

# Fluorinated Photoinitiator for Oxygen Inhibition Resistance and Gradient Photopolymerization

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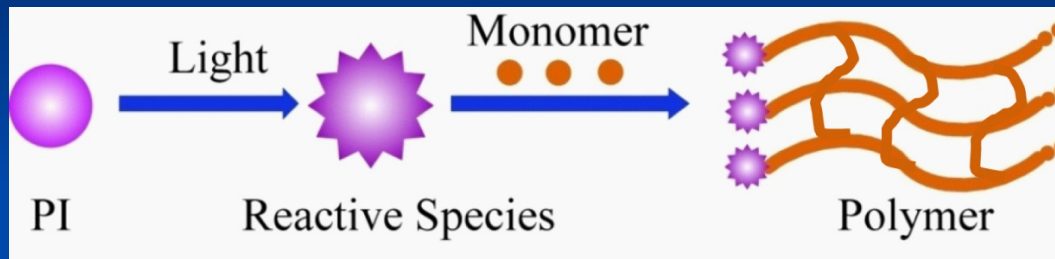
# Outline

## ➤ Background

## ➤ Research and Results

- Synthesis of Photoinitiator
- Oxygen Inhibition Resistance
- Gradient Photopolymerization
- Secondary Polymerization

## ➤ Conclusions

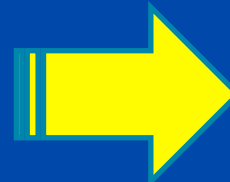
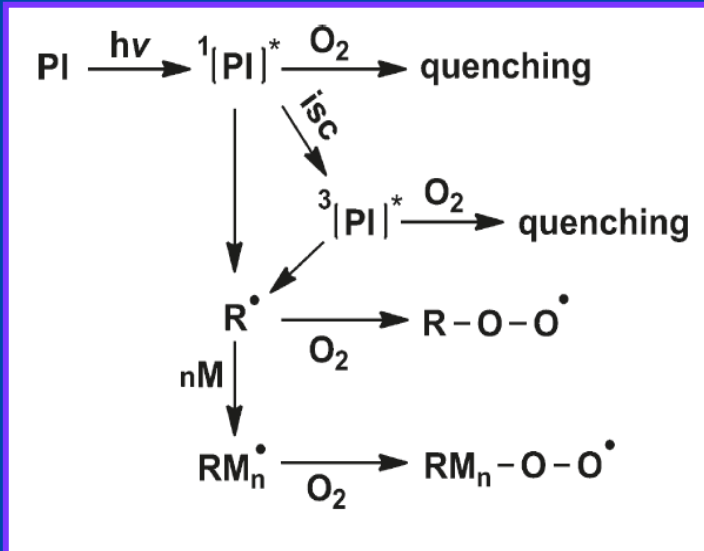
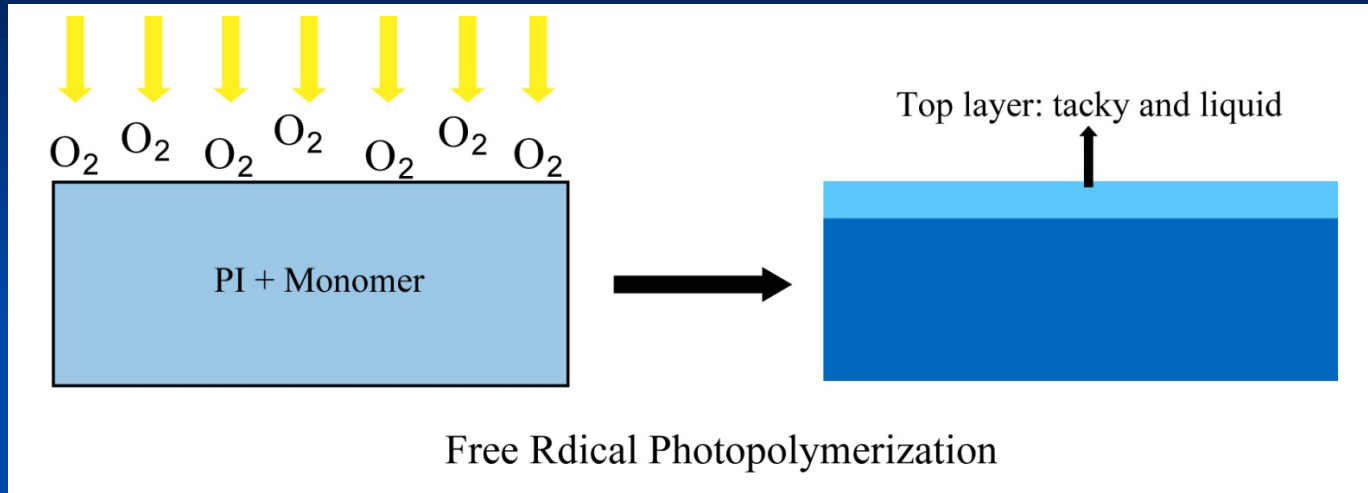


UV-Tech: Economical  
 Energy Saving  
 Efficient  
 Environmental friendly  
 Enabling



# Defect of Free Radical Photopolymerization

## Oxygen Inhibition

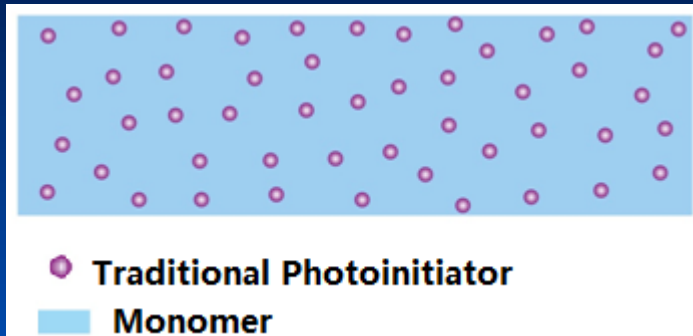


**Low Conversion**

**Small Polymerization Rate**

**Poor Surface properties**

One possible solution—Higher photoinitiator concentration



**Lower polymerization rate**  
**More initiator residue**  
**Worse film properties**

If *Photoinitiator* could have...

