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Oxygen-Initiated Free-Radical Polymerization of Alkyl Acrylates at High Temperatures

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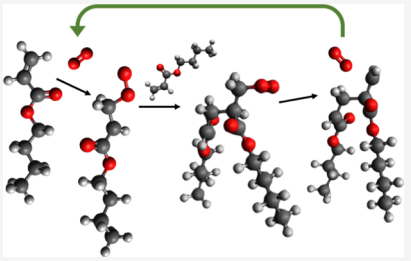
ABSTRACT: Molecular oxygen has been reported to be a strong inhibitor at low temperatures. Here, it is shown that the introduction of oxygen gas into the free-radical polymerization of *n*-butyl acrylate (*n*BA) results in high conversion of the monomer in a very short time at temperatures above 140 °C without the use of any conventional initiators. By conducting first-principles calculations based on density functional theory, this work for the first time identifies and kinetically studies the most-likely reactions via which molecular oxygen contributes to polymer chain initiation. It provides theoretical and experimental evidence that molecular oxygen acts as a catalyst in alkyl acrylate free-radical polymerization at high temperatures. A triplet diradical intermediate is generated from solvated oxygen reacting with an alkyl acrylate monomer. The intermediate then reacts with another monomer and thermally dissociates from molecular oxygen to proceed toward polymerization. This theoretical finding is supported by laboratory experiments showing that in the presence of a very small amount of molecular oxygen and in the absence of any thermal initiators, free-radical polymerization of *n*BA occurs sustainably and proceeds to a very high monomer conversion. This work opens a new path for a more economic and sustainable production of higher-quality acrylic polymers using molecular oxygen as an initiator catalyst.



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INTRODUCTION

Acrylic polymers are used in many products such as paints, coatings, adhesives, fibers, plastics, and cosmetic products. Severe restrictions placed on volatile organic compounds prevent the use of high solvent concentrations, which improve performance during application, in paints and coatings.[1] Therefore, high-temperature (120−220 °C) polymerization processes are employed to synthesize lower average molecular-weight polymers that require less solvent while maintaining brushability. At high temperatures, the rates of secondary reactions such as monomer self-initiation, depropagation, and β-scission are appreciable and produce resins with low average molecular weights.[2−9] Self-initiation of acrylates at high temperatures improves the polymer quality and reduces the operating costs due to less or no use of expensive conventional initiators.[10−17]

Molecular oxygen is known to affect free-radical polymerization strongly.[18] Studying and conducting polymerization without considering the importance and involvement of oxygen leads to an incomplete understanding of the polymerization pathways. A practical concern about the participation of gaseous oxygen in polymerization is its ability to inhibit initiation.[19] Atmospheric oxygen can quench excited triplet-state initiators that provide free radicals during the initiation step, resulting in induction periods.[20−22] The reaction of oxygen molecules with carbon-based secondary propagating radicals generates peroxyl (R−O−O$^{\bullet}$) radicals, which are much less reactive and have lower polymerization rates. Oxygen may also create peroxides or polyperoxides as copolymers with vinyl-type monomers,[23] which are unfavorable for polymerization reactions as well. Different approaches have been developed to mitigate the problem of oxygen inhibition. Physical approaches, such as bubbling and blanketing the reaction medium with inert gas (e.g., nitrogen),[20,24] or introducing barriers against atmospheric oxygen with waxes[25] or polymers (e.g., polyethylene)[19] with low oxygen permeability, are difficult and expensive methods to implement on an industrial scale.

