Determination of Absolute Rate Constants for Elementary Reactions in Radical Polymerization of Diethyl Fumarate

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ABSTRACT: The absolute rate constants of propagation and termination (k_p and k_t) for radical polymerization of diethyl fumarate (DEF) were evaluated to be 0.015 and 164 L mol^{-1} s^{-1}, respectively, by means of a rotating-sector method at 30 °C. The average lifetime of the propagating radical was 166 s under the present polymerization conditions, and the steady-state concentration of the radical was estimated to be as high as 3.6×10^{-5} mol L^{-1}. The presence of the polymer radical in such a high concentration was also confirmed by ESR spectroscopy. The exceptionally small k_p and k_t values were accounted for by the inherently less reactive nature of poly(DEF) radical, probably arising from considerable steric hindrance and slow diffusion of the polymer radical. Because the small rate constants are compensated by the high concentration of the radical, the rates of propagation and termination rationalize high-polymer formation.

Introduction

We have been studying the radical polymerization of a series of α-substituted acrylic ester and acrylonitrile monomers and have quantitatively revealed the contribution of the substituent to the reactivities of the monomers and the polymer radicals as resonance and polar effects.[1-3] Much less attention has been paid to the polymerization of 1,2-disubstituted ethylenes, where a steric effect of the substituent might be a dominant factor in preventing high polymerization.[4] The effect of the substituent on the polymerization of 1,2-disubstituted ethylenes, which may produce a new type of polymer, is not known.

Recently, dialkyl fumarates (DRFs), particularly those bearing bulky ester alkyl groups, have been found to readily polymerize to high molecular weight polymers consisting of the carboalkoxymethylene repeating unit.[5-10] Apparently, the steric factor of the alkyl group plays an important role in facilitating the polymerization, whereas propagation of DRF has been predicted to encounter considerable steric hindrance.[4] Furthermore, the propagating radical of DRF has been shown by ESR spectroscopy to be present in high concentration in homogeneous solution even at room temperature or above, and the spectra have been observed to change with the ester alkyl group.[10]

In previous papers,[11-13] we have used ESR spectroscopy to reveal characteristics of poly(DRF) radical and steric congestion around the radical center arising from the alkyl group and the polymer chain. It is of interest to disclose the features in polymerization of diethyl fumarate (DEF) from the kinetic viewpoint. In this regard, Bengough et al. have reported on the kinetics of DEF radical polymerization based on the overall rate of polymerization (R_p).[14] However, they have not mentioned the peculiarities of DEF and poly(DEF) radical in the polymerization.

In the present paper, we report the determination of the absolute rate constants for DEF polymerization by means of the rotating-sector method. These rate constants could provide a more detailed view of DEF polymerization on the basis of reactivities of the monomer and polymer radical. Because poly(DEF) radical is advantageously detectable in homogeneous solution, consistency of the kinetic data is confirmed by ESR spectroscopy.

Experimental Section

Materials. Commercial DEF was distilled under reduced pressure before use. 2,2′-Azobisisobutyronitrile (AIBN), 2,2′-azobis-2,4-dimethylvaleronitrile (AVN), and 1,1′-azobiscyclohexane-1-carbonitrile (ACN) were recrystallized from methanol. Benzoyl peroxide (BPO) was purified by reprecipitation from chloroform–cold methanol. 1,3,5-Triphenylverdazyl was prepared and purified as described in the literature.[15]

Polymerization Rate. R_p was measured by using a dilatometer of ca. 9-cm^3 volume with capillary tubing of ca. 1-mm i.d. or a sealed tube. AVN and ACN were used as initiators for polymerizations in the dark and under irradiation with a mercury lamp, respectively. A linear relationship between conversion and contraction of the volume of the polymerization mixture was obtained on the basis of the specific gravities of pure DEF and polymer dissolved in the monomer at 30 °C. The hypothetical contraction at 100% conversion was extrapolated to be 12.5%.

The polymerization in the sealed tube was initiated with AIBN, and after a certain polymerization time the contents of the tube were poured into a large amount of aqueous methanol to isolate the polymer. R_p was calculated from the weight of the polymer.

