thermostat at the assigned temperature. The refractive index (n_p) of the solutions were measured at the assigned time by using WDS-I 881617 refractometer (Shanghai, China). The conversions (P) were calculated from the following equation^{17–19}:

$$P = v_1(n_p - n_1) / [v_2n_2 - v_1n_1 - (v_2 - v_1)n_p]$$

where n is the refraction index, v is the volume density (mL/g), and subscripts 1, 2, and p express the ST, polystyrene, and the polymerization solution, respectively.

(e) Measures of 0.6202 g of ECPS and 4.61 mL of ST were added to 63.5 mL benzene solvent. After the mixed solution reacted for 72 h at room temperature, benzene and unreacted ST were removed in vacuum (the temperature was kept at $20 \pm 5^\circ\text{C}$). The coarse product ($M_w = 478$, $D = 1.96$) was obtained at about 3.8 g and separated by using silica gel (H-200-300 mesh) column. The 1,2-adduct was obtained at about 0.09 g (12% yield). (Because further purity is very difficult, there are still a few impurities in the components.)

MS (EI) (m/z , %): 600 (M^+ , 9%), 463 [$M^+ - \text{C}_6\text{H}_3(\text{OCH}_3)_2$, 36%], 389 [$M^+ - \text{C}_6\text{H}_3(\text{OCH}_3)_2 - \text{CO}_2\text{C}_2\text{H}_5 - \text{H}^+$, 20%], 338 [$\text{C}_6\text{H}_3(\text{OCH}_3)_2\text{C}(\text{CN})(\text{CO}_2\text{C}_2\text{H}_5) - \text{CH}(\text{C}_6\text{H}_5)^+$, 33%], 249 [$\text{C}_6\text{H}_3(\text{OCH}_3)_2\text{C}(\text{CN})(\text{CO}_2\text{C}_2\text{H}_5)\text{H}$, 44%], 248 [$\text{C}_6\text{H}_3(\text{OCH}_3)_2\text{C}(\text{CN})(\text{CO}_2\text{C}_5)^+$, 100%], 220 [$\text{C}_6\text{H}_3(\text{OCH}_3)_2\text{C}(\text{CN})(\text{CO}_2\text{H})^+$, 30%], 176 [$\text{C}_6\text{H}_3(\text{OCH}_3)_2\text{C}(\text{CN})\text{H}^+$, 23%], 105 [$\text{C}_6\text{H}_5 - \text{CH}_2 - \text{CH}_2^+$, 8%]. Some fragments originate via McLafferty rearrangements. Elemental analysis (%): calcd for $\text{C}_{34}\text{H}_{36}\text{O}_8\text{N}_2$: C, 68.00%; H, 6.00%; O, 21.33%; N, 4.67%. Found, C, 69.03%; H, 6.43%; O, 20.56%; N, 3.98%. The mass spectra were determined with a ZAB-HS mass spectrometer. The elemental analysis was carried out by using an 1106 elemental analysis instrument (Italy).

The Average Molecular Weight and Dispersion Coefficient

The average molecular weight and dispersion coefficient were carried out with 150 ALL/GPC and μ -Bondage 1E-lin \times 3 + E-100 nm instrument. Dimethyl formamide was used as the solvent, and the temperature was set at 60°C. The capillary flow rate was fixed at 1.0 mL/min.

ESR Detection of ECPS Molten State

The ESR detection was carried out using a Bruker EP 200 D RSC spectrometer with an assembled temperature control instrument W₂-4107 sample chamber. The solid ECPS was put into a capillary. When the temperature of the sample chamber was heated to 130°C, ESR spectrogram was initially recorded. The satisfying ESR spectrogram was obtained at 190°C.

Spectral simulation was performed with laboratory-written software based on the Bloch equation and rigorously accounts for the line broadening caused by electron exchange between the radical and the nonparamagnetic species in solution.²⁰

¹H-NMR Spectra

NMR spectra were run on a Bruker Am-400 NMR spectrometer. Tetramethylsilane ($\delta = 0$ ppm) and chloroform-*d*₃ were used as an internal standard and solvent, respectively.