**High** concentration on the surface layer and **Low** concentration in the bulk.



Our suggestion: Introduce **Fluorine** to Photoinitiator



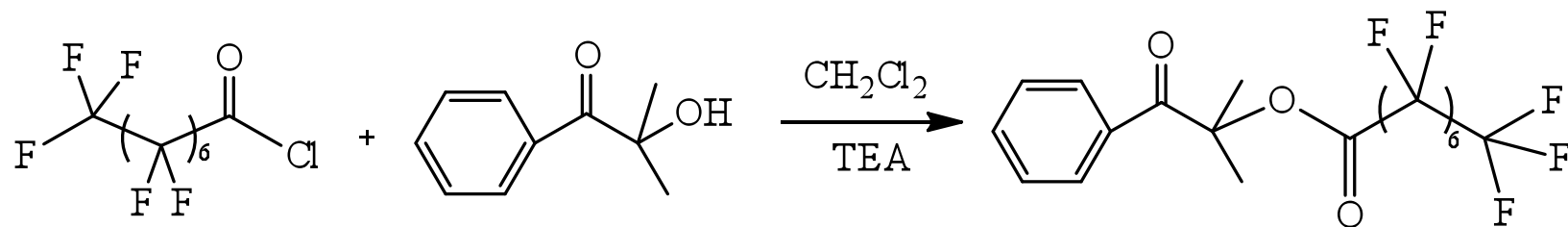
Migratory



Low surface energy  
Low surface tension



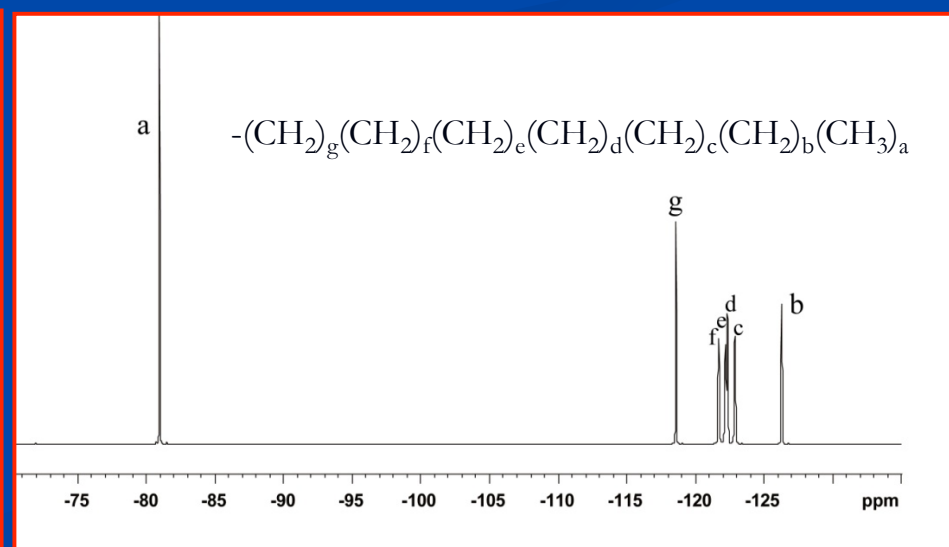
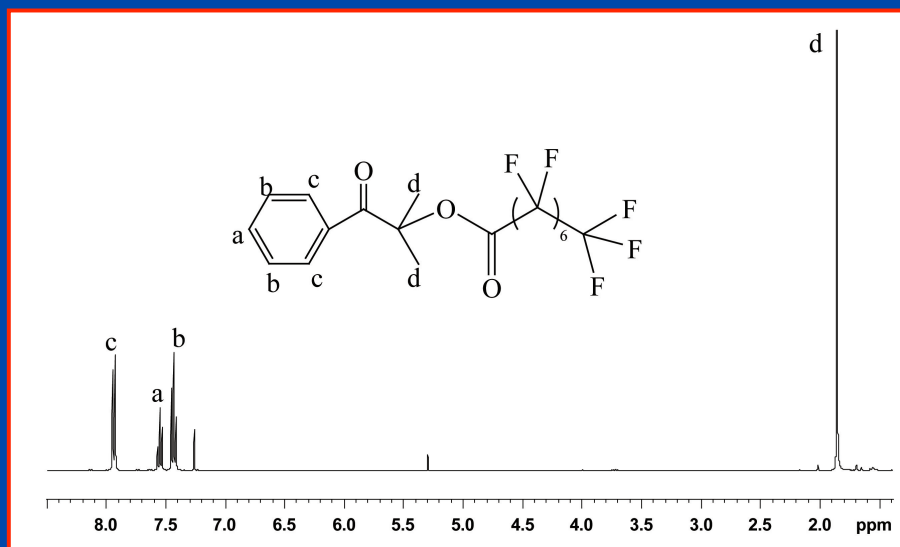
# Synthesis and Characterization of 1173F

