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ESPERANTO Enhancing the Sustainability of PhotopolymERs ANd phoToinduced prOcesses

Funded by the European Union

Synthesis and Application of Castor Oil based MacroPhotoinitiators and their Application for Biobased Polymer Coatings and Gold Nanocomposites

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BOSAD BOYA SANAYİCİLERİ DERNEĞİ THE ASSOCIATION OF PAINT INDUSTRY

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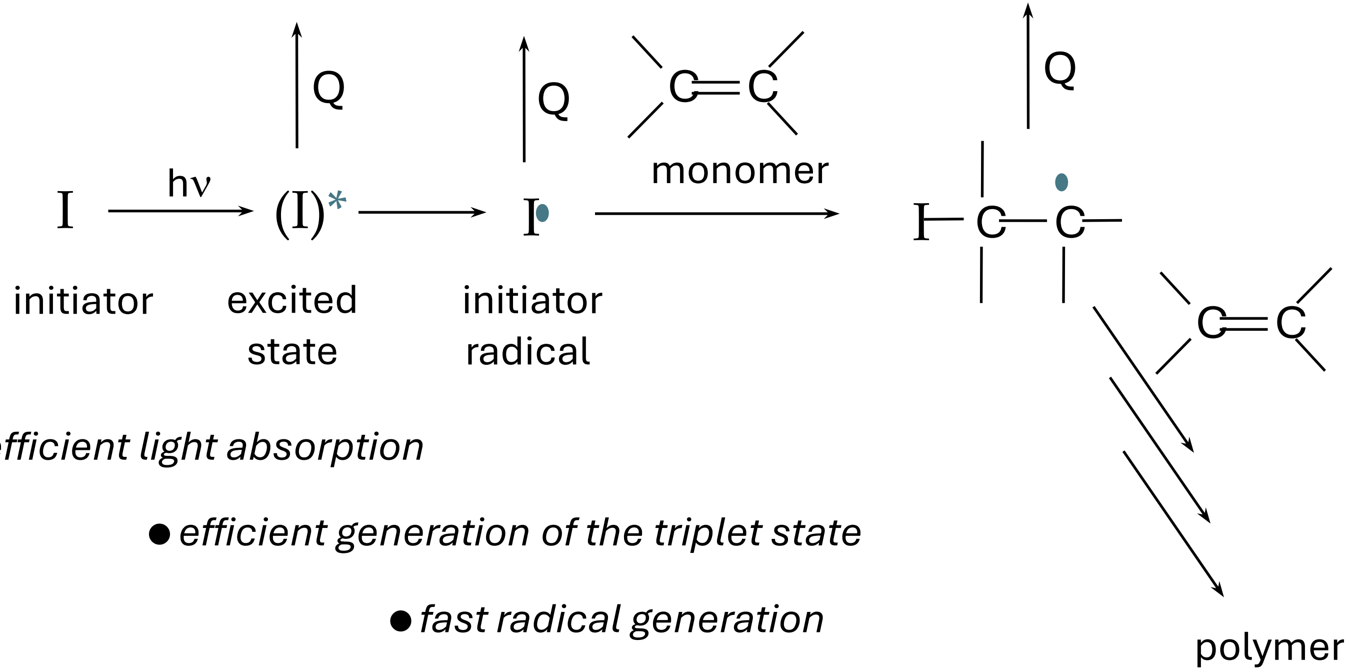
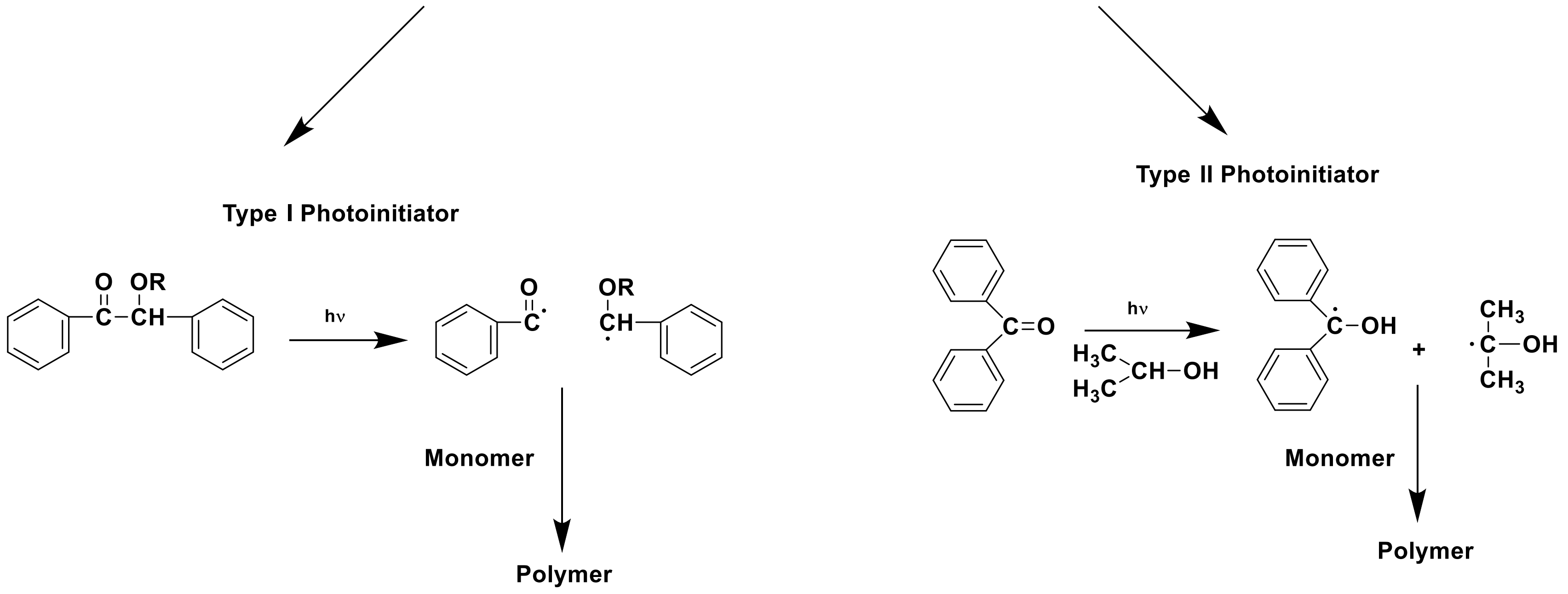
Photoinitiation
of Free Radical Polymerization

