Efficacy modeling of new multi-functional benzophenone-based system for free-radical/cationic hybrid photopolymerization using 405 nm LED

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Abstract

This article presents, for the first time, the kinetics and the general conversion features of a 3-component system, BT(BC)/iodonium/Amine, based on proposed mechanism of Liu et al, for both free radical polymerization (FRP) of acrylates and the free radical promoted cationic polymerization (CP) of epoxides using the new multi-functional initiator of benzophenone-triphenylamine (BT). The additives, iodonium and EDB, have the dual function of (i) regeneration BT and (ii) produce of extra radicals for improved FRP and CP. Analytic formulas are developed to explore the new features including: (i) the conversion efficacy (CE) of FRP is an increasing function of the light intensity, the effective absorption coefficient, and the concentration sum of each of the components, BT, Iod, amine, for transient state. However, CE at steady-state is independent to the light intensity; (ii) the trifunctional hybrid structures of BT3 leads to larger light absorption than other types of BT; it also provides more active sites for the H-abstraction in the presence of EDB, leading to high CE; (iii) the efficacy of FRP is an increasing function of the amine (EDB) concentration, in contrast to that of CP having an opposite dependence; (iv) the consumption rate of BT3 in the BT3/ Iod/EDB system is slower than that of the BT3/Iod system due to photoredox catalytic cycle, and the larger initiator regeneration (RGE) in the three-component system. A comprehensive model is also proposed that the CE (for both FRP and CP) is governed by $(N_j K_j b I)$, whereas more complex formulas are developed; where K_j is an effective rate constant proportional to the electron transfer quantum yield, and the combined effects of other coupling rate constants; b is an effective absorption coefficient given by the light absorption and excited state quantum yield.

Keywords: polymerization kinetics; conversion efficacy; free radical and cationic radical; benzophenone-triphenylamine amine; photoredox catalyst; 3D bioprinting.

1. Introduction

Photopolymerization offers both industrial and medical applications such as dental curing, microlithography, stereolithography, microelectronics, holography [1,2]. Light sources in UV (365 nm) has been conventionally widely, whereas light sources in near-UV (400-410 nm) and visible (430 to 680 nm) and near infrared (700 to 1064 nm) have been explored more recently in various applications such as additive manufacturing (AM), 3D and 4D bioprinting [3,4]. Both spatial and temporal controlled 3D processes were reported using single and multiple wavelength lights [7-11].

Organic dyes used as visible light photosensitizers of polymerization have been extensively studied [12,13], in which high extinction coefficients and their long-living excited states, enabling

the photosensitizers to react efficiently with various additives in the photocurable resins. For cost effective with long-living excited states, copper complexes have been used as a new polymerization approach enabling the formation of acetylacetonate radicals by redox reaction with a phosphine and to initiate the free radical polymerization (FRP) of acrylates or the free radical promoted cationic polymerization (CP) of epoxides [14-17]. Recently, Coumarin as dual function of photoinitiators in photo-oxidation or photo-reduction in visible light were reported [18-20]. The efficiency of copper complex (G1) based photoinitiating systems (G1/iodonium salt (Iod)/N-vinylcarbazole (NVK) was investigated by Mokbel et al [16] for free radical polymerization (FRP) of acrylates and the free radical promoted cationic polymerization (CP) of epoxides using light source (LEDs at 375, 395, 405 nm, halogen lamp). Recently, our group also reported the novel copper photoredox polymerization for in situ synthesis of metal nanoparticles, Tar et al [21], and the associated efficacy and kinetic modeling, Lin et al [22].

More recently, we reported (for the first time) [23] the new initiator benzophenone-triphenylamine (BT), having the bifunctional and the trifunctional hybrid structures, not only strengthened the light absorption, but also provided more active sites for the H-abstraction reaction in the presence of *ethyl 4-(dimethylamino)benzoate* (EDB). It could generate more free radical BT3-H*, in which more dissociative BT3-H* could be fixed via radical-radical self-coupling. For the three-component photoinitiating (PI) system, the free radical photopolymerization (FRP) of acrylates and the cationic polymerization (CP) of epoxides could be promoted with high final function conversions (e.g. 77% for the BT3/iodonium salt/amine system in FRP. Moreover, because of the benzophenone moiety, a monocomponent Type II PI of BT/iodonium salt, was observed, e.g. these compounds could initiate the polymerization alone. We also reported that the 3-component (BT/Iod/Amine) PI system has higher conversion efficacy than that of 2-component (such as BT/Iod) [23].