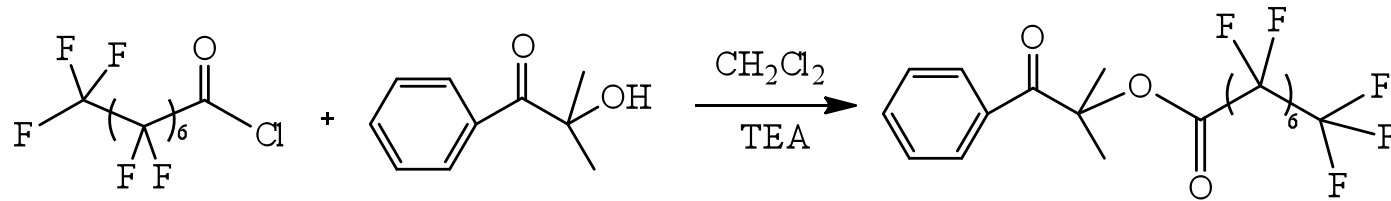


## 1. NMR

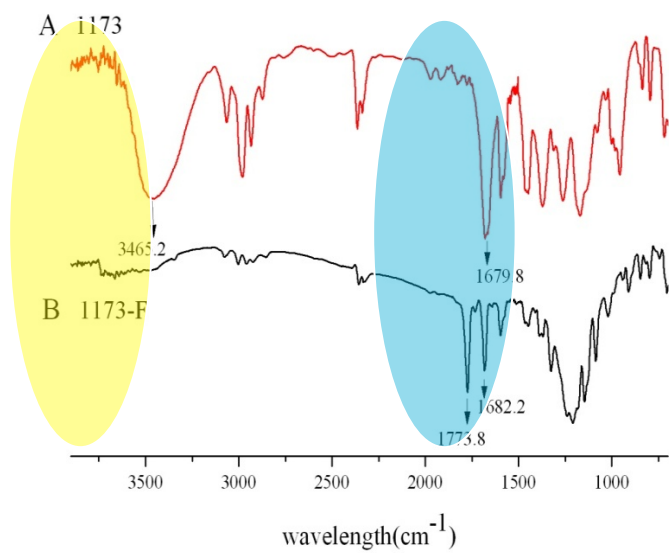
$^1\text{H}$  NMR

$^{19}\text{F}$  NMR

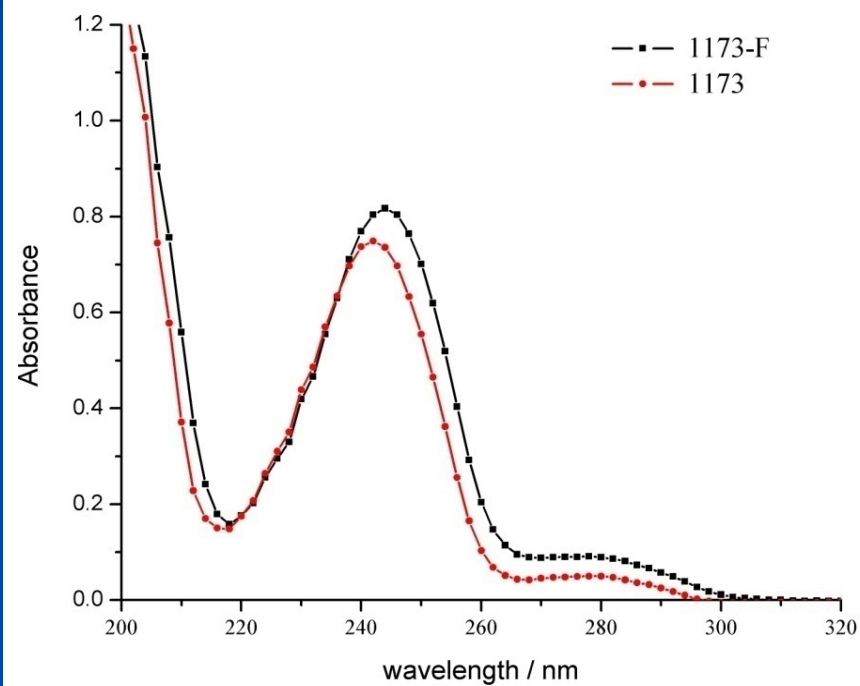




## 2. FTIR

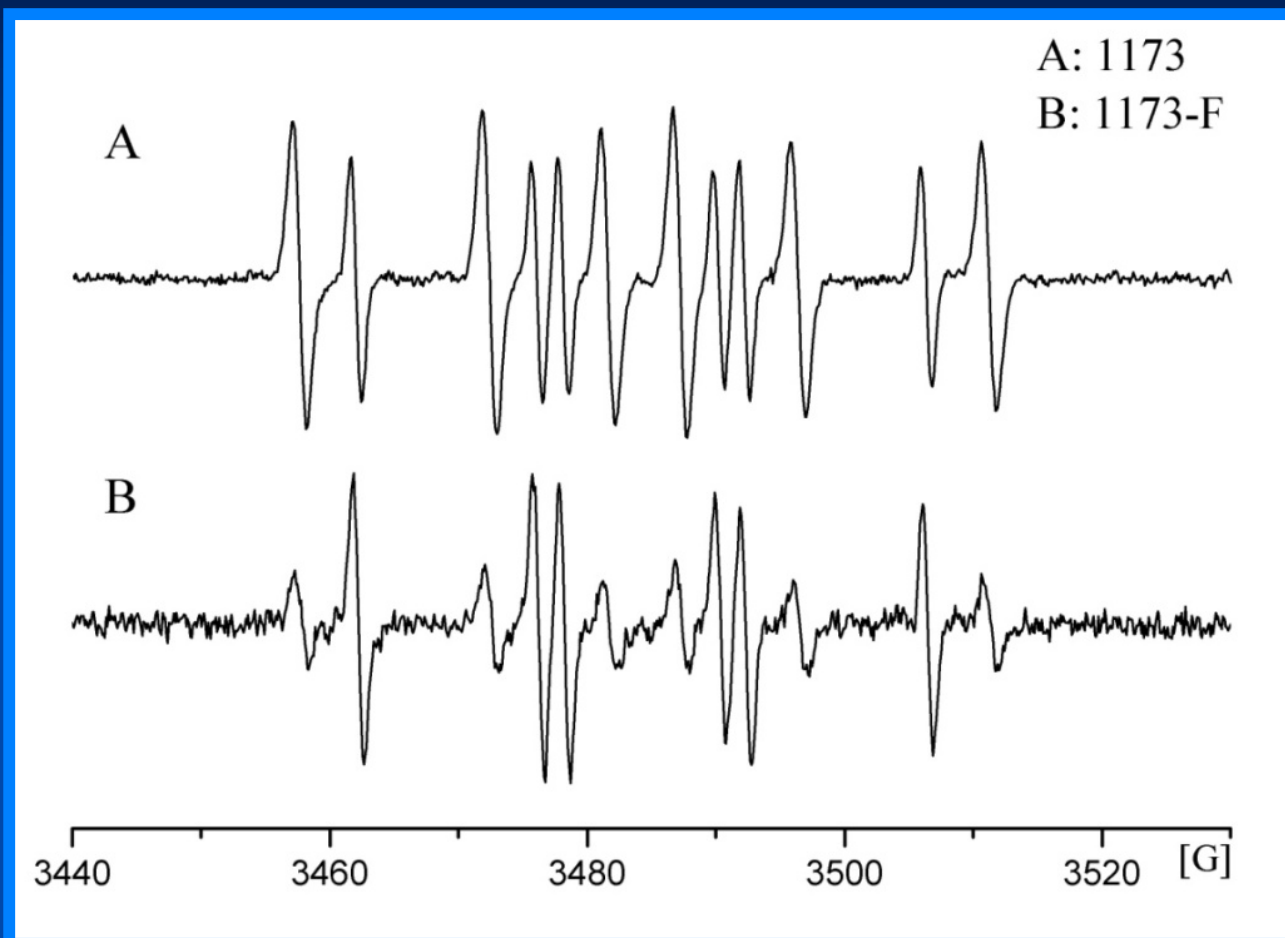


## 3. UV-abs





## 4. EPR (Electron Paramagnetic Resonance )



Radical scavenger: dimethyl pyridine N-oxide (DMPO)  
[M] =  $10^{-2}$  mol/L, 355 nm laser, in acetonitrile solutions

## 5. Laser Flash Photolysis Experiments

$$\frac{1}{A} = \frac{1}{A_L} + \frac{1/\tau_T}{A_L k_q [Q]}$$

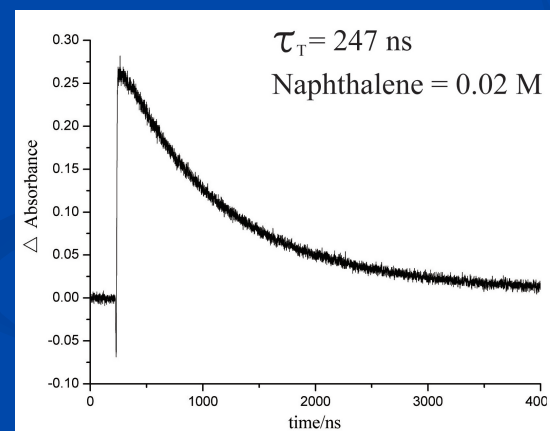
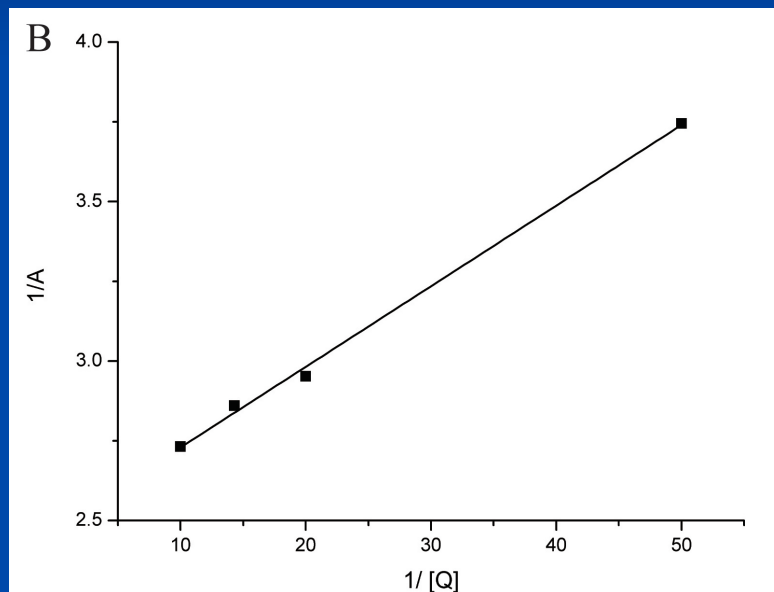
A- the absorbance of naphthalene triplet at 412 nm

$A_L$ - the limiting absorbance

$\tau_T$ - triplet lifetime of 1173-F

$k_q$ - the rate constant for its quenching by naphthalene

[Q] - concentration of naphthalene.

