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 results in high conversions of monomer in a very short time at temperatures above 140°C without use of conventional initiators. By conducting first-principles calculations based on density functional theory (DFT), 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*-butyl acrylate 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.

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 (VOCs) prevent the use of high solvent concentrations, which improve performance during application, in paints and coatings.[1] Therefore, high temperature ($120 - 220^{\circ}$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 longer induction periods.[20–22] The reaction of oxygen molecules with carbon-based secondary propagating radicals generates peroxyl (R-

O-O•) radicals, which are much less reactive and lead to 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 monomers, yet polymerization occurs when oxygen is added.[14] Oxygen also plays a pivotal role in methyl methacrylate polymerization initiated by a copper(II)-ascorbic acid-oxygen system in aqueous medium.[31,32]

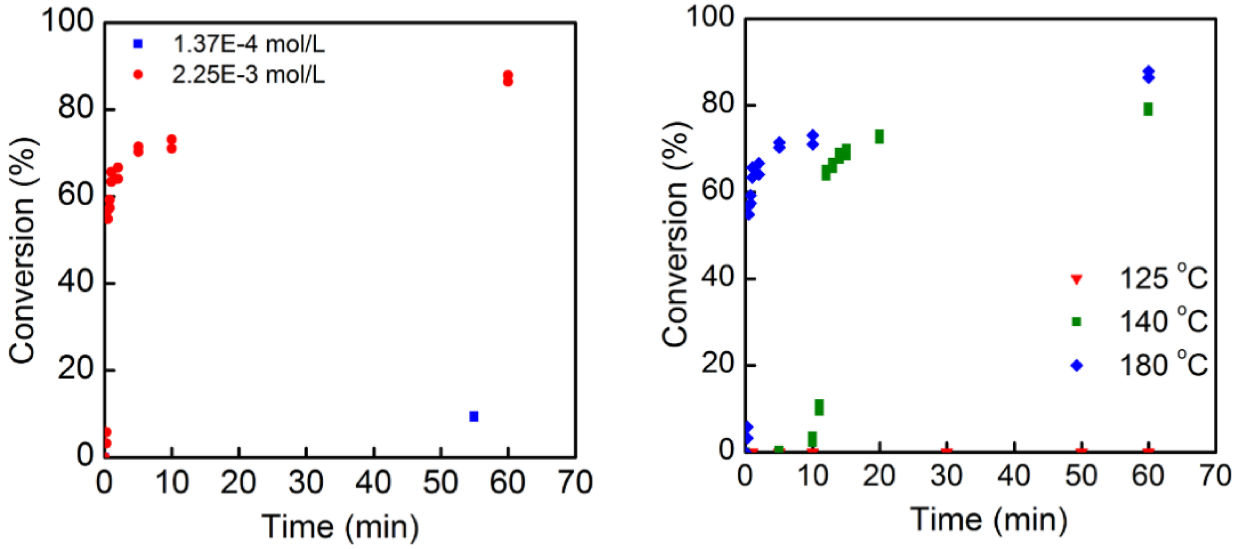
In this study for the first time, we report free-radical polymerization of *n*-butyl acrylate (*n*BA) at different O_2 concentrations and at high temperatures ($140-180^{\circ}$C) in the absence of any added thermal- or photo-initiators. Monomer conversion measurements indicate that *n*BA saturated with air polymerizes vigorously and that the rate of polymerization increases with increasing oxygen concentration and temperature. By 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, the peroxyl radicals decompose with molecular oxygen dissociating from the monomer complex to recover active carbon-based secondary radicals and diatomic oxygen. These results suggest that oxygen acts as an initiator and catalyst for alkyl acrylate free-radical polymerization at $T > 140^{\circ}$C.

Results and Discussion

We explore the temperature dependence of the spontaneous bulk thermal polymerization of ultra-high pure (UHP) N_2-bubbled and air-saturated nBA. The procedure for removal of inhibitor and all the experimental methods, including measuring oxygen content, have been explained in the Supporting Information (SI). From our previous study, we understood that at 140°C there is less than 3% conversion of UHP N_2-bubbled nBA monomer after 240 minutes.[33] 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 nBA bubbled with either UHP N_2 or air at high temperatures are conducted to investigate the participation of O_2 and differentiate this work from conventional works on acrylate free-radical bulk polymerization.[17,33–36] Figure 1a shows that while 10% of the deaerated nBA (1.37×10^{-4} mol/L oxygen) is converted to polymer after 60 minutes at 180°C, a conversion of 50% can be achieved in only 30 seconds for the air-saturated nBA (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 one hour, the final conversion of air-saturated monomer is 86%, which is more than 8.5 times higher than for deaerated nBA 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 polymerization in the presence of oxygen, free radical polymerization of air-saturated nBA is carried out at different temperatures. Figure 1b presents the conversion for air-saturated nBA from $125 - -180$°C. 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