This article will present, for the first time, the kinetics and the general conversion features of the 3-component (BT/Iod/Amine) PI system based on the proposed mechanism of Liu et al [22] for both FRP and CP. The roles of co-additive Iod and EDB, including their dual functions of regeneration of initiator [A] and generation of radicals for improved conversions of FRP and CP. The key factors influencing the conversion rates and efficacy will be explored by analytic formulas derived from a kinetic model for a 3- component and 2-monomer system. Finally, the measured data of Liu et al [23] will be quantitatively analyzed by our formulas, rather than the qualitative discussions. Besides the general conversion features, new finding predicted by our analytic formulas will be explored.

2. Methods and Modeling Systems

2.1. Photochemical Kinetics

As shown by Figure 1, a 3-component system (A/B/E) defined by the ground state of initiator-A, which is excited to its first-excited state A*, and a triplet excited state T having a quantum yield (q). The triplet state T interacts with additive [B] to produce radicals R and R'. It can also interact with the second additive (E) producing radicals S' and S; in which S' can couple with B to form more radical (R) and regeneration of A; and S can couple with E to regenerate A and radical (E'). Monomer M couples with radicals R and S (for FRP), and with couples with radical R' (for CP).

Figure 1. The schematics of a 3-component system, (A/B/E), where A is the ground state of initiator-A, having an excited triplet state T, which interacts with additive [B] to produce radicals R and R'. T can also interact with the second additive (E) producing radicals S' and S; in which S' can couple with B to form more radical (R) and regeneration of A; and S can couple with E to regenerate A and radical (E'). Monomer M couples with radicals R and S (for FRP); and M' couples with radical R' (for CP).

A specific measured system of related to Figure 1 was reported by Liu et al [23], in which their Scheme 4 proposed a 3-component system of BT/Iod/EDB, where BT is benzophenone-triphenylamine photoinitiator, with Iod being the iodonium salt (oxidizing agent), and the amine EDB is ethyl 4-(dimethylamino)benzoate. Monomer rimethylolpropane triacrylate (TMPTA), and (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX) are the functional groups for FRP and CP, respectively, via radicals of Ar* and EDB(-H)* (for FRP), and BT* (for CP). Various amine of BT1, BT2, BT3 and BT4 with different chemical and light absorptions are compared by Liu et al [23], which will be analyzed by the modeling based on Fig.1. In the photo-oxidation process, the electron transfers from T to Iod generating aryl free radical (Ar*) and cation BT*+ as the reactive radicals for the FRP and CP, respectively. In the photo-reduction process, the interaction of T and EDB underwent an electron transfer and a H-abstraction to generate the radical EDB* (-H), which is the species for FRP.

The kinetic equations for our previous systems [24-27] are revised for the new system of Fig. 1 (A/B/E) with 2 monomers, M and M', for FRP and CP, respectively, as follows.