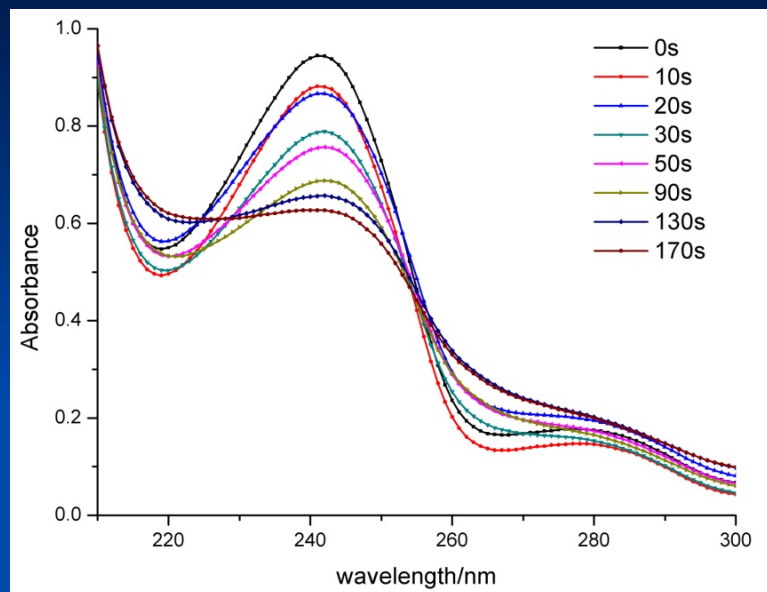


**Triplet lifetime (1173F) = 13 ns**

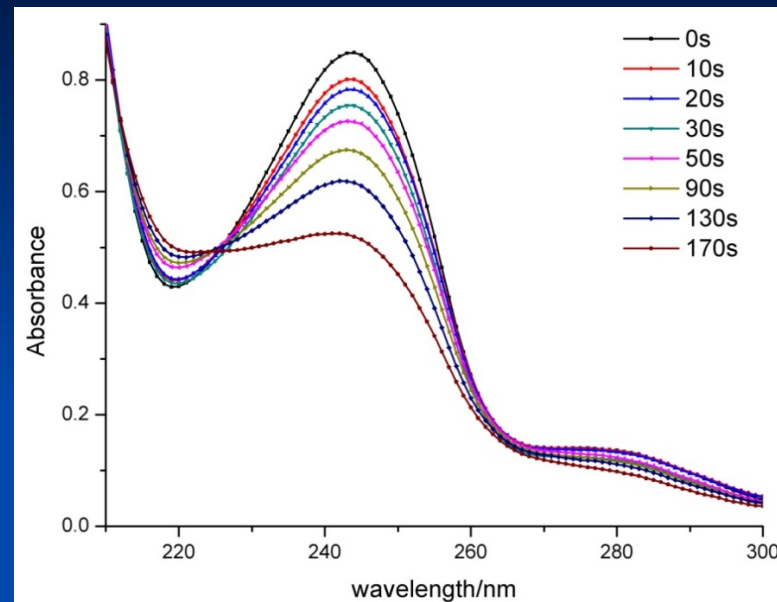
*Macromolecules* 2001, 34, 1610-1626.

## 6. Dissociation rate of Photoinitiator

A: 1173



B: 1173F



$$A = \epsilon c L$$

$$R_d = \frac{-\delta[PI]}{\delta t} = -\left(\frac{[PI]}{A_0}\right) \frac{\delta[A]}{\delta t}$$

$$R_d = I_0 \phi \epsilon [I] = \phi I_a$$

$$R_d(1173F) = 1.46 \times 10^{-7} \text{ molL}^{-1}\text{s}^{-1}$$

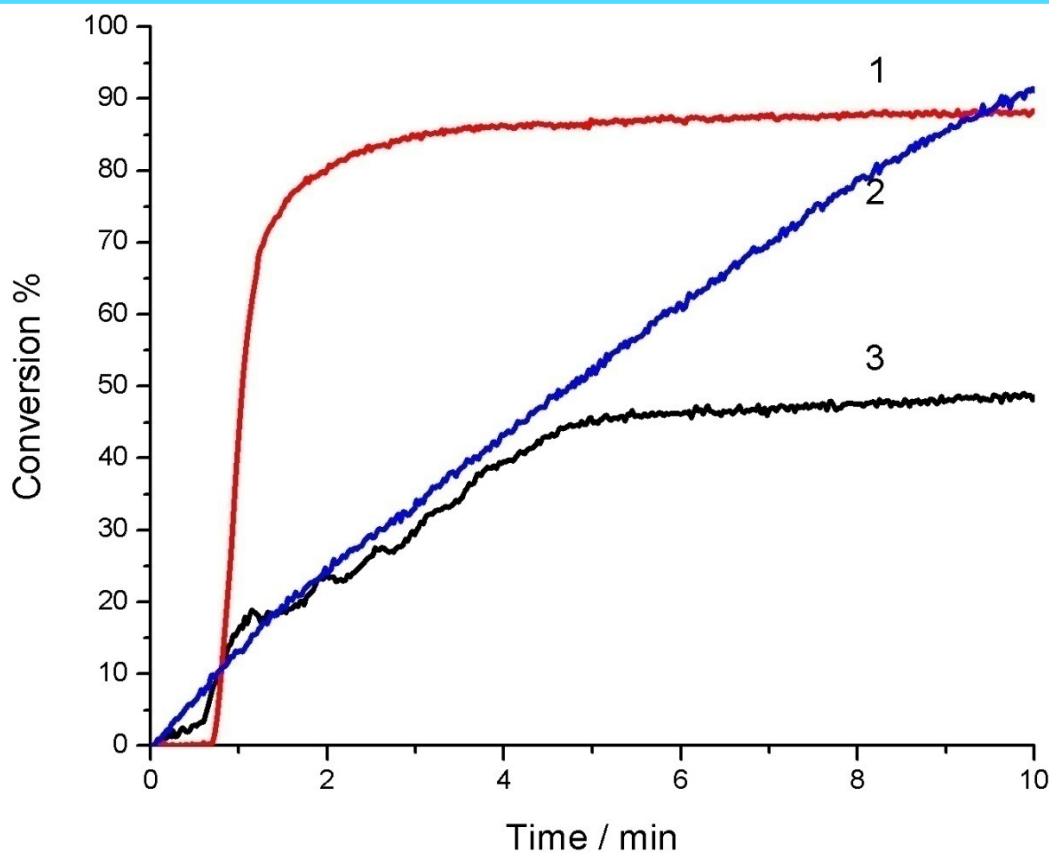
$$R_d(1173) = 2.11 \times 10^{-7} \text{ molL}^{-1}\text{s}^{-1}$$

$$\Phi(1173F) \approx \Phi(1173)$$

All the sample was observed in nitrogen saturated acetonitrile solutions at 23 °C .  
The intensity of UV light was 10 mW/cm<sup>2</sup>. [1173]= 5×10<sup>-5</sup> mol/L, [1173-F] = 5×10<sup>-5</sup> mol/L.

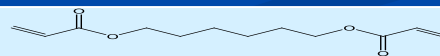
## Oxygen Inhibition Resistance

Polymerization kinetics of HDDA with photoinitiator (1173 and 1173F)