Oxygen has also been reported to act as an initiator. For high-pressure polymerization of ethylene, induction time was observed to decrease with increasing oxygen concentration and temperature.[26−28] Grimsby and Gilliland[29] and Schoenemann[30] proposed that an oxygen molecule reacts with an ethylene molecule to produce two free radicals for propagation. Moreover, oxygen in combination with various organometallic chemicals (especially group III) generates high-performance initiators for free-radical polymerization.[18] For instance, trialkylborane alone cannot polymerize the vinyl-based mono-

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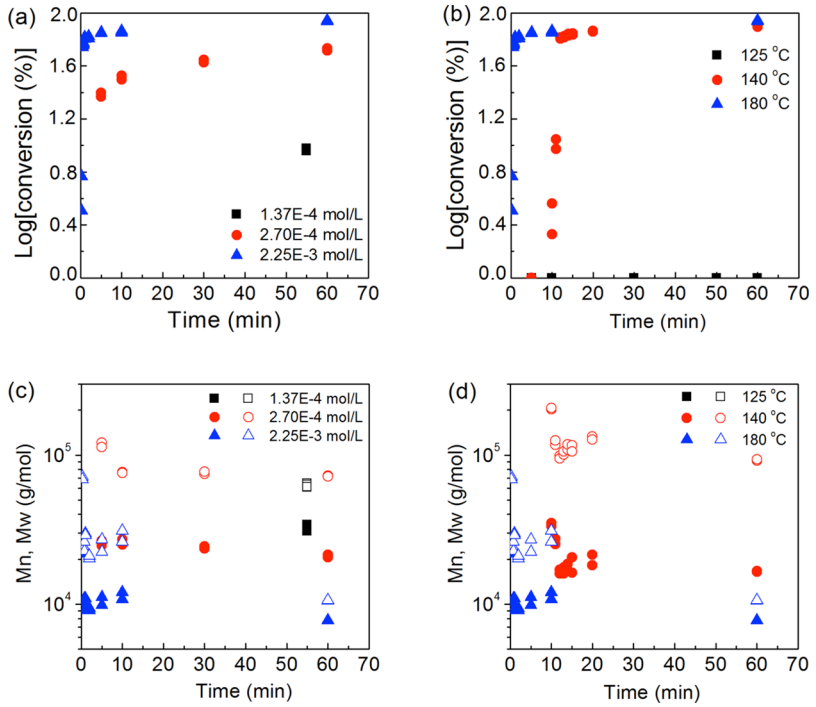

Figure 1. (a) Log of *n*BA conversion *vs* time at 180 °C: black squares, red circles, and blue triangles for the monomer with 1.37×10^{-4}, 2.70×10^{-4}, and 2.25×10^{-3} mol/L dissolved O_2, respectively. (b) Log of conversion of air-saturated *n*BA *vs* time at different temperatures. No conversion is observed at 125 °C. (c) Number-average (filled symbols) and weight-average (empty symbols) molecular weights of the polymer samples in (a). (d) Number-average (filled symbols) and weight-average molecular (empty symbols) weights of the polymer samples in (b).

mers, yet polymerization occurs when oxygen is added.[14] Recent work has also demonstrated diatomic oxygen's role in initiation by activating trialkylborane even in the absence of organometallic species and at ambient conditions.[31,32] Oxygen also plays a pivotal role in methyl methacrylate polymerization initiated by a copper(II)-ascorbic acid-oxygen system in aqueous medium.[33,34]

In this study for the first time, we report free-radical polymerization of *n*-butyl acrylate (*n*BA) at different O_2 concentrations and at high temperatures (140−180 °C) in the absence of any added thermal- or photo-initiators. Monomer conversion measurements indicate that *n*BA saturated with air polymerizes vigorously and that the rate of polymerization increases with increasing oxygen concentration and temperature. Using quantum chemical calculations based on density functional theory (DFT), we understand how oxygen reacts with alkyl acrylate monomers to produce and sustain radicals for initiation. DFT calculations show that at high temperatures, peroxyl radicals decompose with molecular oxygen dissociating from the monomer complex to recover active carbon-based secondary radicals. These results suggest that oxygen acts as an initiator and catalyst for alkyl acrylate free-radical polymerization at $T > 140$ °C.

