Influence of Isomer Ratio and Ring Substituents in Decomposition Activation Energies of $\alpha,\alpha,\alpha',\alpha'$-Tetrasubstituted Dibenzyls

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ABSTRACT: Diethyl-2,3-dicyano-2,3-di-(*X*-substituted phenyl) succinates ($X = p$-OCH$_3$, p-CH$_3$, p-Cl, H, p-NO$_2$) can initiate the free-radical polymerization of styrene. The decomposition rate constant and activation energy were measured by means of a dilatometer, and the results showed that they were strongly dependent on the ratio of meso- and dl-isomers in the polysubstituted dibenzyl compounds and the properties of the ring substituents. On the other hand, it was found that the polystyrenes, which were obtained by initiation with hydrogen, had a much larger average molecular weight than that with p-OCH$_3$ and p-CH$_3$. The experimental phenomena were correlated with the structure of the radical resulting from hydrogen. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2964–2971, 2001

Key words: diethyl-2,3-dicyano-2,3-di-(*X*-substituted phenyl) succinate; initiator; ring substituent; isomer ratio; styrene

INTRODUCTION

$\alpha,\alpha,\alpha',\alpha'$-Tetrasubstituted dibenzyl compounds in vinyl monomers, which are heated to moderate temperatures, can occur via thermal decomposition of the C—C bond and initiate the free-radical polymerization of vinyl monomers.[1–5] These dibenzyl compounds often have two configurational isomers, meso- and racemic isomers, via the different substituents joining on the benzyl carbon. Previous work mainly concentrated on studying the influence of substituent properties on initiator activity.[6,7] Little attention was paid to the effect of the stereochemistry of an intiator on the decomposition energy (E_d). In fact, the different contents of meso- or dl-isomers in an initiator will cause a variation of the initiator activity.

In this article our purpose was to study the effect of the isomer ratio and substituent properties in diethyl-2,3-dicyano-2,3-di-(*x*-substituted phenyl) succinates ($x = $ OCH$_3$, **1**; CH$_3$, **2**; Cl, **3**; H, **4**; NO$_2$, **5**) on the E_d. We also measured the weight-average molecular weights (M_w) of polystyrenes at different conversions by using initiators **1**, **2**, and **4**. It was found that the polystyrenes, which were initiated by initiator **4**, had a much higher M_w than that by **1** and **2**, the results of which are discussed later.
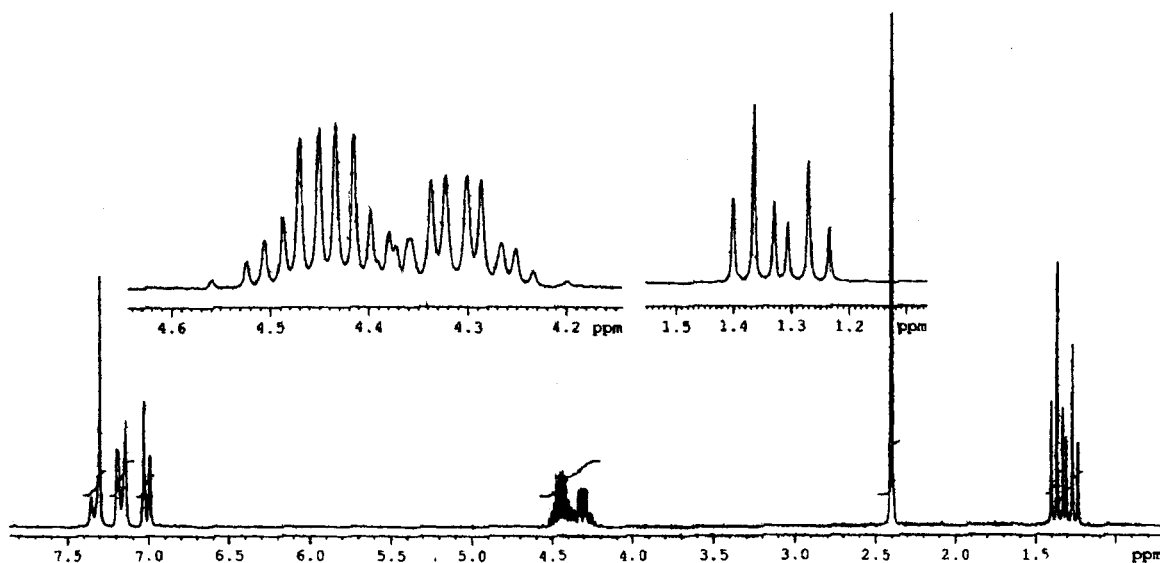
EXPERIMENTAL