Polymerization under Intermittent Irradiation. The rotating sector used was a disk with two 45° cutoffs in symmetrical positions. An appropriate irradiation time was attained by combination of a hysteresis motor and gears (Oriental Motor) or by a manually operated shutter. The polymerization sensitized with ACN (5.6×10^{-2} mol L^{-1}) was initiated upon irradiation with a 400-W high-pressure mercury lamp at 30 °C.

ESR Spectroscopy. All ESR spectra were recorded on a JEOL JES-ME3X X-band spectrometer. After being sealed off under vacuum, a quartz ESR tube of 3-mm diameter containing the polymerization mixture was irradiated with a 100-W high-pressure mercury lamp or heated in the cavity.

Results and Discussion

Characteristics of DEF Polymerization. DEF yields the polymer in the presence of an azo or a peroxide initiator at appropriate temperatures in bulk or in solution at a moderate to slow rate.[5] The overall activation energy of the polymerization (E) was evaluated as 91 kJ mol^{-1} from the Arrhenius plot of R_p for the bulk polymerization initiated with AIBN over the temperature range from 60 to 80 °C. If the polymerization proceeds through a chain mechanism as well as conventional vinyl polymerization, ($E_p - E_t/2$) is calculated to be 26.5 kJ mol^{-1} from the activation energy of decomposition (E_i) for AIBN, 129 kJ mol[-1,16] from the relation

$$E = E_p - (E_t - E_i)/2$$

where the subscripts p and t denote propagation and termination, respectively. The numerical value for (E_p − $E_p/2$) is quite similar to that reported by Bengough et

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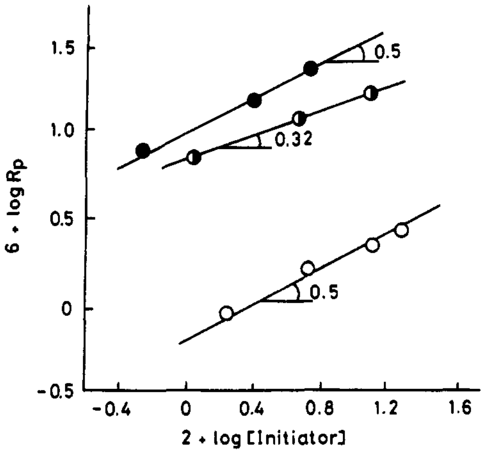

Figure 1. log-log plot of R_p against initiator concentration for DEF polymerization: (○) in bulk ([DEF] = 6.07 mol L^{-1}) with AVN at 30 °C; (●) in bulk with AIBN at 60 °C; (◑) in 50% benzene solution ([DEF] = 3.04 mol L^{-1}) with AIBN at 70 °C.

al.[14] While the absolute values of E_p and E_t for DEF have not been determined yet, the $(E_p - E_t/2)$ value is likely to fulfill the requirement for the chain mechanism.

If the polymerization of DEF follows the standard kinetics, R_p should be expressed by

$$R_p = (2fk_d[I]/k_t)^{0.5}k_p[DEF]$$

where f and k_d denote the efficiency of initiation and the rate constant for decomposition of initiator, respectively.

In DEF polymerization, the kinetic order of the initiator decreased from 0.5 in bulk ([DEF] = 6.07 mol L^{-1}) at 30 and 60 °C to 0.32 in 50% benzene solution (3.04 mol L^{-1}) at 70 °C (Figure 1), suggesting concurrence of bimolecular and primary radical terminations (PRT) at the higher temperature, 70 °C, and the lower DEF concentration, 3.04 mol L^{-1}. Weale has also reported a square root dependency of R_p of DEF on AIBN concentration.[17] A kinetic equation for polymerization involving PRT predicts the lower kinetic order with respect to initiator.[18] However, the same equation indicates that the kinetic order is not sensitive to PRT when the primary radical is more reactive than the propagating radical such as in DEF polymerization. Thus PRT in DEF polymerization could not be completely ruled out.

A plot of R_p versus DEF concentration gave a curve through the origin, and from the log-log plot shown in Figure 2, the apparent kinetic orders with respect to DEF are obtained as 1.66, 1.67, and 1.72 for the polymerizations initiated with AVN at 30 °C, BPO at 60 °C, and AIBN at 60 °C, respectively. It has been confirmed that the propagation as one of elementary reactions involves addition of poly(DEF) radical to DEF.[11-13] Although an apparent kinetic order with respect to the monomer greater than unity has been found in the polymerizations of DRF[8-10] and some other monomers,[19-23] a generally accepted interpretation for this phenomenon is not available.