RESULTS AND DISCUSSION

The measured UV spectra during the reaction of ECPS with ST at room temperature is shown in Figure 1. A new absorption bond appears at $\lambda_{\max} = 360$ nm. It increases with reaction time from zero to a certain period and then keeps almost constant for 2–3 h to begin a slow decay. In addition, we also performed a similar measurement on the reaction of diethyl-2,3-dicyano-2,3-di(*X*-phenyl) succinates (*X* = *p*-CH₃ and H) with ST. It is found that no new absorption bond appears in the wavelength region of 340–400 nm. Those experimental phenomena indicate that the new absorption bond is possibly a result of the formation of reaction intermediate between ECPS and ST. To further explore the structure of the intermediate, ¹H-NMR spectra of 3 : 1 mol ratio of ST and ECPS as well as of pure ECPS in chloroform-*d*₃ are observed (Fig. 2). The chemical shift of the

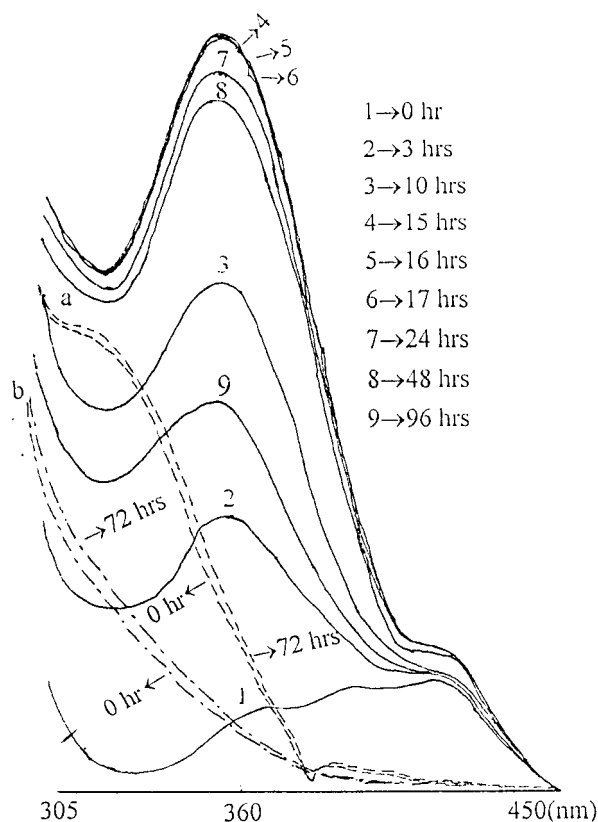


Figure 1 UV absorption spectra recorded during the polymerization reaction of ECPS and ST at room temperature. The absorption lines from 1 to 9 were recorded at different periods. The lines a and b were recorded on the reaction of diethyl-2,3-dicyano-2,3-di(*p*-*X*-1 phenyl) succinate (*X* = CH₃—; line a, H-line b) and ST for 72 h. The initial concentration of ECPS and ST was 0.0092 and 0.4570 mol/L, respectively.

protons of methoxyl in the *meta* of phenyl obviously decreases as a comparison with corresponding protons in pure ECPS. It is possibly because the large conjugated π bond in ST produces a shielding effect on the methoxyl. This shows the presence of the interaction between ST and ECPS. On the other hand, the measurement of the absorbance on the mixed solution of ECPS with ST of a different concentration shows that the absorbance of the new absorption bond grows with increasing concentration of ECPS in the solution,²¹ and the absorbance *A* of the mixed solution is larger than $A_{ST} + A_{ECPS}$ (A_{ST} and A_{ECPS} are the absorbance of ST and ECPS in chloroform, respectively). This demonstrates that the complex interaction between ST and ECPS possibly takes place in the solution. In all probability, the intermediate is the complex of both ST and ECPS. An equation²² described by Rose and Drago is