RESULTS AND DISCUSSION

We explore the temperature dependence of the spontaneous bulk thermal polymerization of *n*BA with three different dissolved oxygen concentrations. The procedure for removal of inhibitors and all experimental methods, including measuring the oxygen content, have been explained in S1 of Supporting Information. From our previous study, we understood that at 140 °C, there is less than 3% conversion of ultra-high purity (UHP) N_2-bubbled *n*BA monomer after 240 min.[35] However, the polymerization rate increased with increasing temperature. At 220 °C, polymerization continues beyond 250 min. The monomer self-initiation rate coefficient increases from 2.2×10^{-14} M^{-1} s^{-1} at 160 °C to 6.8×10^{-12} M^{-1} s^{-1} at 220 °C. These findings, obtained at negligible concentrations of oxygen without solvent, suggested that the monomer self-initiation reaction is intrinsically slow and only plays an appreciable role at $T > 160$ °C.

Free-radical bulk polymerization of *n*BA bubbled with UHP N_2 for various purging times (to adjust oxygen concentration) is conducted at high temperatures to investigate the participation of O_2 and differentiate this study from conventional studies on acrylate free-radical bulk polymerization.[17,35−38] Figure 1a shows that while 10% of the deaerated *n*BA (1.37×10^{-4} mol/L oxygen) is converted to polymer after 60 min at 180 °C, a conversion of 50% can be achieved in only 30 s for the air-saturated *n*BA (2.25×10^{-3} mol/L oxygen). This suggests that oxygen accelerates polymerization significantly and that higher O_2 concentrations also increase the monomer conversion. After 1 hour, the final conversion of air-saturated monomer is 86%, which is more than 8.5 times higher than that for deaerated *n*BA at the same temperature. This suggests that molecular oxygen increases the polymerization rate substantially at 180 °C, which highlights the importance of oxygen in free-radical polymerization at high temperatures.

In order to investigate the temperature dependence, *n*BA saturated with oxygen was polymerized at different temperatures as shown in Figure 1b. At 125 °C, oxygen appears to act as an inhibitor. This temperature is simply too low for initiation with O_2. It is obvious that the spontaneous polymerization rate increases rapidly with temperature and that monomer conversion grows from 78% at 140 °C to 86% at 180 °C. Note that the conversion increases very sharply initially. After

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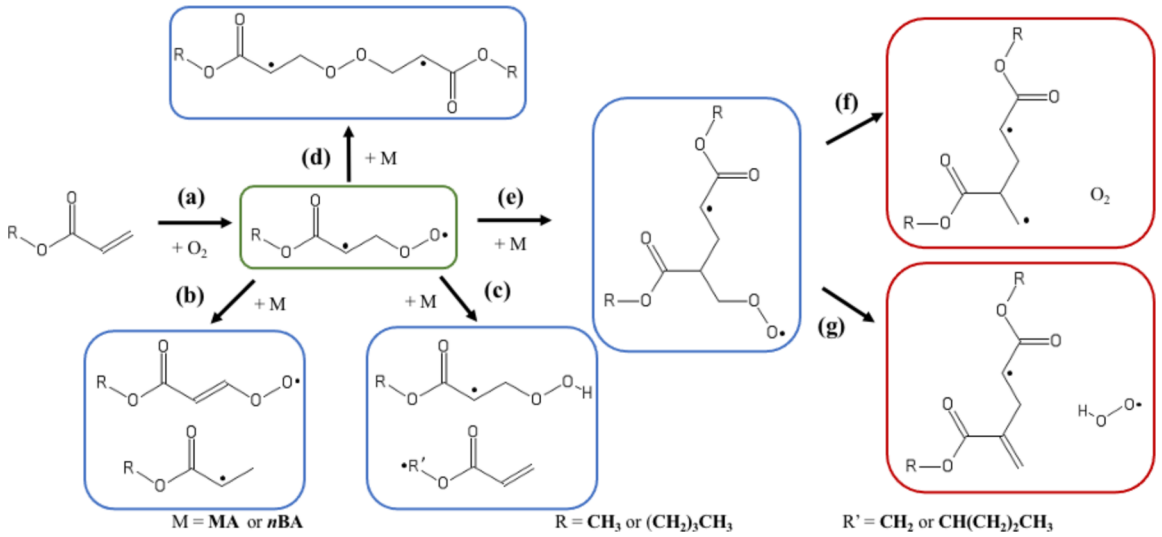