Materials

Commercial styrene (St, Shanghai Third Chemicals) was washed with aqueous NaOH to remove

Figure 1 The ^{1}H-NMR spectrum of **2** (61.9% dl content): 7.355–6.994 ppm (—C$_6$H$_4$—, meso and dl), 4.442 ppm (12, —OCH$_2$—, dl), 4.312 ppm (12, —OCH$_2$—, meso), 2.405 ppm (1, CH$_3$—Ph, meso and dl), 1.365 ppm (3, —CH$_3$, dl), 1.270 ppm (3, CH$_3$, meso).

the inhibitor, dried over CaCl$_2$, and distilled under reduced pressure.

The diethyl-2,3-dicyano-2,3-di-(X-phenyl) succinates (X = p,m-OCH$_3$,**1**; p-OCH$_3$, **2**; p-CH$_3$, **3**; p-Cl, **4**; H, **5**) were synthesized according to the method described by De Jonge et al.[8] Their structures were determined by means of ^{1}H-NMR, IR, mass spectrometry, and elemental analyses.[2] The meso- and dl-isomers were separated by fractional recrystallization in a 9:1 (v/v) mixed solution of tetrachloromethane and ethyl acetate. An X-ray diffraction experiment[9] showed that the low melting isomer is meso and high melting isomer is dl. The pure meso- and dl-isomers were mixed in the same ratio. Because of the different configurations of the two isomers, the protons of the methyl of the ethoxycarbonyl in the dl-isomers had a larger chemical shift than the meso-isomers in the ^{1}H-NMR spectra[10] (Fig. 1). The contents of the meso-isomers and corresponding dl-isomers were calculated by comparing the heighth of the two peaks.

Kinetics Measurement

The 1.732 ± 0.002 × 10^{-3} mol/L solution of initiators in the styrene was accurately made. The experiment was carried out by using a standard dilatometer. The dilatometer volume was 10 mL, and the capillary constant was 0.0285 mL/cm. The dilatometer was filled with styrene containing various initiators and then laid in the ther-

mostat at the assigned temperature (±0.5°C temperature error). The conversions of styrene were measured at certain intervals. (Only a part of curves of conversions with time are depicted in Fig. 2). The decomposition rate constant was calculated by the dead-end polymerization equation[11] (Fig. 3),

$$\ln[1 - \ln(1 - X_t)/\ln(1 - X_\infty)] = -k_d t/2 \qquad (1)$$

where X_t is the fractional conversion at time t (conversion of the thermal polymerization was deducted at t), X_∞ is the conversion at $t \to \infty$, and k_d is the decomposition rate constant of the initiator. The E_d values were calculated by the Arrhenius equation.