(a) (b)

Figure 1: (a) nBA conversion v. time at 180°C: blue square for monomer bubbled with UHP N_2 (1.37×10^{-4} mol/L dissolved oxygen) and red circles for monomer bubbled with air (2.25×10^{-3} mol/L dissolved oxygen). (b) Conversion of air-bubbled nBA v. time at different temperatures. No conversion is observed at 125°C. The induction time decreases as temperature increases. Right after the induction time, conversion initially increases very sharply over a very short time and then increases gradually and steadily.

the spontaneous polymerization rate increases rapidly with temperature and that monomer conversion grows remarkably from 78% at 140°C to 86% at 180°C. An induction period where time passes before considerable conversion is observed for 140°C—180°C. The induction time significantly declines as temperature rises from 11 min for 140°C to less than and 15 s for 180°C. After the induction time, a nearly vertical increase in conversion implies that free-radical polymerization of air saturated nBA is remarkably fast.

To understand the role of oxygen in high-temperature polymerization of alkyl acrylates, we also carry out a systematic, first-principles exploration with GAMESS[37] using density-functional theory (DFT), the Becke-3-Lee-Young-Parr hybrid functional (B3LYP), and the 6-311G** basis set. Further details on computational methods are given in SI. Previous studies employ B3LYP, and its use is well validated for alkyl acrylate and free-radical investigations.[6,7,11,13,38] The solvation entropy is calculated for aerated experimental conditions

($[O_2] = 2.1 \times 10^{-3}$ mol/L) and is accounted for in reaction entropies involving molecular oxygen (see SI). Given the chemical similarity of methyl acrylate (MA) and nBA, we first study various possible reactions of an MA molecule and a triplet ground-state O_2 (see Figure in SI). 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. 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•) are studied where M = MA (see SI). •M-H type mono-radicals result from self-initiation mechanisms[38] and therefore are chosen for this study. DFT calculations predict an electronic energy barrier of 94.21 kJ/mol for peroxyl formation. The rate constant of peroxyl formation decreases appreciably at elevated temperatures while the rate constant of the reverse reaction increases (Table 1).

Table 1: Enthalpy (ΔH), and Gibbs Free Energy (ΔG) in kJ/mol, Entropy (ΔS) in J/molK, and Rate Constants k(T) at Various Temperatures for Peroxyl Formation and Dissociation Reactions for O_2 and MA Mono-radical (•M-H)

	Peroxyl Formation				Peroxyl Dissociation			
T	ΔH	ΔS	ΔG	k(T) ($M^{-1}s^{-1}$)	ΔH	ΔS	ΔG	k(T) (s^{-1})
25°C	-102.8	-121.2	-66.7	7.5×10^{27}	102.8	121.2	66.7	1.3×10^{1}
100°C	-105.0	-121.4	-59.7	5.5×10^{24}	105.0	121.4	59.7	3.4×10^{4}
120°C	-105.6	-121.4	-57.9	1.3×10^{24}	105.6	121.4	57.9	1.7×10^{5}
140°C	-106.2	-121.3	-56.1	3.7×10^{23}	106.2	121.3	56.1	7.0×10^{5}
180°C	-107.3	-121.1	-52.5	4.0×10^{22}	107.3	121.1	52.5	8.4×10^{6}
200°C	-107.9	-120.9	-50.7	1.6×10^{22}	107.9	120.9	50.7	2.5×10^{7}

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 unreacted monomer. These results suggest that molecular oxygen's role as an inhibitor decreases at elevated temperatures.