$$\frac{d[A]}{dt} = - (bI[A] - REG) \quad (1)$$

$$\frac{d[B]}{dt} = -(k_2T + k_3S')[B] \quad (2)$$

$$\frac{d[E]}{dt} = -(k_2T + k_4R')[E] \quad (3)$$

$$\frac{dT}{dt} = bI[A] - (k'' + k_1[B] + k_2[E] + kM)T \quad (4)$$

$$\frac{dR}{dt} = (kM + k_1[B])T + k_3[B]S' - KRM \quad (5)$$

$$\frac{dR'}{dt} = k_1[B]T - k_4R'[E] - K'R'M' \quad (6)$$

$$\frac{dS}{dt} = k_2T[E] - K''MS \quad (7)$$

$$\frac{dS'}{dt} = k_2 T[E] - k_3 [B]S' \quad (8)$$

In Eq. (1) the regeneration (REG) term is given by $REG = k''T + kM + k_3S'[B] + k_4R'[E]$ of of the initiator, $[A]$; $b = 83.6a'wq$, where w is the light wavelength (in cm) and q is the triplet state T quantum yield; a' is the mole absorption coefficient, in (1/mM/%) and $I(z, t)$ is the light intensity, in mW/cm². All the rate constants are defined previously [22] and they are related by the coupling terms. For examples, k_j (with $j=1,2$) are for the couplings of T and [B], and [E], respectively; k_3 and k_4 are for the couplings of S' and [B]; and R' and [E], respectively. The coupling constant K and K'' are for radicals R and S with monomer M (for FRP); and K' for R' with M' (for CP). Here we have excluded the oxygen inhibition effect [23]. We also assume the bimolecular termination can be ignored, or R^2 and S^2 are ignored with a focus on the unimolecular termination due to KRM, $K''SM$ and $K'R'M'$ terms. The weak cross couplings of R and S (or S') are also ignored. The direct coupling of T and M leads to a type-I FRP, whereas the indirect coupling of T and M (or M') via additive produce radicals (R,S, R') are type-II process.

The monomer conversions for FRP and CP are given, respectively, by [22]

$$\frac{dM}{dt} = -(kT + KR + K''S)M \quad (9)$$

$$\frac{dM'}{dt} = -K'R'M \quad (10)$$

Above equations indicate that conversions for FRP and CP are given by the interaction of (T,R,S) and M, and R' and M, respectively. We note that the co-additive, [B] (or Iod) has dual function of FRP (via R and S') and CP (via R'); whereas co-additive, [E] (or amine, or EDB) also has dual function of enhancing FRP by extra R and new radical S. Both [B] and [E] regenerate [A], which enhances FRP and CP as a cycle process to resupply the assumption of [A].

For comprehensive modeling we will use the so-called quasi-steady state assumption [15,18]. The life time of the singlet and triplet states of photosensitizer, the triplet state (T), and the radicals (R, S' and S), since they either decay or react with cellular matrix immediately after they are created. Thus, one may set $dT/dt = dR/dt = dS'/dt = dS/dt = 0$, which give the quasi-steady-state solutions: $T = bIg[A]$, $R = bIg[A](kM + k_1[B] + k_2[E])/(KM)$, $R' = k_1bIg[A][B]$; $S = k_2bIg[A][E]/(K''M)$; and $g = 1/(k'' + k_1[B] + k_2[E] + KM)$, $g' = 1/(k_4[E] + K'M') = [1 - K'M']/(k_4[E])/(k_4[E])$.

Under the above quasi-steady-state solutions, we obtain the simplified equations as follows.

$$\frac{d[A]}{dt} = -(bI[A] - REG) \quad (11)$$

$$\frac{d[B]}{dt} = -k_2bIg[A][B] - k_1bI[A][E] \quad (12)$$

$$\frac{d[E]}{dt} = -k_2bIg[A][E] - bI[A](k_1[B] - K'R'M') \quad (13)$$

where the initiation-A regeneration term is given by $REG = k''T + kM + KRM - K'R'M'$. We note that this REG enhances the conversion of FRP and CP, serving as a catalytic cycle.

The equation for the FRP and CP conversion are given by the solutions of

$$\frac{dM}{dt} = -kbIg[A]M - bI[A](k_1[B] + 2k_2[E]) \quad (14)$$

$$\frac{dM'}{dt} = -k_1bIg[A][B](K'M')/(k_4[E] + K'M') \quad (15)$$

3.. Results and discussion

A full numerical simulation is required for the solutions of Eq. (11)-(16), which will be presented elsewhere. We will focus on comprehensive analysis for special features and the key factors for efficient FRP and CP related to the measured data of Liu et al [22], based on the analytic formulas.