After a solution of 0.5 g of **2** (41.1% dl-isomer) and 321 g of styrene (3.64 × 10^{-3} mol/L) under nitrogen was reacted about 25 min at 100°C (~8% styrene conversion), the solution was diluted with 100 mL of toluene and precipitated with methanol. Then the polystyrene was filtered out. The filtrate was concentrated to dryness *in vacuo* at 30 ± 2°C. The residue was dissolved in chloroform and then washed 3 times in water. After the usual workup (a temperature of < 30°C to prevent meso → dl conversion), about 0.2 g of unreacted **2** was obtained. (There were still a few impurities.) The ^{1}H-NMR spectrum showed that the dl content was 45.2%. [We only compared the peak height of the methyl protons (1.37 ppm) in the dl-isomer to that (1.27 ppm) in the meso-isomer.]
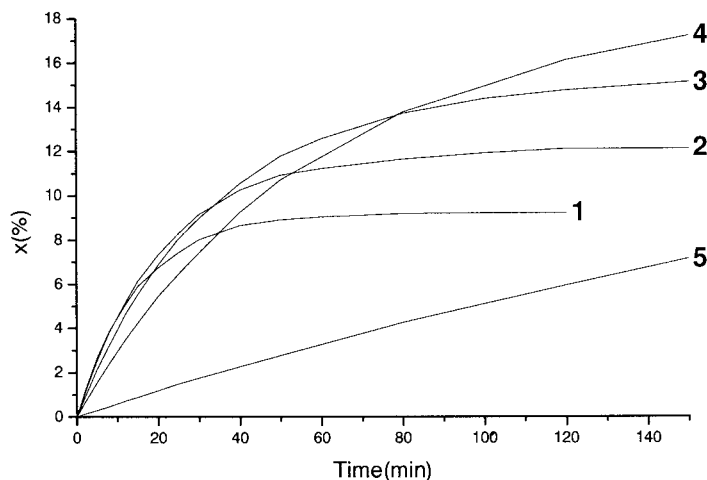
Figure 2   The curves of the conversions with polymerization time: curve 1, **1** (dl, 39.7%); curve 2, **2** (dl, 41.1%); curve 3, **3** (dl, 42.2%); curve 4, **4** (dl, 41.3%); curve 5, **5** (dl, 40.9%).

The concentrations of initiators **1**, **2**, and **4** in styrene were all 0.0217 mol/L. The solution was transferred into 5-mm diameter glass tubes. After sealing, the solutions were laid in the thermostat at the assigned temperature (temperature error $= \pm 0.5°C$). The refractive index (n_p) of the solutions was measured at the assigned time by using a WDS-I 881617 refractometer (Shanghai, China). The conversions (P) were calculated from the following equation[12,13]:

$$P = v_1(n_p - n_1)/[v_2 n_2 - v_1 n_1 - (v_2 - v_1)n_p]$$

where v is the volume density (mL/g); and the subscripts 1, 2, and p are the styrene, polystyrene, and polymerization solutions, respectively.

The solutions of known conversion were dissolved in toluene and then precipitated with methanol. The polystyrenes were filtered off, dissolved in toluene, and precipitated again with methanol. This procedure was repeated once more. The polystyrenes were dried in a vacuum at 80°C and remained there for the GPC measurement.

Physical Analysis

The ^{1}H-NMR spectra were run on a Bruker Am-400 spectrometer. Tetramethylsilane ($\delta = 0$ ppm) and chloroform-d_3 were use as an internal standard and solvent, respectively.

The average molecular weight and dispersion coefficient measurements were carried out
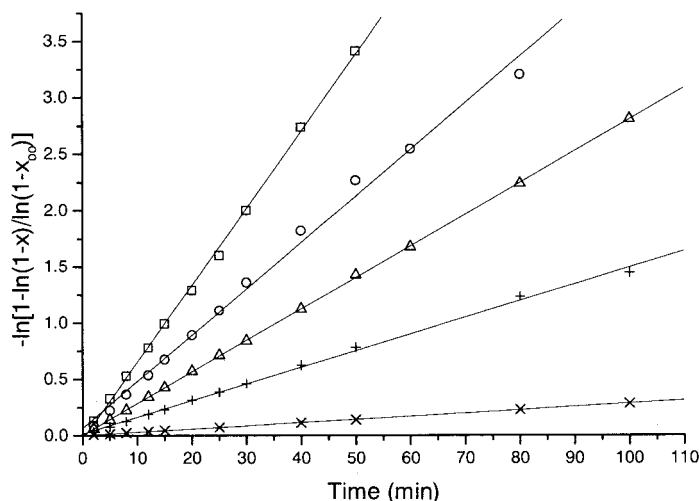
Figure 3   The rate constants of the decomposition of the initiators at 100°C in styrene: (□) **1** (dl, 39.7%), (○) **2** (dl, 41.1%), (△) **3** (dl, 42.2%), (+) **4** (dl, 41.3%), and (×) **5** (dl, 40.9%)
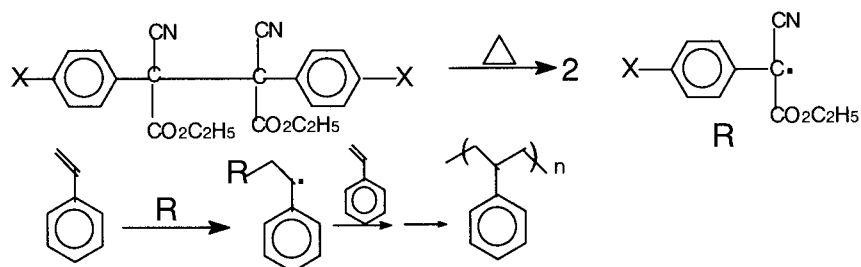
Scheme 1 The reaction equation of the free-radical polymerization of styrene.