Figure 2. (a) Oxygen addition to the monomer forming a diradical intermediate, (b) radical transfer from a secondary carbon to the monomer, (c) radical transfer from peroxyl to the monomer, (d) diradical propagation via the peroxyl radical, (e) diradical propagation via the secondary-carbon radical, (f) C−O_2 bond dissociation, and (g) mono-radical generation by release of •OOH. Corresponding activation energies and rate constants are given in Table 2.

this sharp increase, it increases at a much slower rate and reaches only 86% after 1 h because the viscosity of the reaction media increases sharply with increased conversion, making the reaction diffusion limited (preventing the monomer molecules from reaching free radicals readily). We carried out the same polymerization in the presence of *n*-heptane that does not participate in the polymerization, and we were able to achieve 100% conversion.

An induction period where time passes before considerable conversion is observed for 140−180 °C. The induction time significantly declines as temperature rises from 11 min for 140 °C to less than 15 s for 180 °C. After the induction time, a nearly vertical increase in conversion implies that free-radical polymerization of air-saturated *n*BA is remarkably fast. Figure 1c,d shows the number-average and weight-average molecular weights of the polymer samples, the conversions of which are depicted in Figure 1a,b, respectively. These figures confirm that the polymerization reactions produced long-chain polymers.

To understand the role of oxygen in high-temperature polymerization of alkyl acrylates, we also carry out a systematic, first-principles exploration with GAMESS[39] using DFT, the Becke-3-Lee-Young-Parr hybrid functional (B3LYP), and the 6-311G** basis set. Further details on computational methods are given in S2 of Supporting Information. Previous studies employ B3LYP, and its use is well validated for alkyl acrylate and free-radical investigations.[6,7,11,13,40] The solvation entropy is calculated for aerated experimental conditions ($[O_2]$ = 2.1 × 10^{-3} mol/L) and is accounted for in reaction entropies involving molecular oxygen (see S2.4 of Supporting Information). Given the chemical similarity of methyl acrylate (MA) and *n*BA, we first study various possible reactions of an MA molecule and a triplet ground-state O_2 (see Figure S2). Molecular oxygen may react with the vinyl group of MA by Markovnikov addition, producing a reactive, carbon-based secondary radical and a terminal peroxyl radical (see Figure 2). O_2 is favored to form a bond with the *β*-carbon of MA due to the greater stability of the resulting secondary radical.

Because oxygen inhibits free-radical polymerization at low temperatures, peroxyl formation (•M−H + •OO• → •OOMH) and peroxyl dissociation (•OOMH → •M−H + •OO•) were first studied where M = MA. Thermodynamic parameters and rate constants were calculated using the methods highlighted in S2.3 and S2.5 of Supporting Information, respectively. •M−H type mono-radicals result from self-initiation mechanisms[40] and therefore are chosen for this study. DFT calculations predict an electronic energy barrier of 94.21 kJ/mol for peroxyl formation.

With increased temperature, the rate constant of peroxyl formation decreases appreciably, while the rate constant of the reverse reaction increases (Table 1). At 25 °C, the rate constant of peroxyl formation is approximately 26 orders of magnitude faster than the corresponding dissociation reaction. However, at 200 °C, the rate constant for peroxyl formation is favored over dissociation by 15 orders of magnitude instead. The faster rate constant of peroxyl dissociation at high temperatures may be attributed to the positive entropic consequence of splitting one molecule into two. The kinetic boost that peroxyl dissociation gains with increased thermal energy frees dissolved oxygen to interact more readily with the unreacted monomer. These results suggest that molecular oxygen's role as an inhibitor—forming peroxyl species—decreases at elevated temperatures. This computational insight can help explain the induction