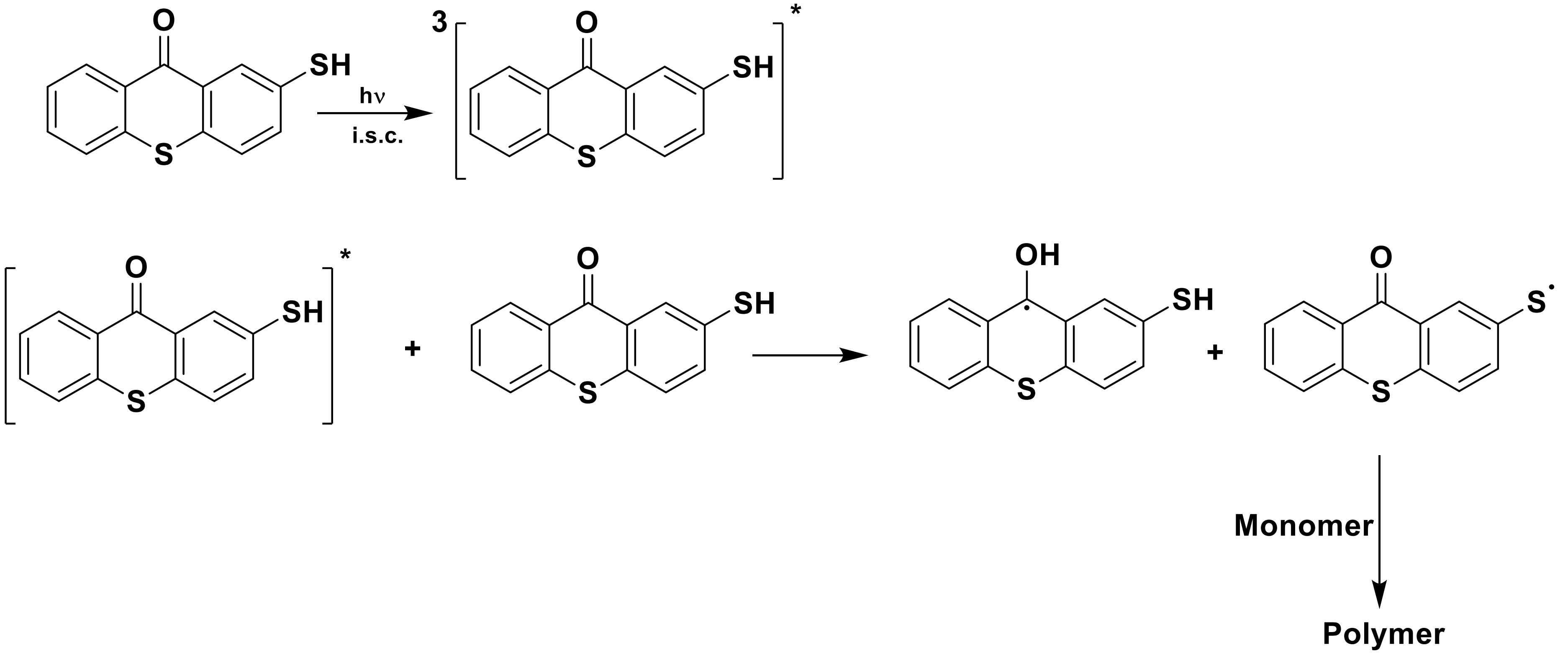


- *efficient light absorption*
- *efficient generation of the triplet state*
- *fast radical generation*
- *high addition rate constant*