with 150 ALL/GPC and a μ-Bondage 1E-lin $\times 3$ + E 100-nm instrument. Toluene was used as the solvent, and the temperature was set at 60°C. The capillary flow rate was fixed at 1.0 mL/min.

RESULTS AND DISCUSSION

Effect of Ring Substituents on Initiator Activity

Initiators **1–5** can initiate the free-radical polymerization of styrene at high temperature be-

Table I Decomposition Rate Constants (k_d) and Activation Energies (E_d)

| Initiators	dl (%)	80°C	90°C	100°C	110°C	E_d (kJ/mol)	ln A
		$k_d \times 10^4$ (S^{-1})		
1	0	11.55	19.11	36.76	48.30	53.6	11.5
1	20.8	8.174	14.95	26.47	45.47	64.3	14.8
1	39.7	5.635	11.28	22.80	40.52	73.9	17.7
1	61.3	4.561	9.690	19.73	38.50	80.1	19.6
1	82.4	3.420	7.790	17.06	35.87	88.3	22.1
1	100	2.531	6.272	14.78	33.42	96.8	24.7
2	0	6.284	11.87	21.93	38.85	68.3	15.9
2	20.7	4.382	8.981	17.71	33.72	76.4	18.3
2	41.1	2.970	6.819	13.75	31.36	88.7	22.1
2	61.9	1.730	4.362	10.43	24.06	98.5	24.9
2	80.9	1.143	3.210	8.412	21.31	109.7	28.3
2	100	0.872	2.668	7.648	20.25	118.7	32.1
3	0	3.436	7.446	15.42	30.79	82.4	20.1
3	19.4	2.239	5.466	12.72	28.10	94.8	23.9
3	42.2	1.312	3.536	9.330	23.85	110.3	28.6
3	58.9	0.756	2.338	6.807	18.75	120.3	31.5
3	80.2	0.363	1.222	3.848	11.53	129.2	33.8
3	100	0.237	0.865	2.941	9.486	138.4	36.5
4	0	1.693	4.026	9.190	20.10	92.7	22.9
4	20.7	1.003	2.682	6.769	16.26	104.5	26.4
4	41.3	0.652	1.888	4.930	13.30	112.8	28.8
4	60.8	0.295	0.966	2.981	8.676	127.2	32.9
4	82.4	0.161	0.575	1.916	5.982	135.4	35.1
4	100	0.074	0.293	1.071	3.705	146.8	38.2
5	0	0.263	0.802	2.300	6.236	118.7	29.9
5	18.9	0.167	0.572	1.826	5.477	130.9	33.6
5	40.9	0.0641	0.257	0.940	3.253	147.2	38.2
5	63.2	0.0307	0.141	0.589	2.268	161.4	42.3
5	80.4	0.0152	0.0819	0.403	1.825	179.3	47.7
5	100	0.0089	0.0523	0.281	1.393	189.4	50.6
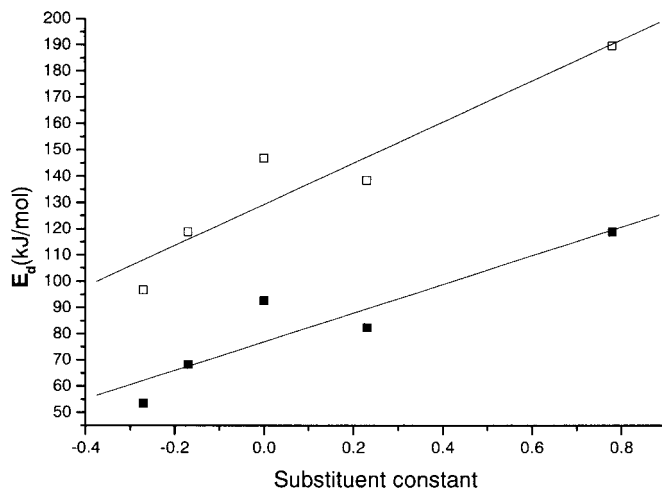
Figure 4 The curves of E_d and substituent constants for (■) meso-isomers and (□) dl-isomers.