1. 1173 close to air
2. 1173F open to air
3. 1173 open to air

Light Intensity: 10 mW/cm<sup>2</sup>



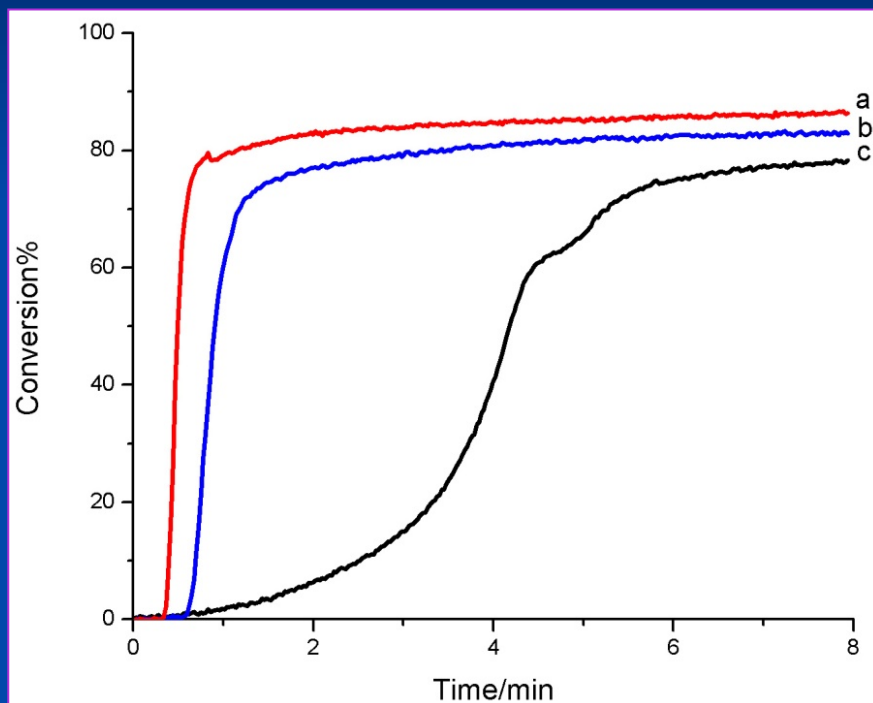
HDDA

# Oxygen Inhibition Resistance

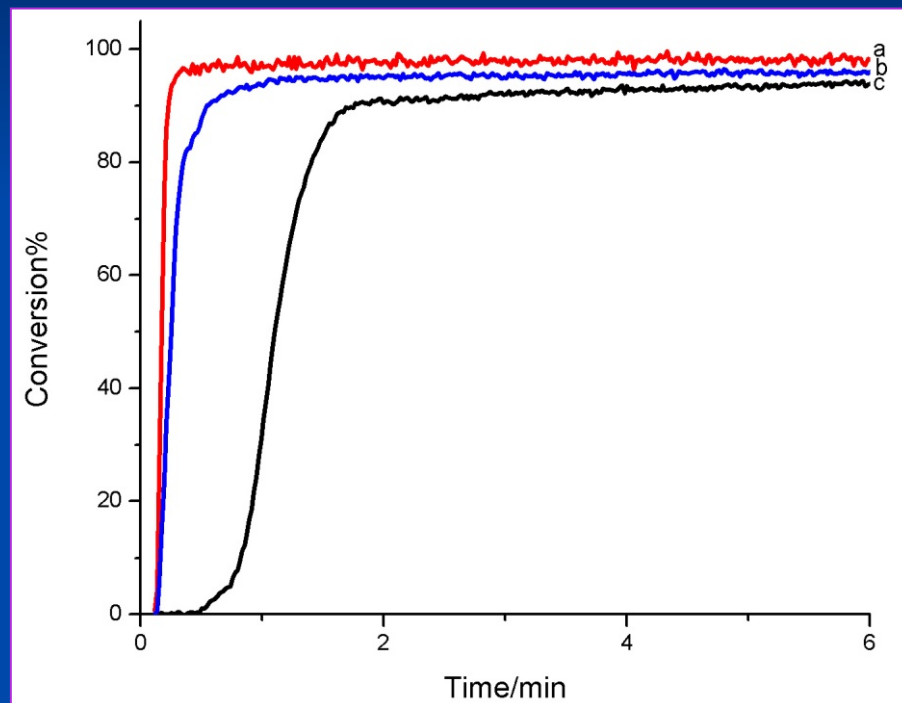
## Conversion of HDDA with 1173 and 1173-F

Close to air

(a. 1173 , b. 1173/1173F=1/1 , c. 1173F)



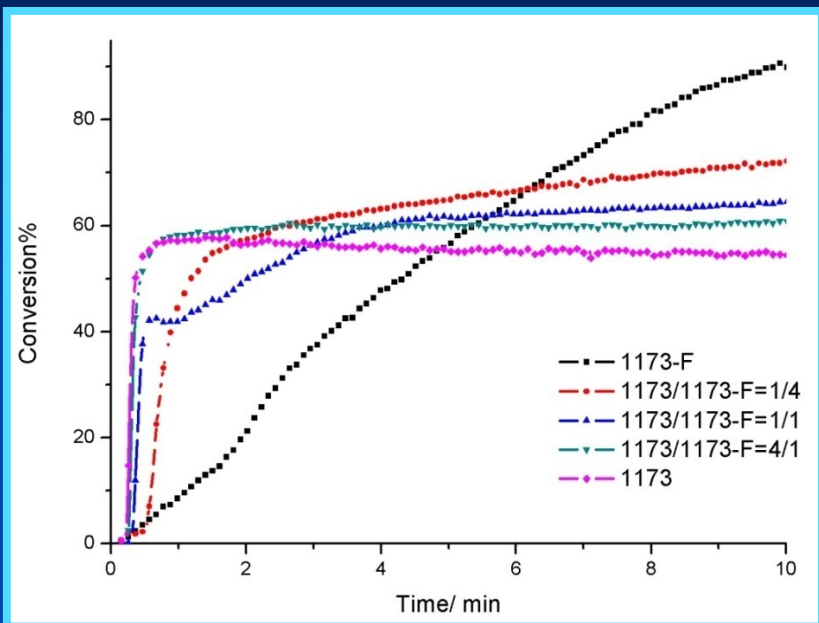
Light Intensity: 10 mW/cm<sup>2</sup>



Light Intensity: 40 mW/cm<sup>2</sup>

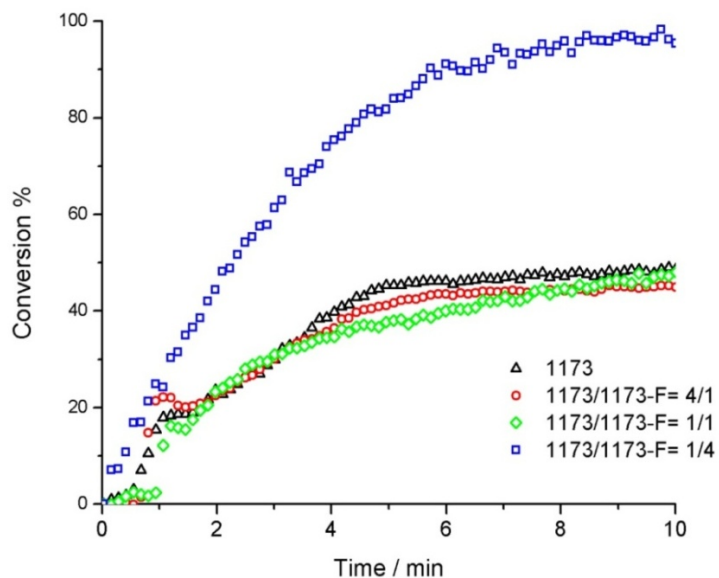
Monomer: HDDA, PI: 0.305 mmol/100g

# Oxygen Inhibition Resistance



Photoinitiator	1173/10 <sup>-4</sup> mol	1173F/10 <sup>-4</sup> mol	Total/10 <sup>-4</sup> mol	HDDA/g
1173	3.05	0	3.05	100
1173/1173F=4/1	2.44	0.61	3.05	100
1173/1173F=1/1	1.525	1.525	3.05	100
1173/1173F=1/4	0.61	2.44	3.05	100
1173F	0	3.05	3.05	100