3.1 Analytic results

Analytic formulas need assumption of strong coupling of T and [B], and $k_1[B] \gg kM$, $k_4[E] \gg K'M'$, such that $g=1/(k_1[B])$, $g'=1/(k_4[E])$. Also RGE is taken as a mean reduction factor (f'), such that $bI[A]$ -RGE = $f'bI[A]$ is time independent having a value of $f'=0.5$ to 1.0. The first-order solutions of Eq. (11) to (13) are found: $[A]=A_0 \exp(-dt)$; with $d=f'bI$; $[B]=B_0 \exp(-H)$, with $H(t)=DE(t)$, with $E(t)=[1 - \exp(-dt)]/d$; $[E]=E_0 \exp(-H)$, with $D=(k_2/k_1)dA_0$.

Eq. (15) and (16) are further reduced to

$$\frac{dM}{dt} = -(k/k_1)bI([A]/[B])M - bI[A](k_1[B] + 2k_2[E]) \quad (17)$$

$$\frac{dM'}{dt} = -K'M'bI([A]/(k_4[E]))[1 - K'M'/(k_4[E])] \quad (18)$$

Solving for Eq. (17), we obtain the first-order solution, for the type-II dominated case that $kM \ll k_1[B] + 2k_2[E]$, $k_1[B]$; that is the major FRP is from radicals R and S, or the last 2 terms of Eq. (17), and the first term for the direct coupling of T and M (type-I FRP) is ignored. We obtain

$$M(t) = M_0 - f'bI(k_1B_0 + 2k_2E_0)P(t) \quad (19)$$

where $P(t)=[1 - \exp(-d't)]/d'$; with $d'=d+D$, with $D=(k_2/k_1)dA_0$, $d=f'bI$. We note that $P(t)$ has a transient state value $P=t$, and steady-state value, $P=1/d$. Therefore, the conversion efficacy of FRP (CE) defined by $1-M(t)/M_0 = f'bIA_0(k_1B_0 + 2k_2E_0)t$ (for transient state), and $CE = A_0(k_1B_0 + 2k_2E_0)$, for steady-state, which is independent to the light intensity, although high intensity has a faster rising profile.

For CP, we solve Eq. (18) to obtain the first-order solution, with $K'M'/(k_4[E])$ term ignored,

$$M'(t) = M'_0 \exp[-P'(t)] \quad (20)$$

where $P'(t)=K'bIA_0Q(t)/(k_4E_0)$, with $Q(t)=[1 - \exp(-D't)]/D'$; $D'=d-D$, $D=(k_1/k_3)d(A_0/G_0)$. Therefore, the conversion efficacy of CP (CE') defined by $1-M'(t)/M'_0$ is given by $CE' = K'bIA_0/(k_4E_0)$, for transient state value; and steady-state value, $K'bIA_0/(D'k_4E_0)$, which is independent to the light intensity, same feature as that of FRP. However, CE (for FRP) is proportional to $A_0(k_1B_0 + 2k_2E_0)$, which is an increasing function of A_0E_0 . In contrast, CE'(for CP) is proportional to $A_0/(k_4E_0)$, which is a decreasing function of E_0 .

We note that $P'(t)$ has a transient state value $K'bIA_0/(k_4E_0)$; and steady-state value, $K'bIA_0/(D'k_4E_0)$, which is independent to the light intensity. We note that Eq. (20) may be used to find the second order solution of Eq. (18), which has reduction correction factor proportional to $K'M'_0/(k_4E_0)$. More accurate CE needs the numerical solutions of Eq. (11) to (15).

3.2 General features and new findings

As shown by Eqs. (17) to (20), the following significant features of the A/B/E, or BT/Iod/EDB, system are summarized as follows (referred also to Scheme 4 of Liu et al [23]). Our modeling has explored the follow general features, in which some new findings are not yet explored in our previous experiment of Liu et al [23], but might be justified in our future works.

(i) The additive [B], or Iod (an oxidizing agent) interacts with excited state (T, or BT*) to produce radicals, R and R', which lead to FRP and CP, respectively.

(ii) The additive, [E] (or amine), has dual functions: interacting with T to produce additional radical (S) which leads to FRP, and another radical S' which then couple with [B] to produce extra radical R, and also regenerate the initiator, [A].