cause of the thermal decomposition of the benzyl carbon–benzyl carbon bond. The reaction equation is generally described as in Scheme 1.

Table I summarizes the k_d and E_d values of initiators **1**–**5**. Introduction of donor ring substituents increases initiator activity. The following order of E_d values was observed: $E_{d\text{-}5} > E_{d\text{-}4} > E_{d\text{-}3} > E_{d\text{-}2} > E_{d\text{-}1}$. This order was in agreement with the order observed for the styrene polymerization with ring substituted benzoyl peroxides.[6] The experimental phenomena can be interpreted from two aspects. As for the first aspect, we found in previous work that the chemical shifts of the carbons of cyano, carbonyl, and methylene of **1**, **2**,

4, and **5** in the ^{13}C-NMR spectra correlated with Hammett σ values for the substituents.[14] Initiator **3** was the exception ($\sigma = +0.23$). This was probably the result of high polarization of the electronic cloud of the chlorosubstituent.[15] This agreed with our present experimental results in which the E_d showed an approximate correlation with its σ values (Fig. 3). On the other hand, the crystal and molecular structure experiments[9] for **1**–**5** showed that the lengths of the benzyl carbon–benzyl carbon bonds were 0.1596 nm (**1**$_{dl}$), 0.1567 nm (**2**$_{dl}$), 0.1578 nm (**3**$_{dl}$), 0.1580 nm (**4**$_{dl}$), and 0.1587 nm (**5**$_{dl}$). The change of the C—C bond lengths did not appear to be as regular as the E_d.
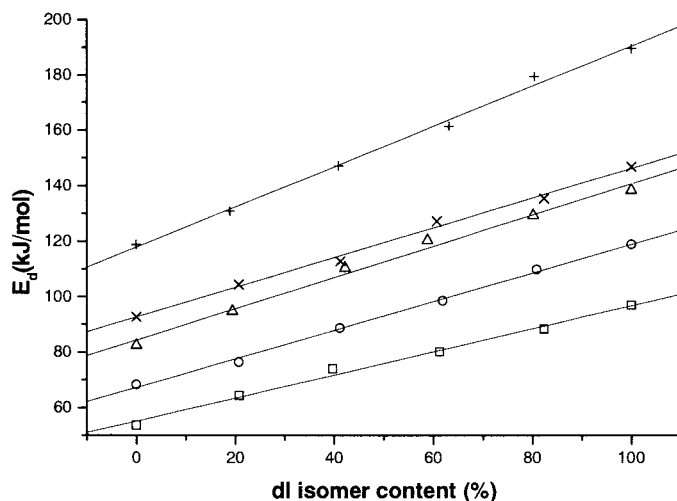
Figure 5 The E_d curves and dl-isomer contents: (+) NO_2 (A_5, 117.83), (×) H (A_4, 92.68), (utri;) Cl (A_3, 84.37), (cir;) CH_3 (A_2, 67.212), and (□) OCH_3 (A_1, 55.076).