# Oxygen Inhibition Resistance



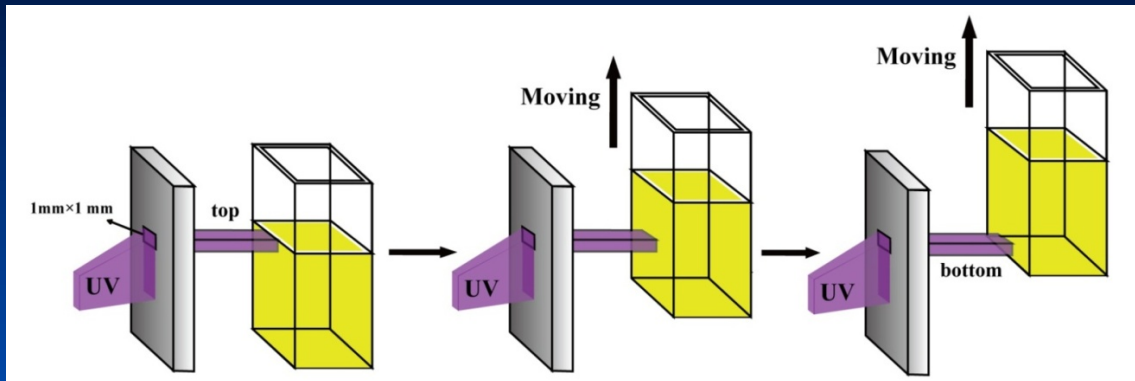
Conversion of HDDA with 1173 and 1173F

*Open to Air!*

Light Intensity: 10 mW/cm<sup>2</sup>

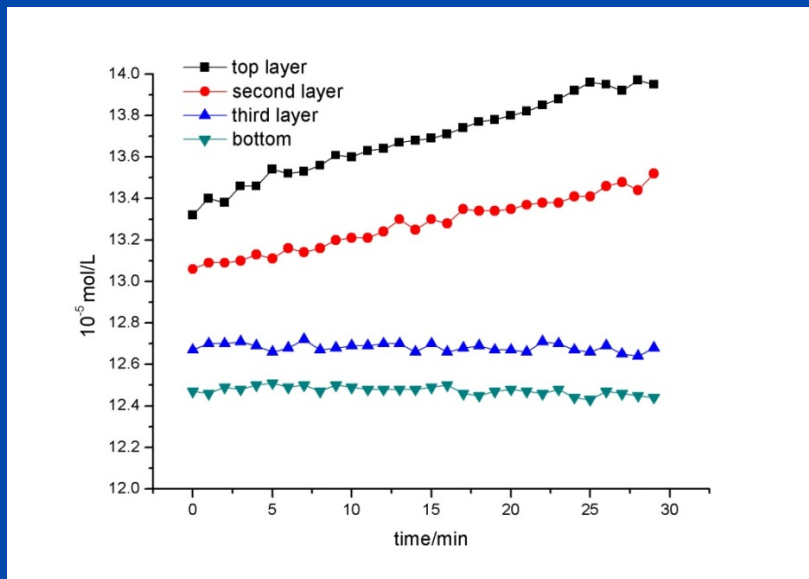
Photoinitiator	1173/10 <sup>-4</sup> mol	1173F/10 <sup>-4</sup> mol	Total/10 <sup>-4</sup> mol	HDDA/g
1173	3.05	0	3.05	100
1173/1173F=4/1	2.44	0.61	3.05	100
1173/1173F=1/1	1.525	1.525	3.05	100
1173/1173F=1/4	0.61	2.44	3.05	100

# Gradient distribution from top to bottom

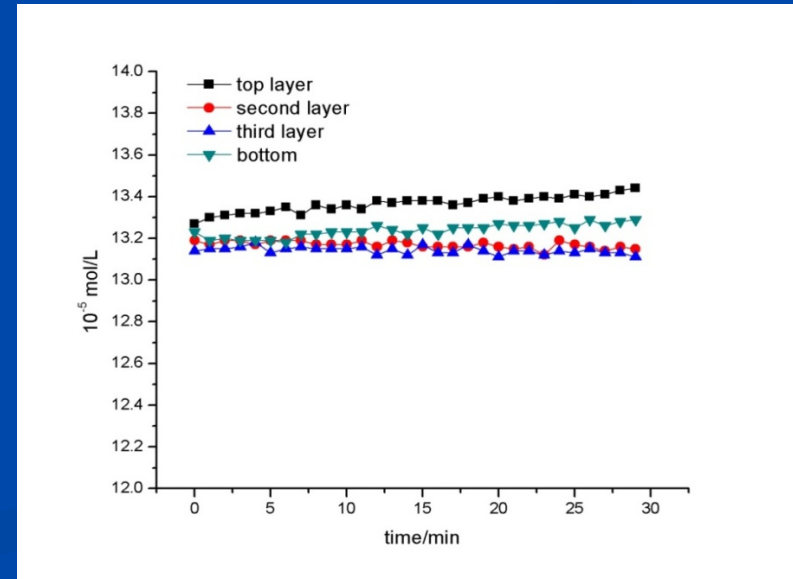


UV Spectrophotometer

## Concentration of 1173 and 1173F in acetonitrile solution



1173F

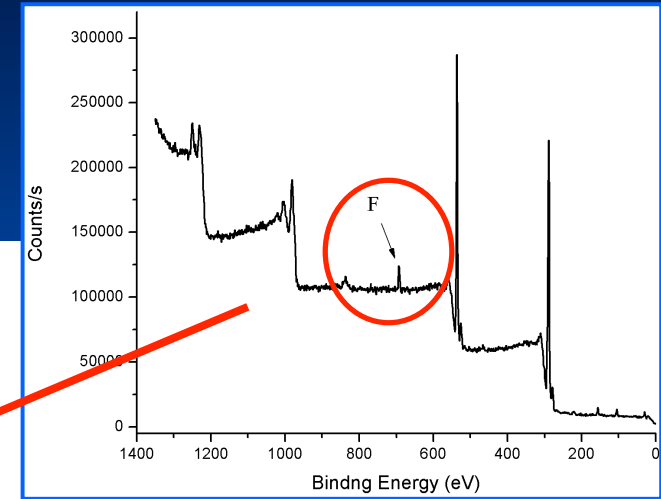
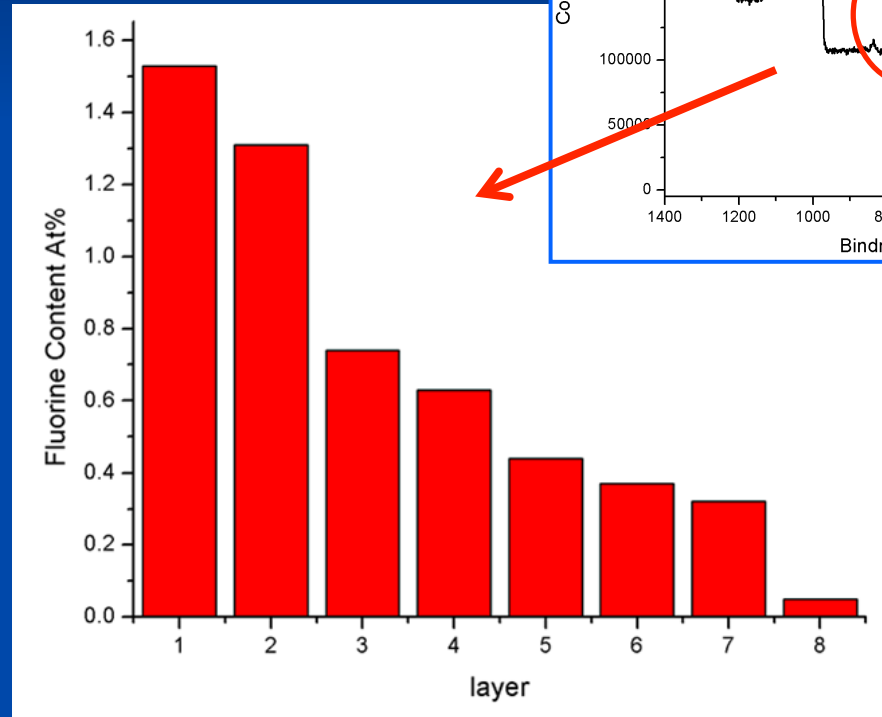
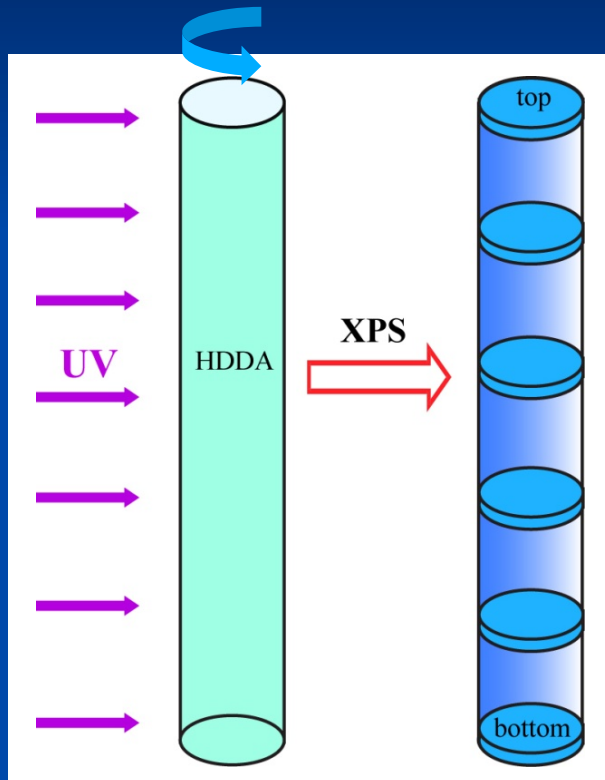


