

# Oxygen as Free, High-Temperature Catalyst for Alkyl Acrylate Polymerization



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## Introduction

**Acrylic polymers** are fundamental to **paint** and **coating** industries. High purity acrylates desired to avoid discoloration and moisture sensitivity.

**Free-radical polymerization (FRP)** conventionally depends on:

- **High operating temperature (T)**: low MW, low solvent resins
- **Thermal- or photo-initiators**: jumpstart polymerization

Conventional initiators **costly** and may **contaminate** final product.

- **Self-initiation mechanisms**: high purity product but **slow**

**Molecular oxygen**- triplet-diradical species observed to **inhibit FRP at low T** (reduces rate and final conversion).

**New Studies**: oxygenated *n*-butyl acrylate (*n*BA) → polymerizes above 120°C and dependence on O<sub>2</sub> concentration.

This computational study proposes an initiation mechanism dictated by **O<sub>2</sub> addition** to an acrylate monomer. This implies O<sub>2</sub> can act as an **initiator-catalyst** in high-T alkyl acrylate polymerization.

## Computational Methods

**Density Functional Theory (DFT)** calculations with GAMESS computational chemistry package.

- **Restricted-open shell Hartree-Fock (ROHF)** constructs wavefunctions as unrestricted-open-shell Hartree-Fock (UHF) introduces **spin contamination**
- The well-validated **Becke-Lee-Parr hybrid functional (B3LYP)** for acrylate systems and Gaussian basis set **6-311G\*\*** were used for stationary point and frequency calculations

**Rate constant k(T)** calculations follow **transition state theory (TST)**

$$k(T) = \kappa(c^\circ)^{1-m} \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(-\frac{\Delta H^\ddagger}{RT}\right) \quad (1)$$

$\kappa$ : Wigner Tunneling corrected transmission coefficient  
 $c^\circ$ : inverse reference volume assumed in ideal gas translational partition function  
 $m$ : molecularity of reaction  
 $h$ : Planck's constant  
 $\Delta S^\ddagger$ : activation entropy  
 $k_B$ : Boltzmann's constant  
 $R$ : ideal gas constant  
 $\Delta H^\ddagger$ : activation enthalpy

Which may be written as an **Arrhenius equation**:  $k(T) = A \exp\left(-\frac{E_a}{RT}\right)$  (2)

For C-O bond dissociation and radical termination, k(T) calculated by

$$k(T) = (c^\circ)^{1-m} \frac{k_B T}{h} \exp\left(-\frac{\Delta G^\ddagger}{RT}\right) \quad (3)$$

**Non-ideality of dissolved O<sub>2</sub>** is approximated by solvation entropy correction based on low solvent and ideal mixing assumptions

$$\Delta S_{\text{solvation}} = R \ln\left(\frac{X_{O_2(g)}}{X_{O_2(dis)}}\right) \quad (4)$$

where  $X_{O_2(g)}$  is oxygen concentration in above gas and  $X_{O_2(dis)}$  is oxygen concentration dissolved in liquid monomer.

## Results

**Methyl acrylate (MA)** monomers M were studied preliminarily due to similar chemical characteristics as *n*BA while less computationally costly