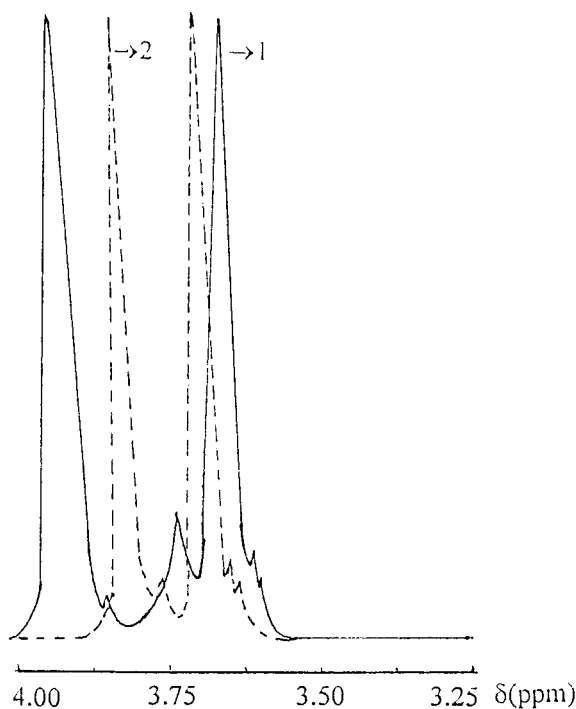
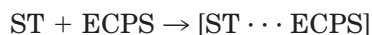


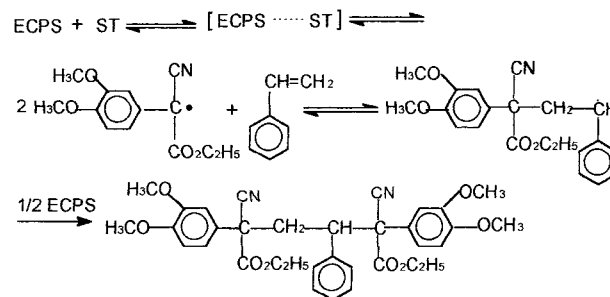
Figure 2 (^1H -NMR spectrum of the methoxyl protons of the *meta* of phenyl was measured on the chloroform- d_3 solution of ECPS (0.40 mol/L) (1) and both ECPS and ST (2) (ECPS = 0.40 mol/L, ST = 1.21 mol/L). The mixed solution of ECPS and ST in chloroform- d_3 was set for 2 h at the room temperature ($20 \pm 2^\circ\text{C}$) and then measured. The obvious change of chemical shift of the other protons in ECPS was not observed as compared to the corresponding protons of pure ECPS in chloroform- d_3 except for the chemical shift of phenyl protons, which has not been assigned.

used to calculate the complex constant. (The maximum absorbance stays unchanged for some time, and therefore, we assume that the reaction of the formation of the complex reaches equilibrium at the time intervals.) The complex constant of 1 : 1 complex of ST and ECPS is 0.605 (L/mol). (The detailed experimental result is described in ref. 21.) The result provides more immediate evidence for the above discussion concerning the formation of the complex between ST and ECPS. The reaction equation is shown as:



It is well known that ST, AN, and MMA all are monomers that can be initiated by the free radical.^{8,9,11} In our research, under room temperature conditions, ECPS can initiate polymerization of

ST, the mixed solution of ST and AN, as well as of ST and MMA, but almost cannot initiate polymerization of AN and MMA. To examine whether light plays a role in the scission of the C—C bond, a comparative test is performed. After the solution of ECPS with ST is sealed in two glass tubes, one glass tube is wrapped in a black cloth and the other is not. It is found that ECPS can still initiate the polymerization of ST in the dark at the room temperature. No significant difference is observed between the two tests. This indicates that light is not responsible for the scission of the C—C bond. In addition, ST is unlikely to reach a 46% conversion ratio for 6 days by selfpolymerization at room temperature. (The dissociation of the π bond of the vinyl in ST needs a thermal energy of about 210 kJ/mol.¹¹) The dissociation energy of the C—C bond in ECPS, which was measured by the kinetic of thermal decomposition of ECPS in ST at 80–110°C, is 64.6 kJ/mol.²³ Therefore, if there is not influence of other factors on ECPS, ECPS is unlikely to initiate ST to polymerize at room temperature ($20 \pm 2^\circ\text{C}$). The polymerization of ST at room temperature could possibly mainly attribute to the complex interaction between ECPS and ST causing the dissociation of the C—C bond. On the other hand, according to product analysis, the 1,2-adduct is obtained from ECPS with ST in chloroform at room temperature. This also indicates that the scission of the C—C bond produces α -cyano, α -ethoxycarbonyl,*p,m*-dimethoxybenzyl radical (CEDR). The 1,2-adduct probably is a result of the CEDR radicals reacting with the vinyl in ST. The discussion about the radical as a reactive intermediate in the 1,2-addition reaction of ECPS with ST is in agreement with the earlier experiments of De Jonge et al.⁸ and Hey and Misra,⁷ where they found the 1,2-addition reactions of some polysubstituted dibenzyl compounds with ST undergoing a radical mechanism.