1173



# Gradient distribution from top to bottom

## XPS (X-ray photoelectron spectroscopy)



Monomer: HDDA , PI: 1173F 5%

## Gradient distribution from top to bottom

### GPC(gel permeation chromatography )

Layer	Mn (1173-F)	Mw(1173F)	PDI(1173F)	Mn(1173)	Mw(1173)	PDI(1173)
1	7544	26012	3.4	14836	40076	2.7
2	24457	39392	1.6	13348	42580	3.2
3	79696	113643	1.4	13203	40849	3.1
4	100839	249292	2.5	12650	38541	3.0
5	107870	338510	3.1	13457	39255	2.9

Monomer: MMA PI: 1173-F 5%

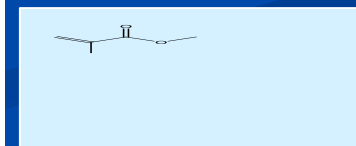
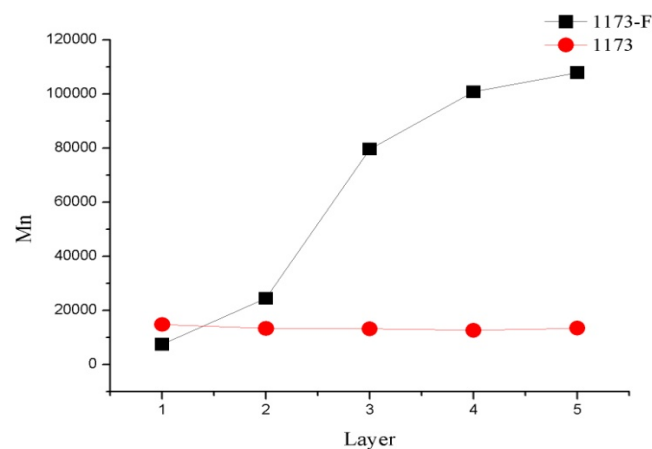
More initiator