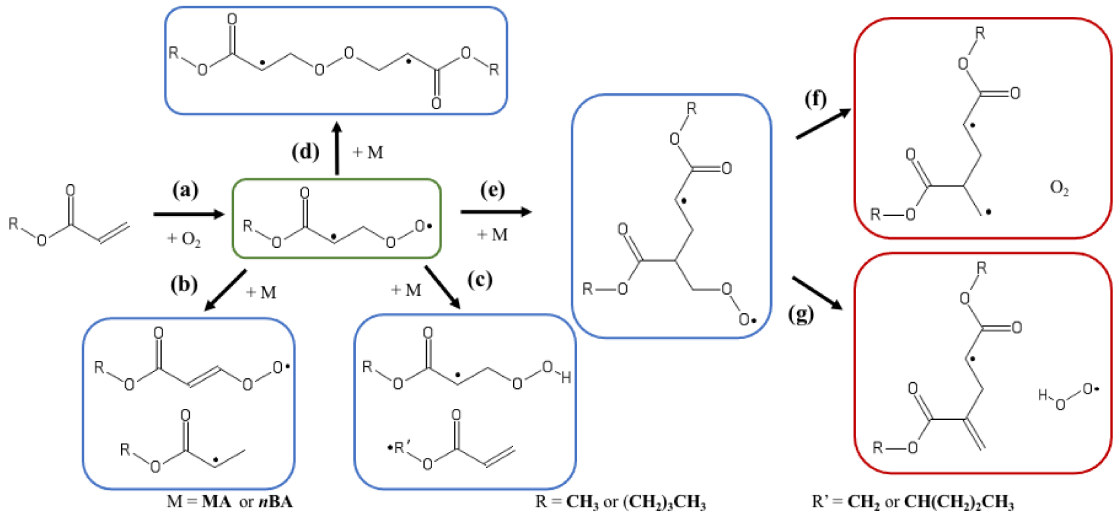


Figure 2: (a) Oxygen addition to monomer forming diradical intermediate, (b) radical transfer from secondary carbon to monomer, (c) radical transfer from peroxyl to monomer, (d) diradical propagation via peroxyl radical, (e) diradical propagation via secondary-carbon radical, (f) C-O_2 dissociation,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

The possible reactions stemming from the active triplet-diradical intermediate formed after oxygen addition to 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. 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 kJ/mol and 121.1 kJ/mol and a relatively low rate constant of 7.4×10^{-9} $M^{-1}s^{-1}$ 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.

Table 2: Activation Energy (E_A) and Gibbs Free Energy ($\Delta G^{\ddagger}$) in kJ/mol, Entropy ($\Delta S^{\ddagger}$) in J/molK, and Rate Constants k(T) at 140° for Oxygen-Monomer Reactions 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)$^{+}$	(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}

$^{+}$ ΔE_0 in place of E_A; ΔG_{rxn} and ΔS_{rxn} in place of $\Delta G^{\ddagger}$ and $\Delta S^{\ddagger}$, respectively (see SI for details).

However, as temperature increases, the oxygen addition rate constant counterintuitively increases to 1.1×10^{-6} $M^{-1}s^{-1}$ at 200°C for MA, demonstrating opposite trends to that of radical termination with O_2 in Table I (see SI for additional tables). While both rate constants are reduced by the entropic cost of gas adsorption, the activation entropy of 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 inter-system crossing process (singlet-triplet crossover) limited by the small spin-orbit coupling of hydrocarbons.[38,39] 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 events, having low activation energy barriers, next take place as opposed to mono-radical generation shown in Figure

2b and 2c. Propagation off 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 events for *n*BA are observed to yield rate constants two orders of magnitude slower than MA. As expected, the peroxyl radical is much less active (two 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 one end.

The oxygen atoms can then leave the live chain two ways, either by C-O_2 bond thermal dissociation or by releasing •OOH. Here, the theoretical C-O_2 bond dissociation energy is 147 kJ/mol, which is comparable to the R-OO• dissociation energy of similar alkyl peroxides (e.g., *n*-butyl peroxyl radical $CH_3(CH_2)_3$-OO•, 145 ± 4 kJ/mol).[40] 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. 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} s^{-1} 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 acrylate monomers as an initiator/catalyst, resulting in a monomer dimer fit for further propagation and chain transfer events without the introduction of peroxide impurities. This finding is supported by experimental observation that at high temperatures, a very low concentration of O_2 vigorously initiates and sustains polymerization.

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 N_2-bubbled monomer is significantly less than that of 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 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 dissociation because the reaction is effectively barrierless and results in a high entropic gain. The oxygen-initiation mechanisms provide 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.

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Supporting Information Available

The following file is available free of charge.

- R194SupportInfo.pdf: Further descriptions of experimental and computational methods.

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Graphical TOC Entry