The 1,2-addition can be considered as a premature termination of the polymerization and shows how the ECPS is built in the polymer.

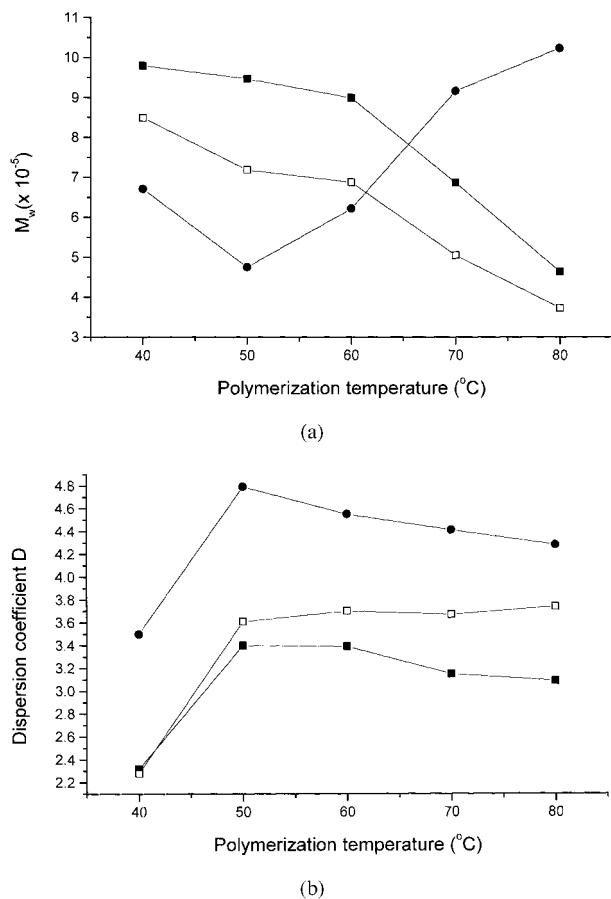


Figure 3 The average molecular weight M_w (a) and the dispersion coefficient D (b) of polystyrenes as a function of the polymerization temperature. (●) ECPS as initiator, (□) BPO as initiator, (■) AIBN as initiator.

The curves of the average molecular weight (M_w) and the dispersion coefficient (D) ($D = M_w/M_n$) via the polymerization temperature are depicted in Figure 3. It can be seen from Figure 3(a) that, when BPO and AIBN (BPO or AIBN : ST = 1 : 400 mol/mol) are used as initiators to initiate polymerization of ST, M_w decreases with rising polymerization temperature. This agrees well with the previous experiments for the two initiators.¹¹ However, when ECPS is used as an initiator for the polymerization of ST, M_w initially decreases and then increases as the polymerization temperature rises. This experimental phenomenon is different from that of BPO and AIBN as well as same-type initiators such as diethyl-2,3-dicyano-2,3-di(*X*-phenyl) succinates ($X = p\text{-OCH}_3$, $p\text{-CH}_3$, $o\text{-OCH}_3$, $p\text{-Cl}$, and H).²⁴ It is possible because the increase in the rate of decomposition of ECPS at a moderate speed with the polymerization temperature rising from 20 to 50 °C leads to an increase in the concentration of the radicals in the polymerization system.