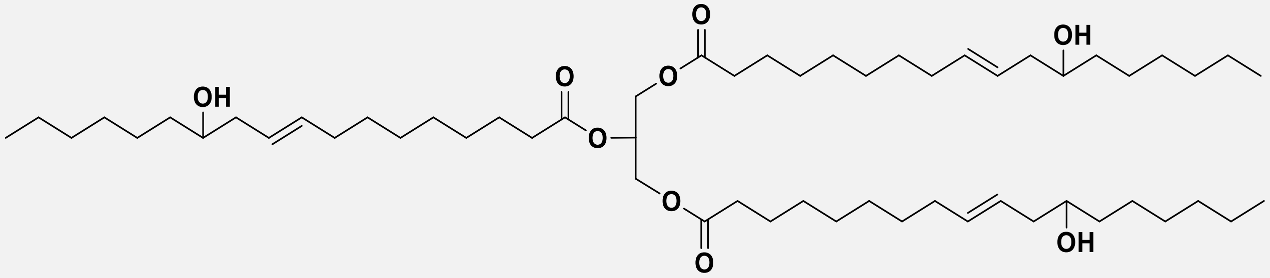
Photoinitiator



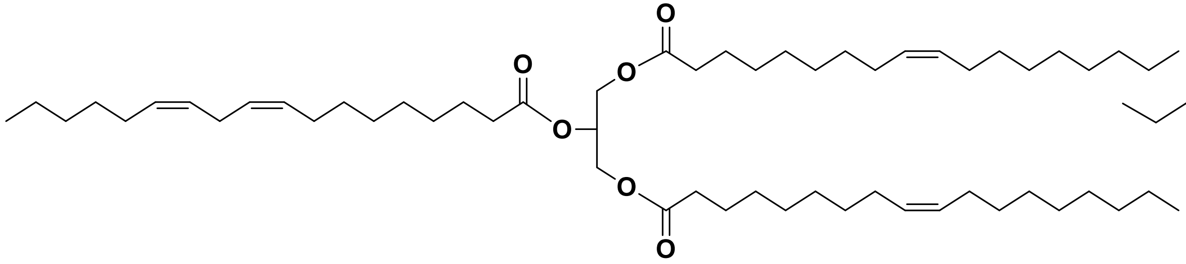
One-component type II photoinitiator



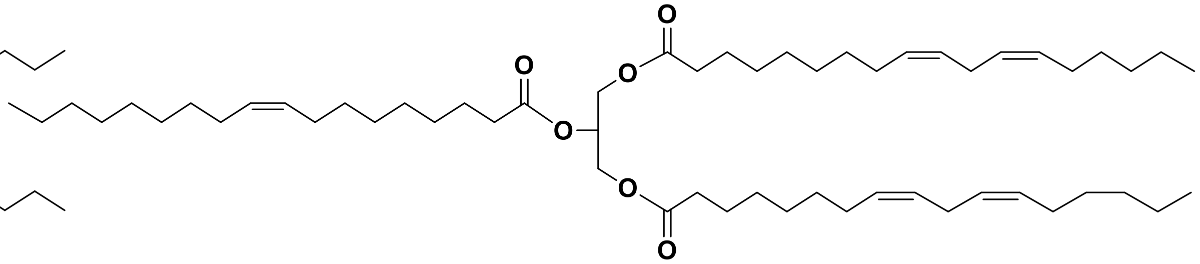
Oils from Renewable Sources



Castor Oil

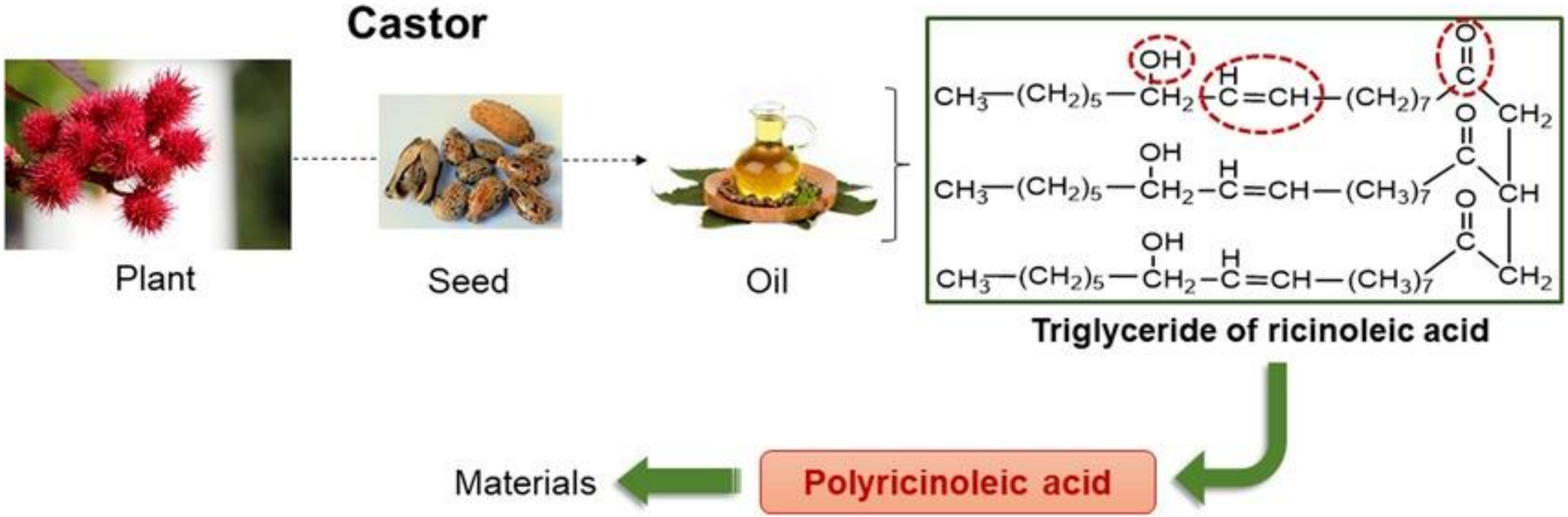