We have speculated that the longer polymer radical terminates with the slower rate, because the steric congestion around the radical center increases with the polymer chain length up to a certain length as evidenced by the spin trap with 2,4,6-tri-*tert*-butylnitrosobenzene (BNB)[11] and change of the ESR spectra of poly(DRF) radicals with the alkyl groups.[12,13] An increase in DRF concentration results in the longer radical, which may terminate with a slower rate. Consequently, the apparent kinetic order with respect to the monomer could be greater than unity.

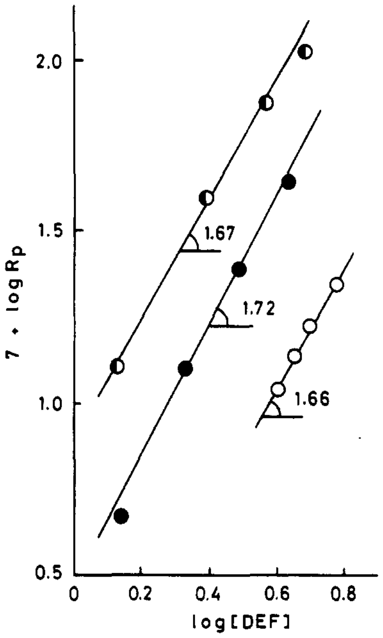

Figure 2. log-log plot of R_p against DEF concentration for polymerization initiated with different initiators: (◐) [BPO] = 1.0 × 10^{-2} mol L^{-1} at 60 °C; (●) [AIBN] = 3.0 × 10^{-3} mol L^{-1} at 60 °C; (○) [AVN] = 1.2 × 10^{-1} mol L^{-1} at 30 °C.

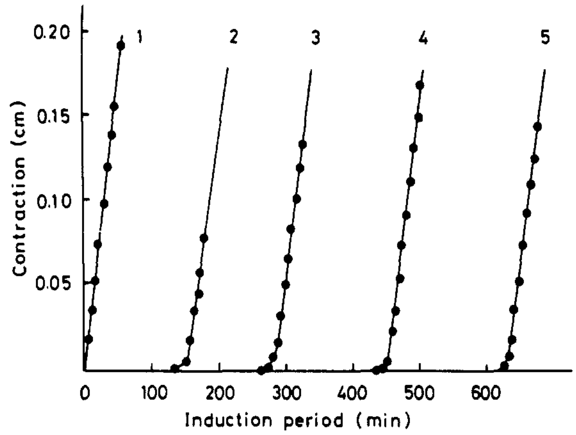

Figure 3. Bulk polymerization of DEF initiated with AVN in the presence of different amounts of verdazyl ([AVN] = 0.118 mol L^{-1}): (1) [verdazyl] = 0; (2) 8.67 × 10^{-4} mol L^{-1}; (3), 1.73 × 10^{-3} mol L^{-1}; (4) 2.60 × 10^{-3} mol L^{-1}; (5) 3.47 × 10^{-3} mol L^{-1}.

Another possibility for the higher kinetic order is the relatively slow addition of the primary radical to DEF. The rate of this reaction should be first order with respect to DEF. From the half-power dependency of R_p on the initiator concentration in the bulk polymerization of DEF, we can safely conclude that decomposition of the initiator is the rate-determining step; however, this consideration does not completely rule out the slower or comparable rate of the addition to DEF, especially at a lower concentration of monomer.[17] R_p of DEF is concluded to be proportional to the square root of AIBN concentration, and the determination of the absolute rate constants by the rotating-sector method is practical.