The decrease of M_w and increase of D mainly attributes to the increase in the termination reaction occurring by the combination between the growing radical chain and CEDR, as well as between growing radical chains. However, when the polymerization temperature rises from 50 to 80 °C, the quick increase in the primary radical concentration will bring about a greater increase in the probability of the termination reaction between the radicals. A large number of ECPS are consumed at an earlier stage of reaction, so, when the polymerization reaction with time reaches a certain degree, the concentration of the radical originating from ECPS is low in the polymerization system. Figure 4 shows that the conversion rate increases considerably with the temperature rising from 20 to 50 °C, but when the temperature exceeds 50 °C, the temperature rise can result in an increase in the rate only at the earlier stage of polymerization reaction. At a later stage, it can be seen from Figure 4 that the rate at 60 °C is faster than at 70 and 80 °C. The lower radical concentration can lead to the increase in M_w during the prolonged polymerization reaction. This discussion is in agreement with the result in which D of polymers have a large value in the range of polymerization temperature from 50 to 80 °C. In this temperature range, the quick depletion of the primary radicals probably is correlative with the complex interaction of ECPS with ST. The interaction can increase the formation of primary radicals. In other similar experiments, it is found that M_w of polyacrylonitrile (ECPS : AN = 1 : 800 mol/mol) decreases when the polymerization temperature rises from 50 to 65 °C [M_w ($\times 10^{-4}$) is 58.62 ($D = 6.71$, 50 °C), 44.58 ($D = 6.00$, 55 °C), and 29.89 ($D = 5.66$, 65 °C)].²⁵ This also indicates that the complex interaction between ECPS and ST probably

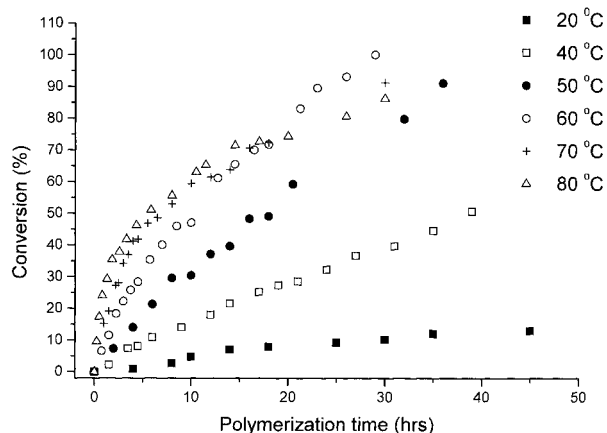


Figure 4 The conversion of ST as a function of time.

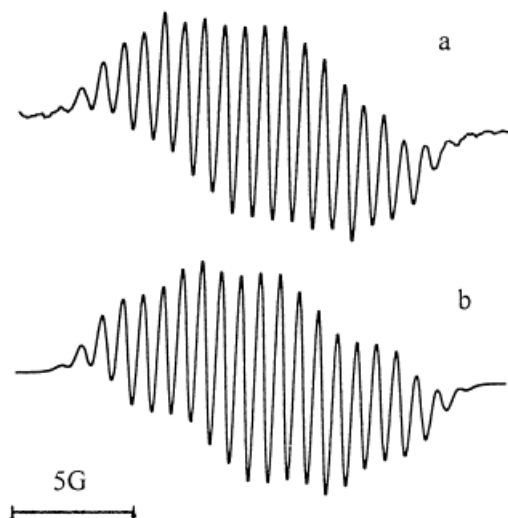
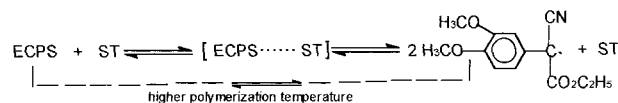


Figure 5 (a) the ESR spectrum obtained in the molten state of ECPS. g factor = 2.0060. (b) Simulated ESR spectrum, linewidth $\Delta H_{pp} = 0.30\text{G}$, the hyperfine splitting constants (G) are 0.21 (3H), 0.94 (3H), 0.90 (1H), 3.30 (1H), 4.93 (1H), 1.70 (1N), and 0.75 (2H), respectively.

plays a role in the increase of M_w of polystyrene with the rise in polymerization temperature.

ECPS almost cannot initiate the polymerization of AN or MMA at room temperature, but can effectively above 50°C .²⁵ This shows that AN or MMA does not produce a complex interaction with ECPS, and the formation of CEDR at a high temperature is more probable as a result of thermal decomposition of the C—C bond. The C—C bond joining two benzyls has a longer bond length (0.1581 nm^{16}) than the normal C—C bond (0.154 nm). The bond is decomposed easily compared to the normal C—C bond at high temperature. The ESR measurement provides immediate evidence for the discussion. The CEDR is observed in the molten state of ECPS ($\text{mp} = 143^\circ\text{C}$) (Fig. 5). The initiation mechanism is depicted as follows.



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