Soybean Oil



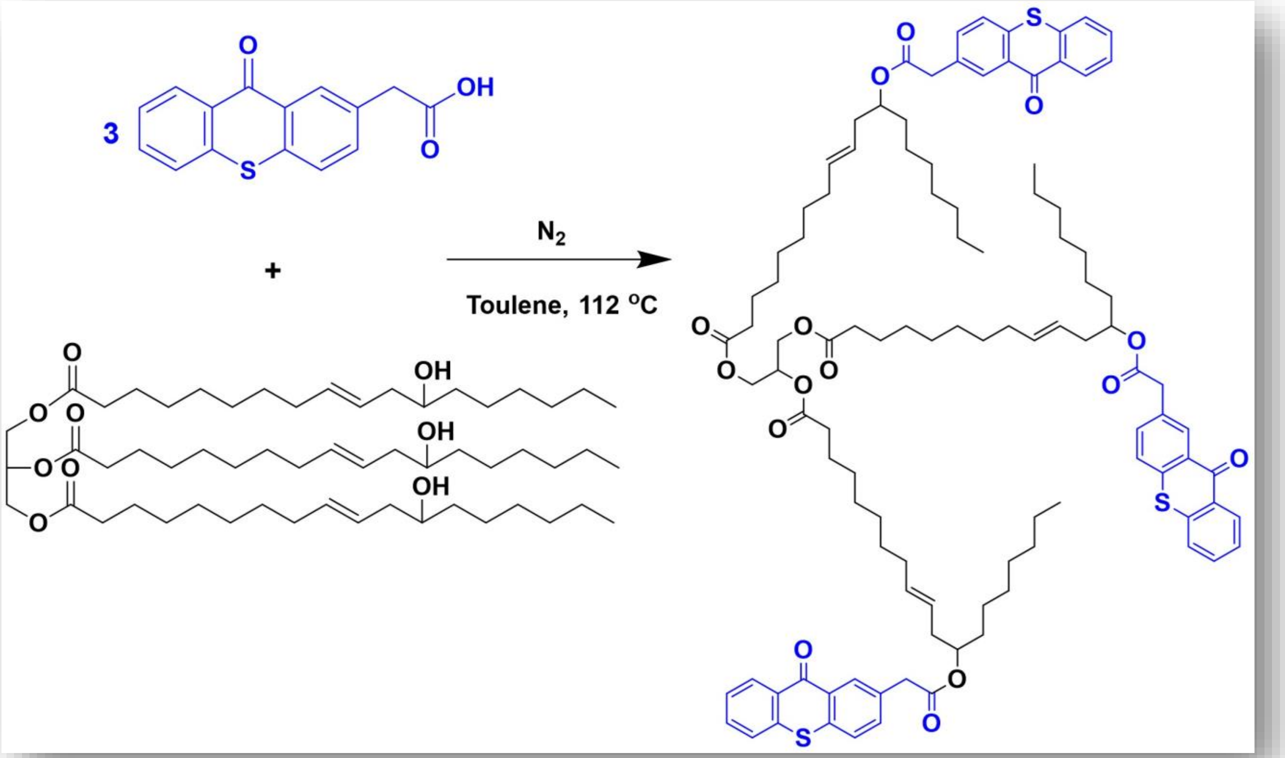
Canola Oil

Castor Oil


Castor
Plant
Seed
Oil
OH
H
O
CH3—(CH2)5—CH2—C=CH—(CH2)7
CH2
CH3—(CH2)5—CH2—C=CH—(CH3)7
CH
CH3—(CH2)5—CH2—C=CH—(CH3)7
CH2
Triglyceride of ricinoleic acid
Materials
Polyricinoleic acid