Low molecular weight



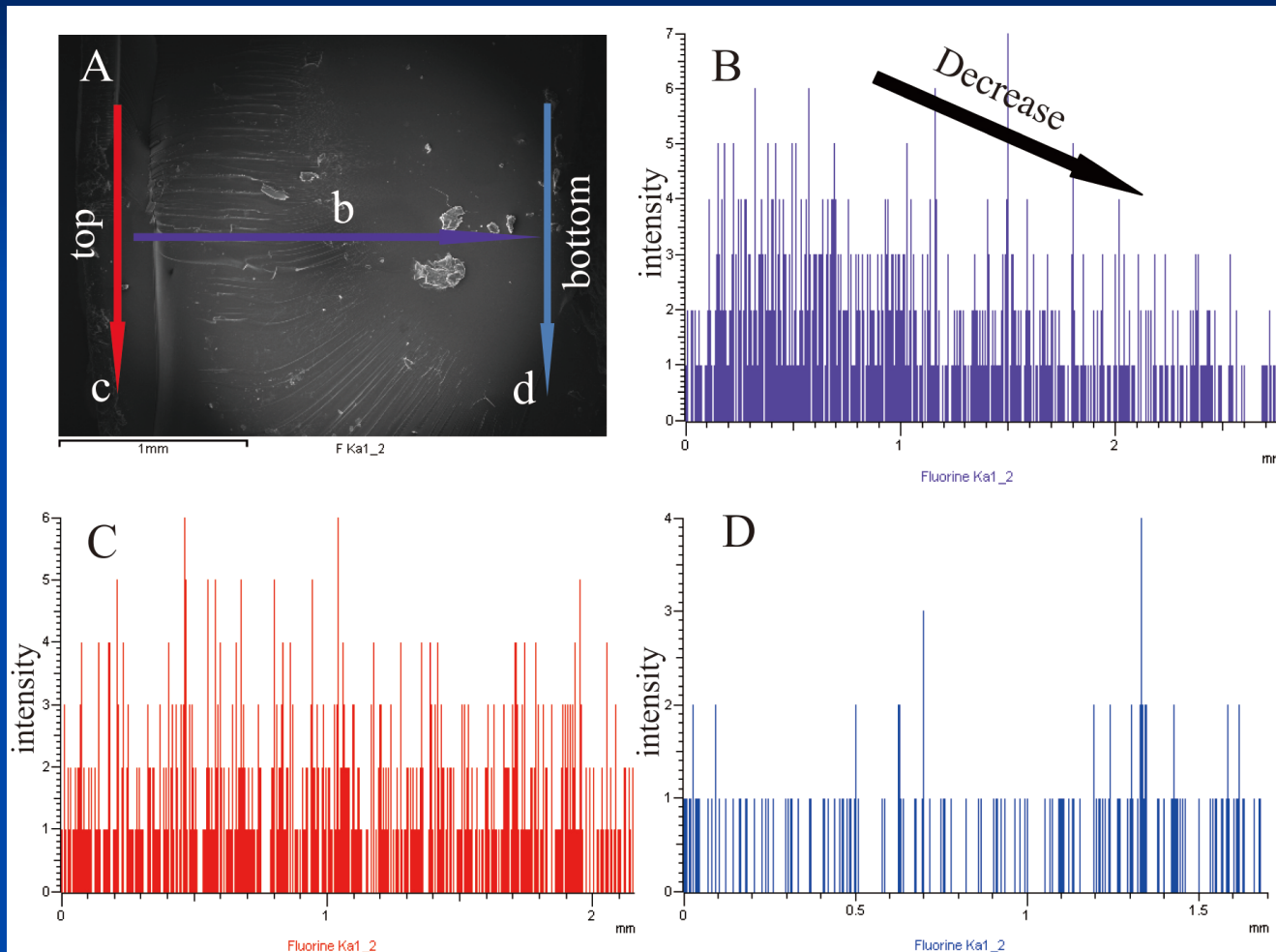
Gradient polymerization



MMA

# Gradient distribution from top to bottom

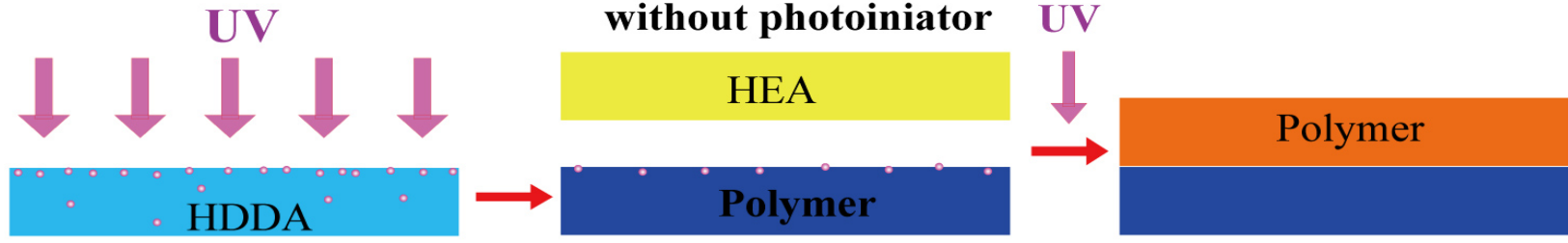
## SEM EDS line mapping



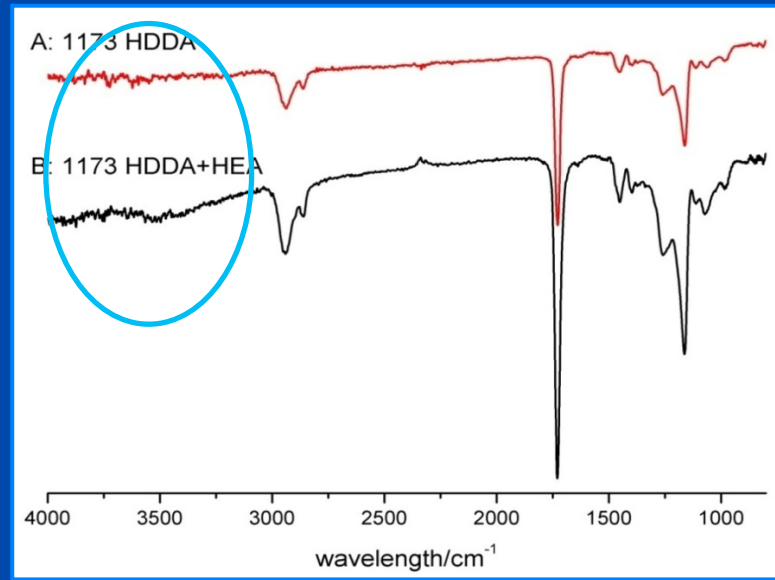
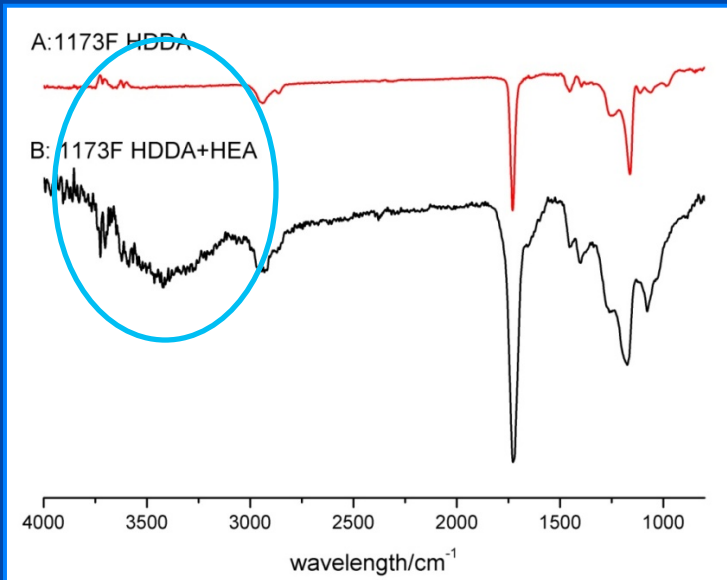
Monomer: HDDA PI: 1173F 5%

# Secondary polymerization

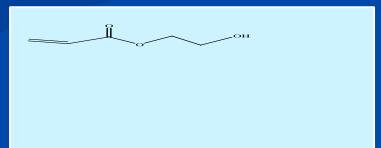
PI: 1173F



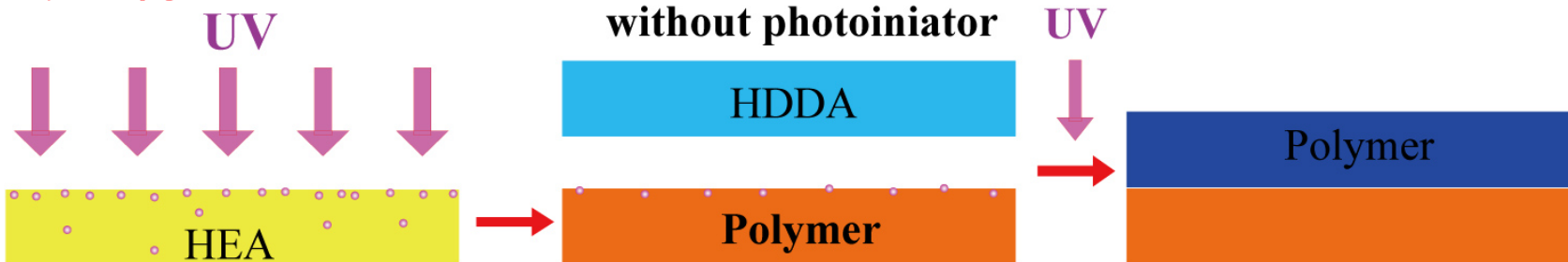
## ATR (Attenuated Total Reflection)



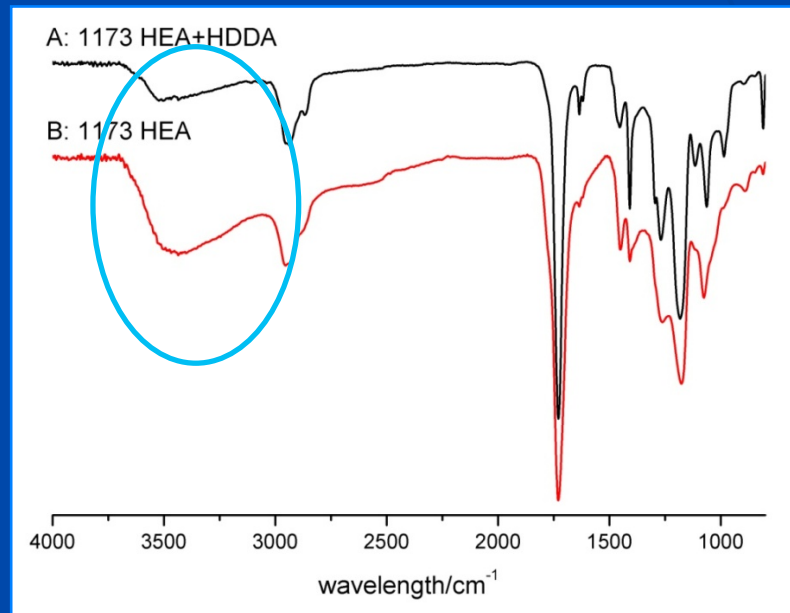
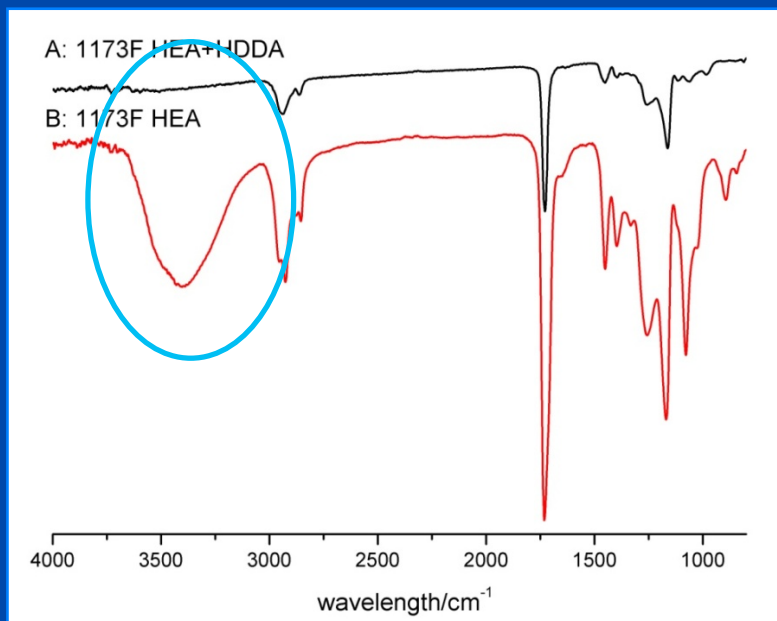
HEA



**PI: 1173F**



## ATR (Attenuated Total Reflection)



# Conclusions

- Fluorinated photoinitiator had excellent migratory ability
- 1173F had better qualities in surface photopolymerization
- 1173F decreased oxygen inhibition effectively without any other additives or co-initiator
- A simple method to overcome oxygen inhibition
- A method to prepare gradient polymer

**Thank you for your attention!**