This clearly proved that purely steric interactions were not the main factor affecting the E_d. It was probably that the donor groups in the phenyls increased the dipolar repulsion among the nitrile groups and carbonyl groups. Therefore, the increase in the withdrawing electron properties of the substituents in phenyls caused the increase in the stability of the dibenzyl compounds. The second aspect was that the electron spin resonance (ESR) spectrum of the radical decomposing from melting state **5** showed that the single electron could transfer from the benzyl carbon to the strong electron acceptor nitro.[16] (The hyperfine splitting constant was 9.07 G in the nitrogen oxide radical.) This indicated that the stability of the primary radicals resulting from initiators **1** to **5** probably decreased with the increase in the donor properties of the substituents.

Effect of Isomer Ratio on Initiator Activity

Table I shows that the E_d values increased with increasing content of dl-isomer in the initiator. The results indicated that dl-isomers had lower initiating activity than the corresponding meso-isomers. This was in agreement with the earlier experiment of Drefahl et al.[17] They found that the dl-isomer of 2,3-diphenylsuccinonitrile was more stable than the corresponding meso-isomer. It can be seen from the plots in Figure 4 that there was linear relationship between the E_d and dl-isomer content. The curves can be described by the following equation (Fig. 3):

$$E_d = E_{d(\text{meso})} + AX$$

where X is the content (%) of the dl-isomer in the initiator; $E_{d(\text{meso})}$ is the activation energy of the pure meso-isomer; and A is a parameter that is relative to the molecular structure of the initiator, reaction system, and so forth.

   It is well known that dibenzyl compounds can occur from thermal isomerization between meso- and dl-isomers.[8,18] To explore the conversion of the meso- to dl-isomers during polymerization, the polymerization was terminated and the residual initiator was separated when the conversion of styrene reached 8% at 100°C (41.1% dl-isomer **2** as initiator). The 45.2% content of the dl-isomer was determined by means of the ¹H-NMR spectrum. This result showed that only insufficient radicals were found during thermal isomerization. This was probably because of the low initiator concentration and high polymerization tem-

Table II   Weight-Average Molecular Weights (M_w) and Dispersion Coefficient (D)

Initiators	Conversion (%)	T (°C)	$M_w \times 10^4$	D
1	10.7	60	6.91	3.06
1	46.3	60	7.55	2.96
1	76.2	60	9.62	2.32
1	12.5	70	5.63	3.14
1	43.2	70	6.32	2.77
1	71.4	70	8.01	2.54
2	12.9	60	8.18	2.80
2	49.6	60	8.64	2.07
2	81.7	60	15.81	2.24
2	20.2	70	6.40	2.68
2	48.6	70	7.06	1.88
2	63.6	70	8.32	1.96
4	11.5	60	121.2	4.82
4	35.4	60	132.6	4.10
4	69.8	60	148.2	3.13
4	8.3	70	86.42	4.36
4	48.7	70	97.55	2.05
4	69.3	70	113.0	4.18

perature in our research system; the radicals easily diffused out of the solvent cage to initiate styrene polymerization and the diffusing radicals had little probability to recombine. Hence, the E_d was a direct ratio to the contents of the dl-isomers in the initiators.