Results and Discussion

Esterification reaction of Castor Oil with $TXCH_2COOH$ (PICO I)



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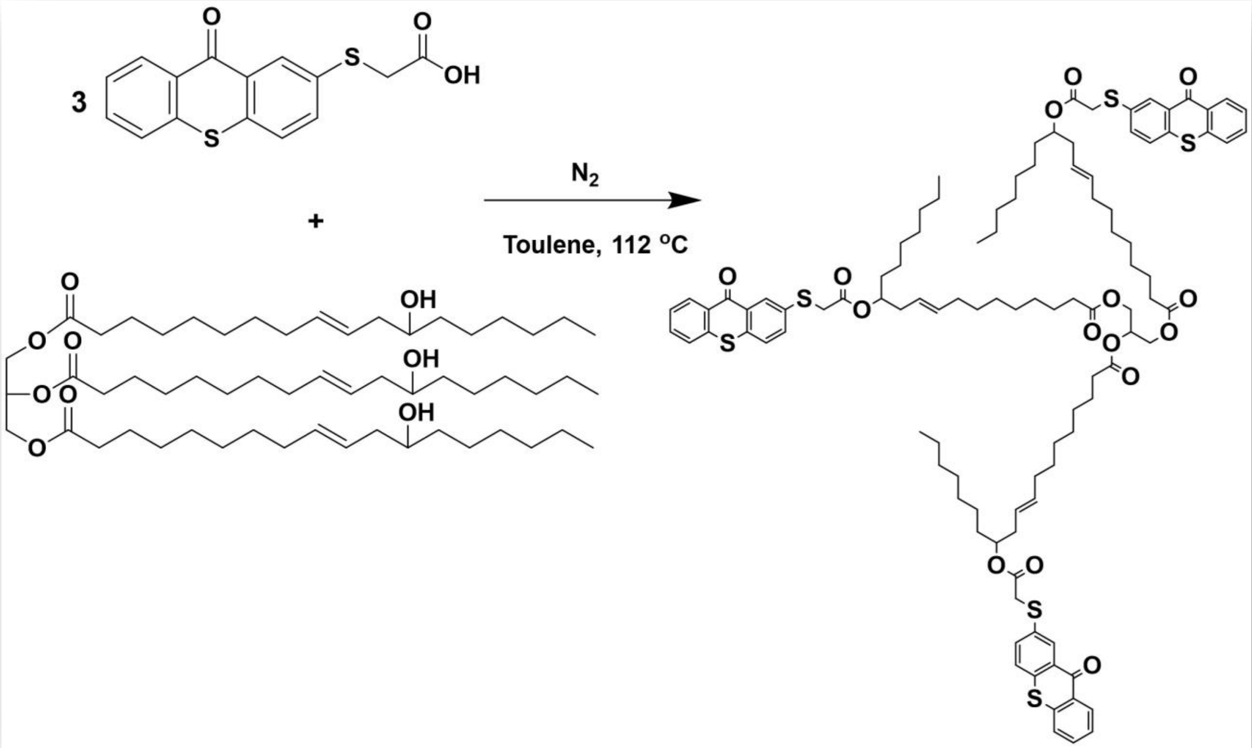