### O<sub>2</sub> Inhibition for Methyl Acrylate

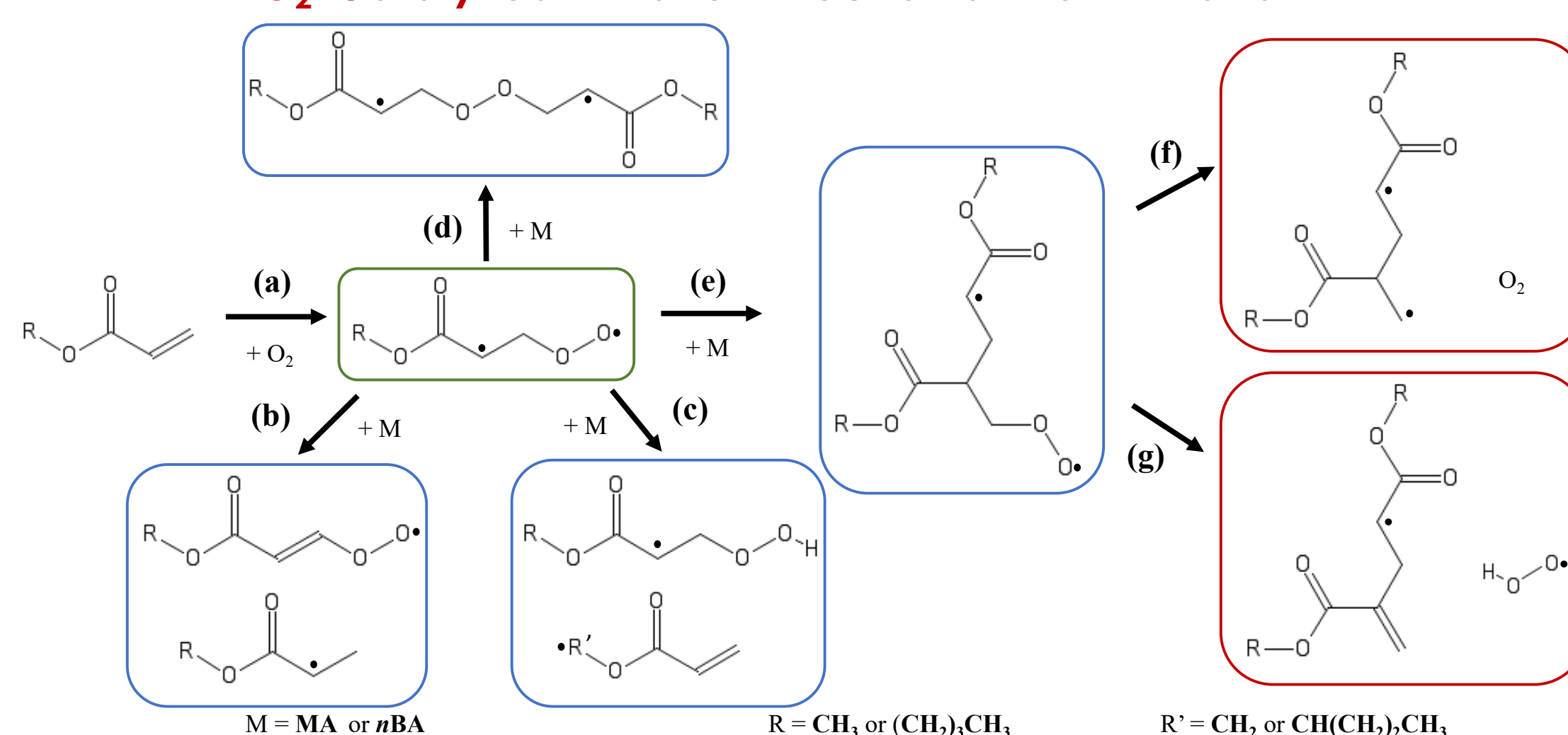
Table I: Gibbs Free Energy ( $\Delta G$ ) and  $\Delta S^\ddagger$  in kJ/mol and Rate Constants  $k(T)$  at Various Temperatures for Radical Termination (*forward*) and C-O Dissociation (*reverse*) Reactions for O<sub>2</sub> and MA Mono-radical •M-H with B3LYP/6-311G\*\*

		273 K	298 K	393 K	413 K	453 K	473 K
$\Delta G^\ddagger$	<i>forward</i>	-48.5	-45.3	-33.2	-30.7	-25.6	-23.1
$\Delta S^\ddagger$	<i>forward</i>	-34.6	-37.8	-50.0	-52.5	-57.4	-59.9
$k(T)$	<i>forward</i> (M <sup>1</sup> s <sup>-1</sup> )	2.4 x 10 <sup>23</sup>	1.3 x 10 <sup>22</sup>	6.9 x 10 <sup>18</sup>	2.2 x 10 <sup>18</sup>	3.2 x 10 <sup>17</sup>	1.4 x 10 <sup>17</sup>
	<i>reverse</i> (s <sup>-1</sup> )	3.0 x 10 <sup>3</sup>	7.1 x 10 <sup>4</sup>	3.1 x 10 <sup>8</sup>	1.1 x 10 <sup>9</sup>	1.0 x 10 <sup>10</sup>	2.8 x 10 <sup>10</sup>

+  $\Delta G_{\text{reverse}} = -\Delta G_{\text{forward}}$  and is not included for brevity (as follows for  $\Delta S_{\text{reverse}}$ )

- Oxygen inhibition, on self-initiation mono-radicals
- MH, **decreases** with **increasing temperature**. The converse is true for C-O dissociation
- Instability for O<sub>2</sub> inhibiting mechanisms at elevated temperature

### O<sub>2</sub>-Catalyzed Initiation Mechanism for MA and *n*BA



**Figure 1:** (a) oxygen addition to monomer, (b) propagation off peroxy radical, (c) mono-radical generation by hydrogen transfer to monomer, (d) mono-radical generation by hydrogen transfer from monomer, (e) propagation off secondary-carbon radical, (f) C-O dissociation, (g) mono-radical generation by backbiting.