Table 1. Enthalpy (Δ*H*) and Gibbs Free Energy (Δ*G*) in kJ/mol, Entropy (Δ*S*) in J/mol K, and Rate Constants *k*(*T*) at Various Temperatures for Peroxyl Formation (Forward) and Dissociation (Reverse) Reactions for O_2 and MA Mono-Radical (•M−H)[a]

T (°C)	$\Delta H_{forward}$	$\Delta S_{forward}$	$\Delta G_{forward}$	$k_{forward}(T)$ (M^{-1} s^{-1})	$k_{reverse}(T)$ (s^{-1})
25	−102.8	−121.2	−66.7	7.5×10^{27}	1.3×10^{1}
100	−105.0	−121.4	−59.7	5.5×10^{24}	3.4×10^{4}
120	−105.6	−121.4	−57.9	1.3×10^{24}	1.7×10^{5}
140	−106.2	−121.3	−56.1	3.7×10^{23}	7.0×10^{5}
180	−107.3	−121.1	−52.5	4.0×10^{22}	8.4×10^{6}
200	−107.9	−120.9	−50.7	1.6×10^{22}	2.5×10^{7}

[a]Note: for brevity, $\Delta H_{reverse}$, $\Delta S_{reverse}$, and $\Delta G_{reverse}$ omitted as $\Delta H_{reverse} = -\Delta H_{forward}$, and so forth.

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Table 2. Activation Energy (E_A) and Gibbs Free Energy ($\Delta G^{\ddagger}$) in kJ/mol, Entropy ($\Delta S^{\ddagger}$) in J/mol K, and Rate Constants $k(T)$ at 140 °C for Oxygen-Monomer Reactions, as Shown in Figure 2, for MA (Shading) and *n*BA (No Shading)

	Initiation	Mono-Radical Generation		Diradical Propagation		Peroxyl Radical Dissociation	
	(a)	(b)	(c)	(d)	(e)	(f)[a]	(g)
E_A	121.6	85.6	75.1	31.5	16.7	146.8	118.5
	121.1	85.4	63.4	31.4	15.6	146.7	118.9
$\Delta G^{\ddagger}$	155.4	146.5	133.4	97.6	76.1	102.4	119.7
	161.8	157.6	127.4	108.8	84.6	106.1	121.4
$\Delta S^{\ddagger}$	-98.3	-164.0	-157.8	-176.5	-160.6	136.4	-11.5
	-115.3	-191.5	-171.7	-203.9	-183.6	127.1	-14.3
$k(T)$	7.6×10^{-9} $M^{-1}s^{-1}$	2.8×10^{-7} $M^{-1}s^{-1}$	9.4×10^{-6} $M^{-1}s^{-1}$	1.6×10^{-1} $M^{-1}s^{-1}$	7.5×10^{1} $M^{-1}s^{-1}$	3.3×10^{3} s^{-1}	9.5×10^{-3} s^{-1}
	1.2×10^{-9} $M^{-1}s^{-1}$	1.1×10^{-8} $M^{-1}s^{-1}$	5.5×10^{-5} $M^{-1}s^{-1}$	6.0×10^{-3} $M^{-1}s^{-1}$	6.4 $M^{-1}s^{-1}$	1.1×10^{3} s^{-1}	5.9×10^{-3} s^{-1}

[a] ΔE_0 in place of E_A; ΔG_{rxn} and ΔS_{rxn} in place of $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively (see S2.5 of Supporting Information).

period observed in the experiment at 140 °C as both inhibitory and initiator behaviors are observed. Yet, at 180 °C, the lack of a measurable induction period may be attributed to the inhibitory role of oxygen decreasing as it is freed from quenching radicals more readily.