Figure 3 shows inhibition with verdazyl, which is a typical stable free radical. DEF polymerized without retardation after the induction period. Based on the relation between the concentration of verdazyl and the length of the induction period, the initiation rate was determined to be 9.95 × 10^{-8} mol L^{-1} s^{-1} at 0.118 mol L^{-1} AVN. The efficiency of initiation was estimated to be 0.4 by using k_d of AVN, 1.02 × 10^{-6} s^{-1}, at 30 °C.[24] Substituting R_p = 2.17 × 10^{-6}

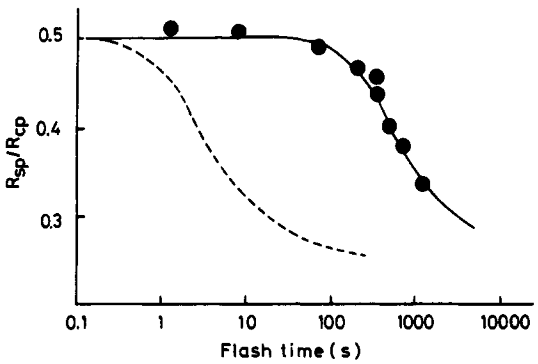

Figure 4. Change of R_p under intermittent irradiation, R_{sp}, relative to R_p under continuous irradiation, R_{cp}, with flash time: (- - -) theoretical curve for $t = 1$ s; (—) theoretical curve for $\tau = 166$ s.

mol L^{-1} s^{-1} into

$$k_p^2/k_t = R_p^2/R_i[\mathrm{DEF}]^2$$

we obtained

$$k_p^2/k_t = 1.28 \times 10^{-6}\ \mathrm{L\ mol^{-1}\ s^{-1}}$$

Lifetime of Propagating Radical. Since the rotating sector used brought about a ratio of the light period to the dark period of 1:3, the ratio of R_p's under intermittent to continuous irradiation (R_{sp} and R_{cp}, respectively) should decrease from 0.5 to 0.25 by elongation of the light period. Determination of τ was carried out by shifting the theoretical curve for τ of 1 s so as to find the best fit to the experimental points, where τ is defined by

$$\tau = 1/(k_t[\mathrm{DEF}^\bullet]) = k_p[\mathrm{DEF}]/(k_t R_{cp})$$

From Figure 4, τ was found to be 166 s by using $R_{cp} = 3.25 \times 10^{-6}$ mol L^{-1} s^{-1}. Hence

$$k_p/k_t = 8.88 \times 10^{-5}$$

No thermal polymerization took place in the dark.

Although one of the possibilities for the large τ is the lower radical concentration than that in ordinary polymerization where τ is likely to be around 1 s, this is in contradiction with ESR detection of the polymer radical. Slow termination resulting from the smaller k_t value is reasonably anticipated.

Absolute Values of k_p and k_t. The absolute rate constants for the bulk polymerization were evaluated from the numerical values of k_p^2/k_t and k_p/k_t: $k_p = 0.015$ L mol^{-1} s^{-1} and $k_t = 164$ L mol^{-1} s^{-1}. A k_p value as small as that for DEF has never been determined, and this implies the presence of considerable steric hindrance against propagation. While recently the k_p and k_t values of some monomers bearing bulky substituents have been found to be quite small,[21-23] the rate constants for DEF are decreased further from them by 2 orders.

Apparent fluidity of the polymerization mixture did not explain such an anomalous k_t value. It has been pointed out that poly(DRF) radical is highly susceptible to steric hindrance of the reaction site.[11,13] The effect of the carbethoxy groups surrounding the radical center and overcrowdedness along the polymer chain[9] are considered to be responsible for the slow termination as well as the slow diffusion arising from the less flexible nature of the polymer chain.

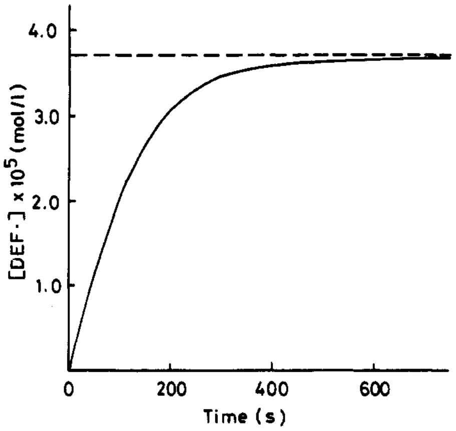

Figure 5. Increase in radical concentration with time at the beginning of polymerization; $[\mathrm{DEF}^\bullet]_s = 3.7 \times 10^{-5}$ mol L^{-1} and $k_t = 164$ L mol^{-1} s^{-1}.