**Proposed Mechanism:**

- 1) Markovnikov addition M + O<sub>2</sub>, producing triplet-diradical intermediate (a)
- 2) New M propagates off active carbon radical (e)
- 3) O<sub>2</sub> leaves triplet-diradical dimer by C-O dissociation, driven by entropy (f)

**C-O dissociation (f) or Backbiting (g) at elevated T?**

- Similar entropic contributions
- Exothermicity favors C-O dissociation
- Enthalpic difference approximately C-H bond formation

### O<sub>2</sub> functions as a true catalyst

Self-initiation

- **k(413) = 1.1 x 10<sup>-14</sup> M<sup>-1</sup>s<sup>-1</sup>**
- Slow singlet-triplet intersystem crossing

O<sub>2</sub>-catalyzed initiation

- **k(413) = 1.5 x 10<sup>-7</sup> M<sup>-1</sup>s<sup>-1</sup>**
- (a) rate limiting, O<sub>2</sub> adsorption onto M,  $\Delta S^\ddagger < 0$

**7 orders** of magnitude quicker than self-initiation mechanism

$$k(473) = 2.0 \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1} \rightarrow \mathbf{T \text{ boosts } O_2 \text{ initiation}}$$

## Conclusions

**Character of Molecular Oxygen in Alkyl Acrylate Polymerization**

Low Temperature Inhibitor High Temperature Initiator-Catalyst

**DFT calculations** reveal and support that

- Rate limiting step- O<sub>2</sub> opening monomer vinyl group to form **active triplet-diradical**
- Monomer readily propagates off triplet-diradical intermediate
- O<sub>2</sub> thermally dissociates from active triplet-diradical dimer

In studying oxygen's participation as an **initiator-catalyst**, oxygen initiation mechanisms provide **faster reaction times** compared to thermal self-initiation.

Table II: Activation Energy ( $E_a$ ) and Gibbs Free Energy ( $\Delta G_{rxn}$ ) in kJ/mol, Entropy ( $\Delta S_{rxn}$ ) in J/molK, and Rate Constants  $k$  at 413K for Oxygen-Monomer Reactions in Figure 4 for MA (*no shading*) and *n*BA (*shading*) with B3LYP/6-311G\*\*

	Initiation	Mono-Radical Generation	Diradical Propagation	Peroxy Radical Termination	(f) <sup>+</sup>	(g)
$E_a$	(a)	(b)	(c)	(d)	(e)	
	132.8	90.8	77.2	47.7	34.5	135.0
	133.2	91.8	66.7	50.9	37.1	135.8
$\Delta G_{rxn}$	168.9	151.6	135.5	113.8	94.0	74.7
	176.3	164.1	133.2	127.5	108.7	73.5
$\Delta S_{rxn}$	-104.1	-164.0	-157.8	-176.5	-160.6	137.7
	-121.0	-191.5	-177.6	-202.1	-190.0	142.7
$k(413)$	1.5 x 10 <sup>-7</sup> M <sup>-1</sup> s <sup>-1</sup>	6.2 x 10 <sup>-5</sup> M <sup>-1</sup> s <sup>-1</sup>	5.0 x 10 <sup>-3</sup> M <sup>-1</sup> s <sup>-1</sup>	1.4 M <sup>-1</sup> s <sup>-1</sup>	4.2 x 10 <sup>2</sup> M <sup>-1</sup> s <sup>-1</sup>	3.1 x 10 <sup>3</sup> s <sup>-1</sup>
	1.7 x 10 <sup>-8</sup> M <sup>-1</sup> s <sup>-1</sup>	1.6 x 10 <sup>-6</sup> M <sup>-1</sup> s <sup>-1</sup>	1.0 x 10 <sup>-2</sup> M <sup>-1</sup> s <sup>-1</sup>	2.6 x 10 <sup>-2</sup> M <sup>-1</sup> s <sup>-1</sup>	5.7 M <sup>-1</sup> s <sup>-1</sup>	8.5 x 10 <sup>-1</sup> s <sup>-1</sup>

+  $\Delta G_{rxn}$  and  $\Delta S_{rxn}$  are given for the difference between products and reactant, not transition state and reactant(s)

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