The possible reactions stemming from the active triplet-diradical intermediate formed after oxygen addition to the monomer are explored for both MA and *n*BA homo-polymerization (Figure 2). Table 2 reports the activation energies and rate constants, calculated with DFT using B3LYP/6-311G** and transition-state theory, relevant to the initiation of MA and *n*BA polymerization at 140 °C. Detailed tables for 120, 140, 180, and 200 °C are given in S3 of Supporting Information. We find that the initiation step, oxygen addition to the C═C double bond of the acrylate, is kinetically and thermodynamically rate limiting. For both MA and *n*BA polymerization, this step has a high activation energy of 121.6 and 121.1 kJ/mol and a relatively low rate constant of 7.4×10^{-9} and 1.2×10^{-9} M^{-1} s^{-1}, respectively. A low rate constant is expected as adsorption of molecular oxygen onto a monomer is penalized for a significantly negative activation entropy.

However, as temperature increases, the oxygen addition rate constant counterintuitively increases to 2.4×10^{-7} M^{-1} s^{-1} at 180 °C for MA, demonstrating opposite trends to that of radical termination with O_2, as listed in Table 1. While both rate constants are reduced by the entropic cost of gas adsorption, the activation entropy of the Markovnikov addition is less negative than the reaction entropy of O_2 radical termination. This trend suggests that elevated temperatures favor oxygen initiation while hindering oxygen inhibition, which agrees with experimental observations despite the relatively low theoretical rate constant. It is also noted that the oxygen-MA initiation reaction is still 5−6 orders of magnitude faster than self-initiation, which has a non-adiabatic rate constant of 1.1×10^{-14} M^{-1} s^{-1} at 140 °C due to a slow intersystem crossing process (singlet−triplet crossover) limited by the small spin−orbit coupling of hydrocarbons.[40,41] It, therefore, becomes more favorable for O_2 to initiate MA and *n*BA polymerization rather than for monomers to self-initiate at elevated temperatures.

Following oxygen initiation, it is more likely that propagation reactions, having low activation energy barriers, next take place as opposed to mono-radical generation shown in Figure 2b,c. It is noted here that $^{\bullet}$OH is not expected to be generated as the abstraction of a hydrogen by the peroxyl radical has a slow rate constant for both MA and *n*BA (Table 2). Propagation of both radical sites may occur at high temperatures, where a moderate rate constant of 1.6×10^{-1} M^{-1} s^{-1} follows for the peroxyl radical and a relatively fast rate constant of 7.5×10^{1} M^{-1} s^{-1} follows for the secondary carbon-based radical in MA polymerization. Diradical propagation reactions for *n*BA are observed to yield rate constants 2 orders of magnitude slower than MA. As expected, the peroxyl radical is much less active (2 orders of magnitude slower) than the carbon radical toward chain propagation for both MA and *n*BA polymerization. This may translate into highly asymmetric chain growth, with the peroxyl radical capping at one end.

Few peroxide species of the type $^{\bullet}$MOOM$^{\bullet}$ are expected to be generated over the course of the reaction. Additionally, this triplet diradical is not favored for O−O dissociation, having a calculated bond dissociation energy (BDE) of 210 kJ/mol, which is high relative to the energy barriers of the pathways proposed here. The high BDE may be attributed to the triplet product $^{\bullet}$MO$^{\bullet}$ being a high energy intermediate due to the proximity of its radical centers. This BDE is comparable to those of studied peroxides, both experimentally and by other DFT studies.[42] The rate constant of forming $^{\bullet}$MO$^{\bullet}$ is 1.4×10^{-3} s^{-1} for M = MA at 140 °C, which is rather slow. Therefore, R−O$^{\bullet}$ type initiator species are not predicted to be generated by this mechanism, reducing the likelihood of O_2 being consumed over the course of the reaction.