The steady-state concentration of the radical is estimated to be 3.6×10^{-5} mol L^{-1} by using the following relation:

$$[\mathrm{DEF}^\bullet] = R_p/(k_p[\mathrm{DEF}])$$

These kinetic parameters and the concentration of the radical are quite different from those expected for radical polymerizable monomers. From the beginning of the polymerization until the steady state is reached, the radical concentration gradually increases with time as a consequence of concurrence of initiation and termination:[25]

$$(1/[\mathrm{DEF}^\bullet]_s)\tanh^{-1}([\mathrm{DEF}^\bullet]/[\mathrm{DEF}^\bullet]_s) = k_t t$$

where the subscript s refers to the steady state. Figure 5 shows the curve obtained according to this equation, and it requires less than 10 min to establish the steady state. After this period, the polymerization would proceed under a constant radical concentration.

Because the steady-state concentration of the polymer radical has been proved to be of the order of 10^{-8} mol L^{-1} in vinyl polymerization,[26] DEF polymerization can be featured by compensation of the small rate constants with the high concentration of the radical. The propagation and termination rates calculated from the present study rationalize formation of poly(DEF):

$$\bar{P}_n = k_p[\mathrm{DEF}]/(k_t[\mathrm{DEF}^\bullet]) = 15$$

Actually, poly(DEF) of much higher $\bar{P}_n$ has been obtained,[8] and the lower estimate is ascribable to fast initiation by using a high concentration of ACN.

Rate Constants for Cross Propagations. According to Giese and co-workers, DEF is as reactive as methyl acrylate (MA) toward a less bulky radical,[27] and hence the much smaller k_p for DEF than for MA ($k_p = 720$ L mol^{-1} s^{-1} at 30 °C[28]) may indicate the low reactivity of the poly(DEF) radical as described in the preceding section. Despite 1,2-disubstitution of ethylene encounters unfavorable hindrance against addition, conversion of the carbon–carbon double bond to the single bond concomitant with relief of steric strain undoubtedly facilities polymerization.

Rate constants for cross propagations can be evaluated from combination of the monomer reactivity ratios for copolymerization of M$_1$ and M$_2$ ($r_1 = k_{11}/k_{12}$ and $r_2 = k_{22}/k_{21}$) with the k_p's of the respective monomers (k_{11} and k_{22}). The monomer reactivity ratios, r_1 and r_2, for copolymerization of DEF (M$_1$) with St (M$_2$) are 0.02 and 0.29, respectively,[29,30] and k_p for St is 55 L mol^{-1} s^{-1} at 30 °C.[28] The value of k_{12} for addition of poly(DEF) radical to St and the k_{21} value for addition of poly(St) radical to

Table I
Rate Constant for Cross Propagation in Copolymerization of DEF or MA (M_1) with St (M_2) at 30 °C

polymer radical	monomer	rate constant, L mol^{-1} s^{-1}
DEF	St	0.75[a]
MA	St	4000[a]
St	DEF	190[b]
St	MA	73[b]

[a] Evaluated as k_{12} from r_1 and k_p for DEF or MA. [b] Evaluated as k_{21} from r_2 and k_p for St.

DEF are calculated as in Table I.

The rate constants for cross propagations in copolymerization of MA (M_1) with St (M_2) were also calculated from the monomer reactivity ratios, $r_1 = 0.18$ and $r_2 = 0.75$,[31] and are given in Table I. Although the reactivity of DEF in homopolymerization is distinctive from that of dimethyl fumarate,[5] the type of ester alkyl group in EA or MA and poly(EA) or poly(MA) radical[28,31] is unlikely to contribute significantly to differentiate the reactivities of the fumarate and acrylate monomers and polymer radicals. We confirm again that poly(DEF) radical is much less reactive than poly(MA) radical by a factor of 5000, showing that poly(DEF) radical can be regarded as an inherently less reactive species not only in termination but also in propagation. However, DEF as monomer is more reactive toward poly(St) radical than MA, in agreement with the result of addition of small radicals.[27]

Recently, Fukuda and co-workers have emphasized the importance of the penultimate effect on the propagation rate constant of copolymerization.[32] The steric factor of the DEF unit and the highly alternating tendency might result in the penultimate effect on copolymer composition. According to their study, however, copolymer composition is not sensitive to the penultimate effect, because the numerators and denominators of the r_1 and r_2 expressions involve approximately the same amount of effect from the penultimate unit.[33] Careful reexamination of the results of the copolymerization of DEF with St did not show significant improvement with the penultimate treatment, and the contribution of the penultimate unit was not estimated definitely. We evaluated the rate constants for cross propagations using the terminal model.