(iii) Eq. (9) shows that the FRP is contributed by 3 components: from the direct coupling of monomer (M) with T (the type-I process); and coupling with R, and S.

(iv) Eq. (19) shows that the conversion efficacy (CE) of FRP is proportional to and $CE = f' b I t A_0 (k_1 B_0 + 2k_2 E_0)$, which is an increasing function of the light intensity (I), the effective absorption coefficient (b), and the concentration sum of $A_0 (k_1 B_0 + 2k_2 E_0)$, for transient state. However, CE at steady-state is independent to the light intensity, i.e., low and high light intensity lead to the same saturated CE, although high intensity has a faster rising profile. Above features are for the type-II dominated case, and with unimolecular coupling of KRM term in Eq. (5). For the situation of a strong bimolecular termination, we need to include the coupling of R^2 (or S^2) in Eq. (5), and leading a CE which is proportional to the square-root of bI (for transient state); and inverse proportionally to square-root of bI at steady-state, i.e., higher intensity leads to a lower steady-state CE than lower intensity. These special features have been explored in many systems [25,27].

(v) The conversion efficacy of FRP (CE) is proportional to $A_0 (k_1 B_0 + 2k_2 E_0)$, which is an increasing function of the amine (or EDB) initial concentration (E_0). In contrast, CE' (for CP) is proportional to $A_0 / (k_4 E_0)$, which is a decreasing function of E_0 . This opposite trend may be easily realized by Fig. 1 (Chart) that the presence of additive [E] always enhances the FRP via its producing of extra FRP-radicals (S and R); whereas [E] will reduce the amount of CP-radical (R') produced by [B], as shown mathematically by the (negative) $k_4 R' [E]$ term in Eq. (6). In comparison, FRP-radicals (R and S) are produced by the (positive) $k_2 T [E]$ term in Eq. (7) and (8). Therefore, higher concentration of [E] will enhance the CE of FRP, but it also suppresses the CE of CP, a competing effect. By controlling the relative amount of $A_0 (k_1 B_0 + 2k_2 E_0)$, and $K' A_0 / (k_4 E_0)$, and also the types of monomers, one should be able to control the intended relative amount of FRP and CP. These features for the role of amine (or EDB) initial concentration (E_0) are not yet explored in Liu et al [23], and we plan to conduct in our future studies.

(vi) In our previous system of PI/Iod/EDB (0.3%/1%/1%, mol/mol/mol) systems in TMPTA (for FRP) and in EDB (for CP) in Liu et al [23]. These concentration might not be optimized, specially the concentration of EDB, which might be too low for maximum CE of CP, but it is too high if for maximum CE of CP, as predicted by our formulas of Lin et al [23]. Our modeling provides some guidance for future studies using optimal and controlled concentrations for both FRP and CP. Furthermore, in the studies of Liu et al [23], we used a fixed LED light intensity. We intend to vary light intensity for future study to confirm the predicted features of the CE dependence on light intensity, in transient and steady states, for both FRP and CP, as shown by Eq. (19) and (20), respectively.

(vii) In the studies of Liu et al [23], various types of BT were reported, including BT1 to BT 4, BC1 to BC3, which have different quantum yields for electron transfer (or kinetic rate constants, K_j), and quantum yields for excited state (BT*). We will discuss further as follows. For a comprehensive analysis, we propose that the CE is proportional to $(N_j K_j b I)$ for both FRP and CP, noting that a more precise and complex formulas are as shown by Eq. (19) and (20), respectively; where N_j is the number of moiety of t initiator and the amine; K_j an effective rate constant proportional to the electron transfer quantum yield, and the combined effects of other coupling rates, k_j (with $j=1$ to 4), and K (for FRP) and K' (for CP); b is an effective absorption constant defined by, $b=83.6 a' w q$, where w is the light wavelength and q is the quantum yield of the initiator triplet excited state; a' is

the mole extinction coefficient of the initiator. For a given light wavelength, the CE is an increasing function of the product ($N_i K_i a' q$), rather than just N_i , K_i , a' or q .