The oxygen atoms can then leave the live chain two ways, either by C−O_2 bond thermal dissociation or by releasing $^{\bullet}$OOH. Here, the theoretical C−O_2 BDE is 147 kJ/mol, which is comparable to the R−OO$^{\bullet}$ dissociation energy of similar alkyl peroxides [e.g., *n*-butyl peroxyl radical $CH_3(CH_2)_3$−OO$^{\bullet}$, 145 ± 4 kJ/mol].[43] Furthermore, despite the large activation energy, the rate constant for C−O_2 dissociation is relatively fast for both MA and *n*BA due to the significant, positive contribution of entropy to the reaction free energy. As shown in Figure 2g, the peroxyl radical abstracts one hydrogen atom from its backbone and then dissociates. This reaction also has a moderately slow rate constant of 9.5×10^{-3} and 5.9×10^{-3} s^{-1} for MA and *n*BA, respectively, making it less likely to occur at high temperatures. The reaction's activation entropy is less favorable than the reaction entropy of C−O_2 thermal dissociation because of the backbiting mechanism's low entropy, coordinated transition state that forms an O−H bond while breaking a C−O bond. It is therefore suggested that O_2 returns to the reaction medium as a true catalyst by C−O_2 thermal dissociation. Molecular oxygen is predicted to leave the two-monomer-unit diradical and return to the reaction media, thus acting as an initiator/catalyst. The diradical product can then react with a third monomer to generate two mono-radicals. This finding is supported by experimental observation that at high temperatures, a very low

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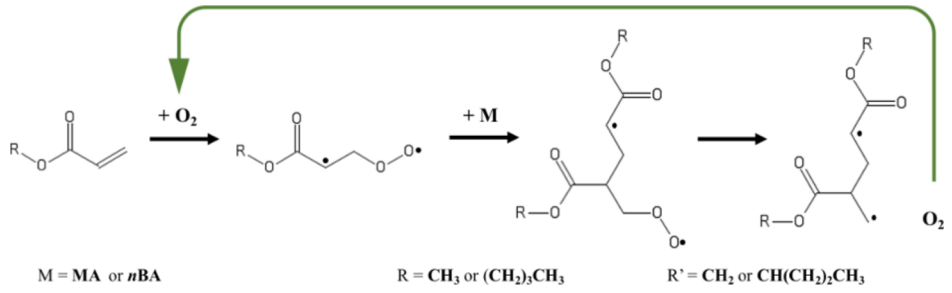

Figure 3. Catalytic role of molecular oxygen in MA and *n*BA polymerization.

concentration of O_2 vigorously initiates and sustains polymerization. The overall catalytic pathway of O_2 in MA and *n*BA polymerization is illustrated in Figure 3.

CONCLUSIONS

Using DFT calculations, the known inhibiting role of O_2 in free-radical polymerization was found to diminish substantially with increased temperature. These theoretical findings are in agreement with our experimental observations at $T > 140$ °C that show the presence of molecular oxygen dramatically increases the polymerization rate in comparison to the monomer self-initiation processes. Particularly, we showed that the conversion of the deaerated monomer is significantly less than that of the air-saturated monomer at 180 °C. Our DFT studies provide insights into the mechanism of MA and *n*BA free-radical polymerization in the presence of molecular oxygen. First, O_2 initiates polymerization by bonding to the monomer vinyl group to form an active triplet diradical. Another monomer is then attached via propagation off the reactive secondary-carbon radical. Finally, O_2 leaves by thermal dissociation. This sequence of reactions illustrates the catalytic role of O_2. The first step, oxygen addition to the monomer, was predicted to be the rate-limiting step due to the entropic cost of dissolved gas adsorption; however, this step becomes faster at elevated temperatures, in agreement with experimental observations. Molecular oxygen is then favored to leave dimerized monomers by C−O_2 bond dissociation because of the high entropic gain. The oxygen-initiation mechanism provides a faster reaction pathway for mono-radical generation compared to thermal self-initiation. Thus, oxygen-catalyzed initiation of free-radical polymerization of alkyl acrylates is promising for future cost-efficient and sustainable polymer production.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.macromol.1c00669.

Further descriptions of experimental and computational methods, select energies of optimized structures, and additional information on kinetic parameters (PDF)

All optimized structures (ZIP)

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Notes

The authors declare no competing financial interest.

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