We have noted the steric effect arising from the polymer chain on the BNB spin trap.[11] However, the addition of poly(DEF) radical to St or MA, which are not sterically so crowded, is not likely to suffer from the effect of the chain length.

ESR Spectroscopy. During the polymerization of DRF, the propagating radical is detectable by ESR spectroscopy.[10] Actually, the same spectra were observed during the polymerizations initiated with AIBN and BPO (Figure 6). After the irradiation was discontinued for the polymerization sensitized with ACN, the intensity of the signal in the dark diminished by termination (Figure 7). It was assumed that the amplitude of the spectrum was proportional to the radical concentration, and Figure 8 shows the plot according to the second-order rate equation

$$[\mathrm{DEF}^\bullet]_0/[\mathrm{DEF}^\bullet]_t = 1 + k_t[\mathrm{DEF}^\bullet]_0 t$$

where $[\mathrm{DEF}^\bullet]_0$ and $[\mathrm{DEF}^\bullet]_t$ denote concentrations of poly(DEF) radical at reaction time 0 and t, respectively.

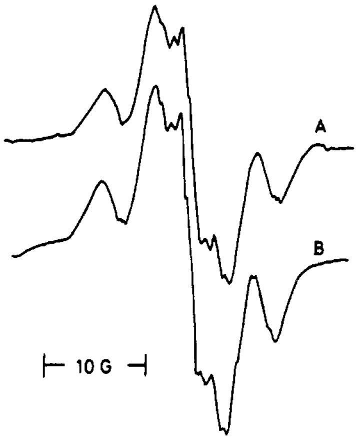

Figure 6. ESR spectra detected during DEF polymerization in bulk initiated with AIBN (A) and BPO (B) under irradiation with a high-pressure mercury lamp.

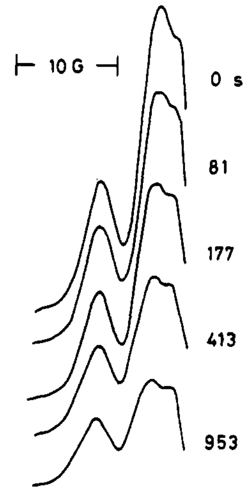

Figure 7. Decay of ESR signal due to poly(DEF) radical after interception of irradiation.

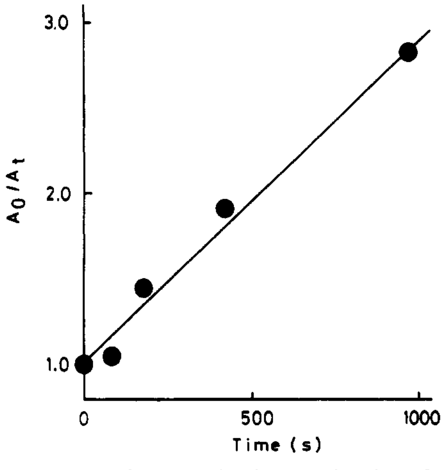

Figure 8. Second-order rate plot for termination of poly(DEF) radical based on the ESR signal in Figure 7: A_0, initial height of the signal; A_t, height of the signal after leaving in the dark of t s.

The linear relationship obtained evidences bimolecular termination of the polymer radical. The slope of the straight line corresponds to $k_t[\mathrm{DEF}^\bullet]_0$, and the reciprocal of this gives τ. The slope is equal to 1.9×10^{-3} s^{-1}, and τ is 556 s. The concentration of poly(DEF) radical is calculated to be 1.15×10^{-5} mol L^{-1} from the k_t already determined. The ESR method monitored the decay of poly(DEF) radical solely by mutual termination in the absence of PRT, because decomposition of the sensitizer did not occur in the dark. The k_t value determined involves a considerable contribution of PRT, and the radical concentration estimated by the ESR method should be lower than the actual concentration. These findings that the estimates of the ESR method are in the same order with those by the rotating-sector method may qualitatively corroborate the extremely small k_t value and the high steady-state concentration of the radical.

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Registry No. DEF, 623-91-6; AIBN, 78-67-1; BPO, 94-36-0; AVN, 4419-11-8; 1,3,5-triphenylverdazyl, 2154-65-6.