Effect of Molecular Structure on Average Molecular Weight

The M_w values of polystyrenes at different conversions are summarized in Table II. These results showed that the M_w rose with the decline of the polymerization temperature and with the increase in the withdrawing electron property of substituents in the phenyls. The experimental phenomena correlated to E_d and could be interpreted by the usual polymerization theory.[19] In addition, a comparison of the M_w values of polystyrenes obtained by using initiator **4** with those using **1** and **2** showed that the M_w was much larger in the initiator **4** system than in **1** or **2**. The result could not be attributed simply to the change of the E_d. On one hand, it was correlated with the high decomposition energy of the C—C bond. On the other hand, it was probably correlated with the structure of radical **4**. Radical **4** electron transfer can take place by π–π conjugation. The H of the para position of phenyl has a high hyperfine splitting constant of 5.57 G in the
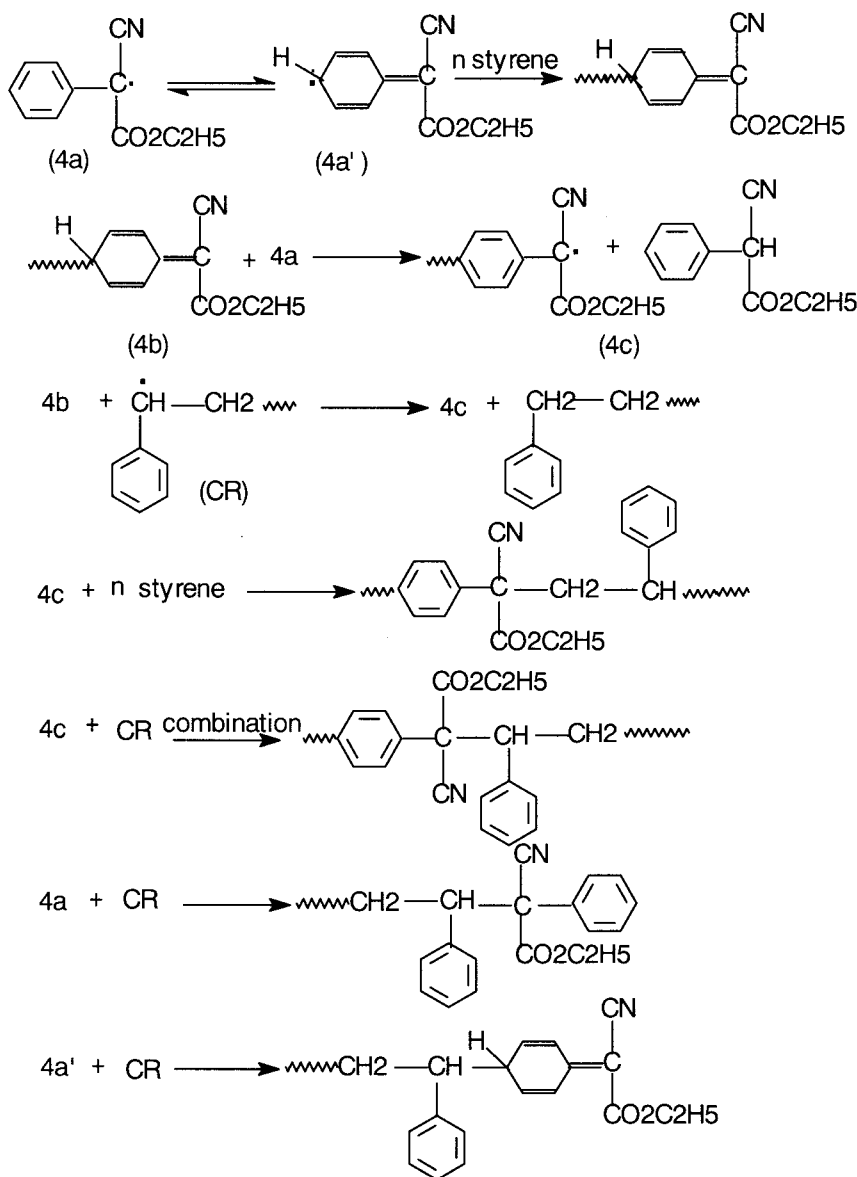
Scheme 2 The polymerization mechanism of initiator **4**.

ESR spectrum.[16] There are two activation centers to react with styrene or chain radicals. The two activation centers of radical **4** are advantageous to propagate the macromolecular chains of the polymer and increase the molecular weight of the polymer. [The trimer (about 15%) and tetramer (about 6%) of radical **4** were obtained by refluxing in chlorobenzene for about 3 h.[20]] This polymerization mechanism is shown in Scheme 2.

CONCLUSIONS

Meso-diethyl-2,3-dicyano-2,3-di-(X-substituted phenyl) succinates have lower activation energies than the corresponding dl-isomers. The E_d rises with the increase in the content of dl-isomer in the dibenzyl compounds. It is found that purely steric interactions are not the main affects on the decomposition of the benzyl carbon–benzyl carbon bond, and the dipolar repulsion among polar groups plays an important role in the decomposition. In addition, the experimental results also show that the E_d is correlated to the Hammett substituent constant. The donor substituent in phenyl is beneficial to the decrease in the E_d.

The structure of the primary radical has an obvious influence on the M_w of polystyrene. The two activation centers of radical **4** are important causes for the resulting high M_w.

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