Besides the above described general features, other special features concluded by the measured data of Liu et al [23] are analyzed as follows. Also refer to Fig. 2 and 3 of Liu et al [23], which show the CE dynamic profiles of FRP and CP, respectively, for various types initiators (BT and BC), with monomer EDB (for FRP) and EPOX (for CP).

Example (A). Liu et al [23] reported K_i for the BT1/EDB, BT2/EDB, BT3/EDB, BT4/EDB and BC3/EDB systems are 0.46, 0.51, 0.56, 0.52 and 0.37, respectively. BC3-based systems (with a lower electron transfer quantum yield, or K_i), has lower CE than those of the BT1/BT2/ BT3/BT4-based systems, although it has a high molar extinction coefficient at 405 nm. Liu et al [23] also reported more reaction sites are provided for H-abstraction behavior from EDB in trifunctional benzophenone–triphenylamine hybrid structures, which can promote the FRP more efficiently. These features may be analyzed by our comprehensive formula proposing the CE is proportional to ($N_i K_i b I$). For the same $N_i K_i$, an initiator with $a'=12,000$ ($1/(M\text{ cm})$) and $q=0.3$, will have similar CE as that of a lower $a'=6,000$ ($1/(M\text{ cm})$), but higher $q=0.6$. Similarly, for the same $N_i q$, the CE is governed by the product of $a' K_i$.

Example (B). The UV-visible absorption of BT3 alone did not initiate FRP, but FRP was observed in the presence of Iod. This feature is shown mathematically by our Eq. (17), for the case when $k_{\text{I}} \gg k_1$, the first term (for direct type-I coupling of T and M) is neglectable and the last 2 terms due to radicals (R and S) are dominate (type-II).

Example (C). The consumption rate of BT3 in the BT3/ Iod/EDB system seems to be slower than that of the BT3/Iod system. It is probable that there is a photoredox catalytic cycle in the three-component system. We have shown mathematically in Eq. (1), the regeneration of the initiator is given by $\text{REG} = k''T + k_M + k_3 S' [B] + k_4 R' [E]$, which may enhance the CE. In addition, the catalytic coupling cycle of [B] and [E] producing radicals R, R', and S, as shown in Fig. 1, and our Eq. (17), where the CE for FRP is proportional to the cycle couplings of [A], [B] and [E], regenerating [A] and producing radicals R and S. Our formulas also show that the 3-component system, BT3/ Iod/EDB, has higher CE and also larger RGE than that of 2-component system, BT3/ Iod/EDB which has a less $\text{RGE} = k''T + k_M T + k_3 S' [B]$, with $[E]=0$. The RGE term reduces the depletion rate of the initiator [A], as shown by Eq. (1). In the extrem case of high $\text{RGE} = bI[A]$, $d[A]/dt=0$, such that [A] is not depleted leading to the highest CE for both CP and FRP. The present modeling develops, for the first time, this RGE effects quantitatively, and using its exact functional form, proportional to the initial concentration sum of T, [B] and [A], which in general is time dependent. Moreover, $\text{REG} = (k'' + k_M)T$, for the case that $KRM = K'R'M'$, the rate function of [A] becomes $bI [1(k'' + M)/(k_1[B] + k_2[E])]$, which is an increasing function of [B] and [E], such that [A] is a slower decreasing function and leading to a higher CE.

Example (D). For CP, the highest epoxy function conversion $\text{CE} = 47\%$ was obtained in the BT3/Iod system. Conversely, BC1 and BC2 based systems had low $\text{CE} = 26\%$ and 27% , respectively, due to unfavorable molar extinction coefficients at 405 nm. Even though a high extinction coefficient is observed, BC3 exhibited worse performance than ITX. This can be ascribed to the tertiary amine groups in the BC3 structure, which had a negative effect on the cation reactivity. Besides, the interaction of initiators with Iod and the kinds of cations could also be associated with the performance of CP. As noted earlier that CE is proportional to the ratio of $K'A_0/(k_4 E_0)$, as also shown by Eq. (18), (20), the CE is governed by (K'/k_4) depending on types of amine and types of cations; and the ratio (A_0/E_0) , which can be optimized for CE higher than the measured value of 47% . Liu et al [23] report a TMPTA system with $\text{CE}=77\%$, in PI/Iod/EDB ($0.3\%/1\%/1\%$, mol/mol/mol), which may also be enhanced by optimized concentrations of A_0 , B_0 and E_0 (for FRP), and the ratio (A_0/E_0) for CP.