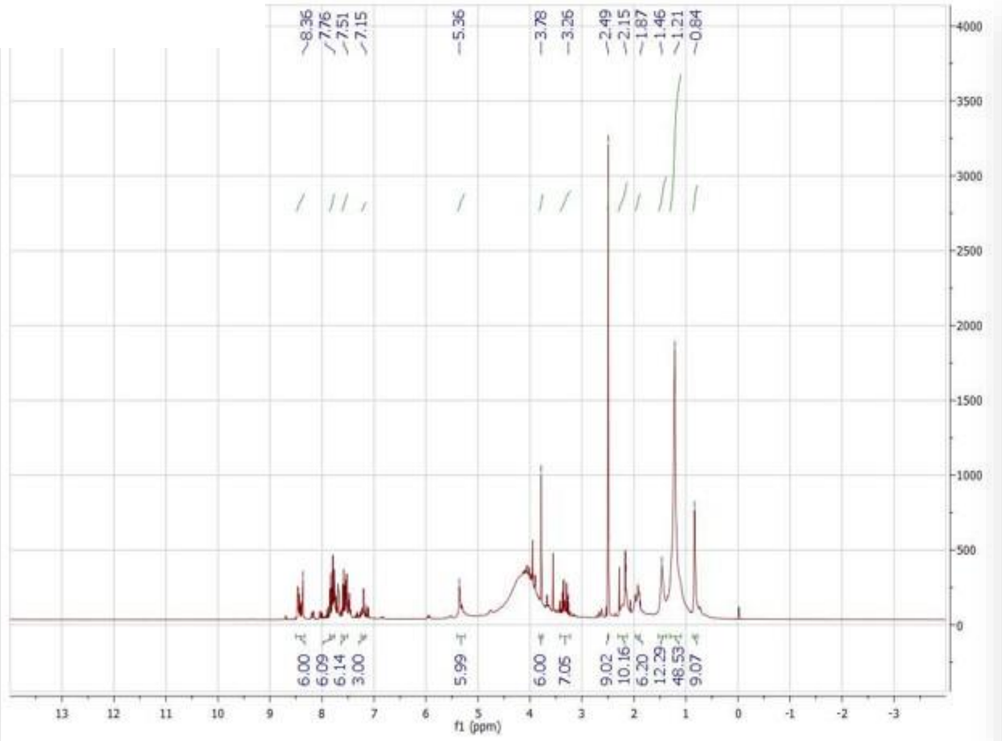
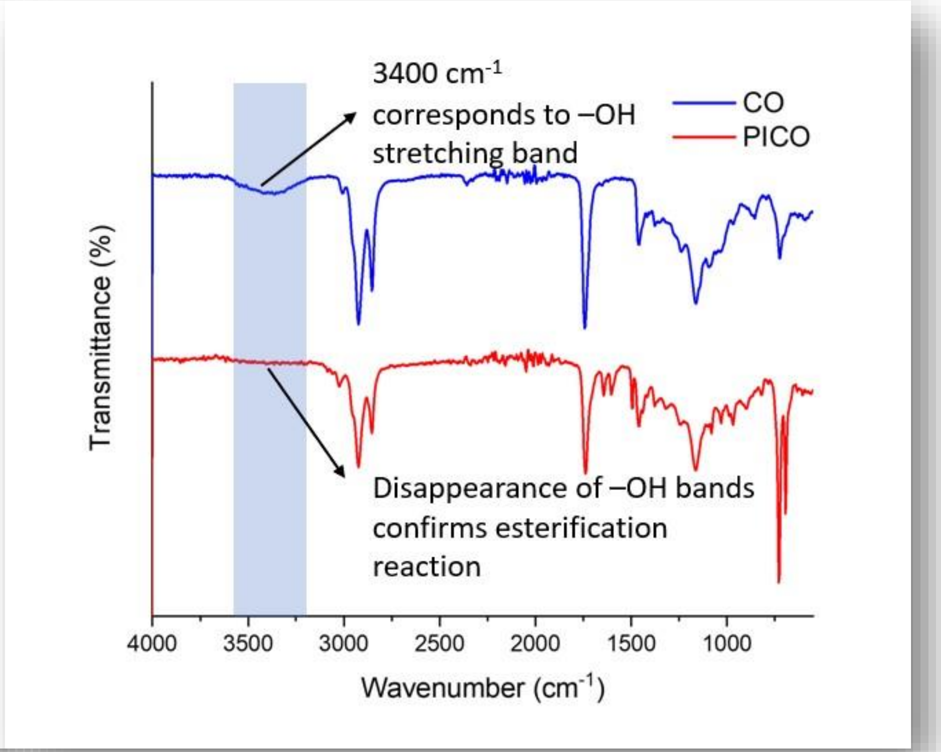
Esterification reaction of Castor Oil with $TXSCH_2COOH$ (PICO II)