Exapes (E). Our measured data, Liu et al [23], showed a weak interaction of BC3 and EDB, which could be attributed to the amine groups in the BC3 structure, so that the BC3/EDB system had an unfavorable performance, or low CP efficacy. In addition, the amine groups were also to the disadvantage of the cation

species. So, low conversion of epoxy functions was found in the presence of the BC3/Iod system. These features may be analyzed, quantitatively, by our Eq. (6), (15), (18) and (20). (i) Weak interaction of BC3 and EDB, means the small coupling term $k_1[B]T$ leading to a small rate function for the CR-radical, R' , shown by Eq. (6), comparing to that of FRP-radical (S) having a rate function of $k_2[E]T$, shown by Eq. (7) and (8); (ii) The CP efficacy shown by Eq. (15) and (18), is a decreasing function of $k_4[E]$ (or the amine group, EDB), in contrast to Eq. (14) which shows the FRP efficacy is enhanced by EDB. Moreover, the FRP radicals (R and S) are increasing function of $k_2[E]T$, as shown by Eq. (4), (6) and (7); noting that R is indirectly related to $k_2[E]T$ via Eq. (7) for S'. The opposite role of EDB (or $k_4[E]$) on the efficacy of FRP and CP are also discussed earlier.

Example (F). Our earlier studies showed that for benzophenone–triphenylamine PI, the bifunctional and the trifunctional hybrid structures not only strengthened the light absorption properties but also provided more active sites for the H-abstraction reaction in the presence of EDB. As a result, BT2, BT3 and BT4 demonstrated better photoinitiation performance. As shown in Scheme 4 of Liu et al [23], in the presence of EDB, BT3 with a trifunctional character could generate more free radical $BT3-H^*$. Through radical–radical self-coupling, more dissociative $BT3-H^*$ could be fixed. In addition, the low migration properties were found for BT3 due to the trifunctional character and high molecular weight. Above measured features may be analyzed by our comprehensive model that the CE (for both FRP and CP) is governed by $(N_j K_j b I)$, or a more precise and complex formulas shown by Eq. (19) and (20), respectively, for FRP and CP; where N_j is the number of moiety of the initiator and the amine; K_j is an effective rate constant proportional to the electron transfer quantum yield, and the combined effects of other coupling rates, k_j (with $j=1$ to 4), and K (for FRP) and K' (for CP).

4. Conclusion

We have presented, for the first time, the kinetics and the general features of BT/ Iod/EDB, and BC/Iod/EPOX systems based on the proposed mechanism of Liu et al [19]. Analytic formulas are developed to explore the new features including: (i) the trifunctional hybrid structures of BT3 leads to larger light absorption (at 405 nm) than other types of BT; it also provides more active sites for the H-abstraction in the presence of EDB, leading to high CE; (ii) efficacy of FRP is an increasing function of the light intensity (I), the effective absorption coefficient (b), and the concentration sum of $A_0(k_1 B_0 + 2k_2 E_0)$, for transient state. However, CE at steady-state is independent to the light intensity; (iii) the efficacy of FRP is an increasing function of the amine (EDB) concentration, in contrast to that of CP which has an opposite dependence; (iv) the consumption rate of BT3 in the BT3/ Iod/EDB system is slower than that of the BT3/Iod system due to photoredox catalytic cycle, and the larger initiator regeneration (RGE) in the three-component system. A comprehensive model is also proposed that the CE (for both FRP and CP) is governed by $(N_j K_j b I)$, whereas more complex formulas shown by Eq. (19) and (20), respectively, for FRP and CP; where K_j is an effective rate constant proportional to the electron transfer quantum yield, and the combined effects of other coupling rates, k_j (with $j=1$ to 4), and K (for FRP) and K' (for CP).

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