Characterization by NMR and FTIR

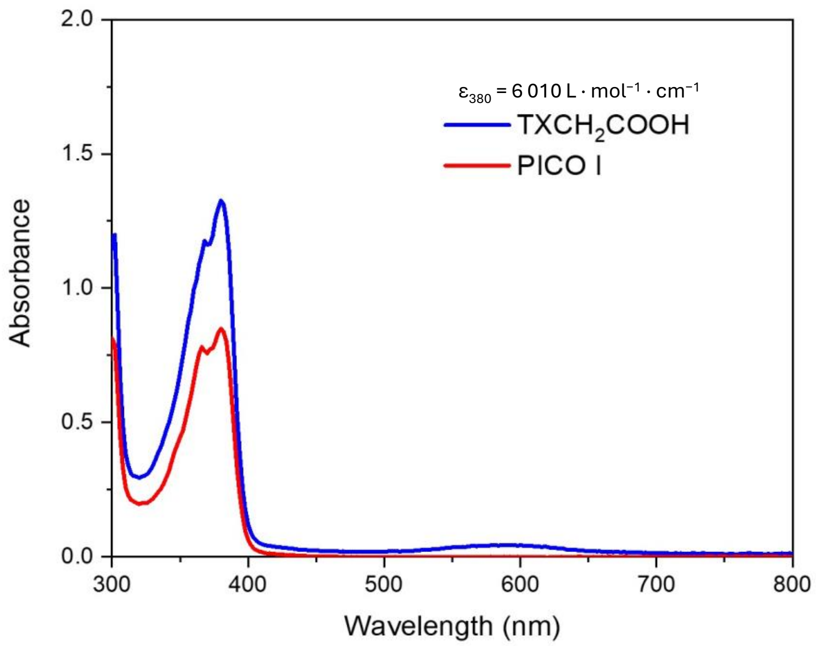




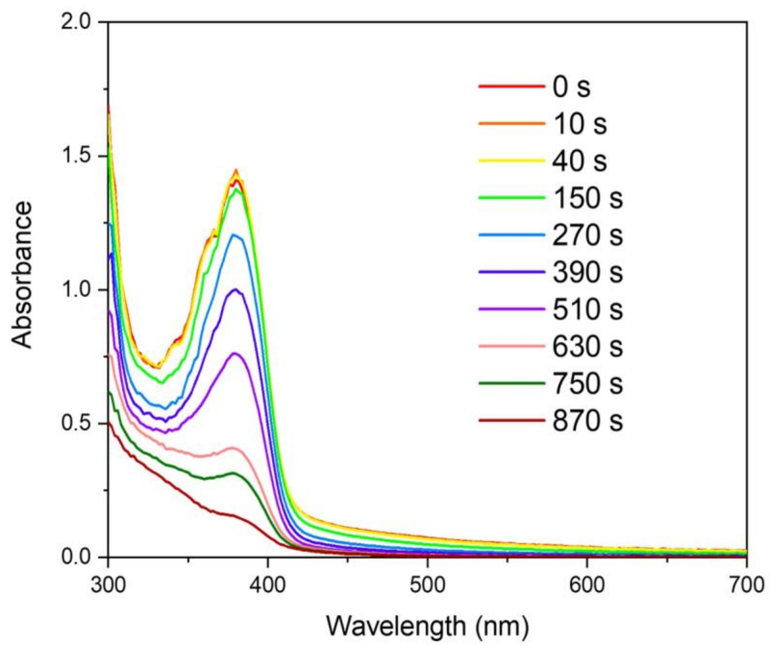
^{1}H NMR (DMSO-d_6): δ (ppm) = 0.83(t, J=6.8H_2, 9H(CH_3)$_3$), 1.21(m, 48H, CH_2), 1.46(br s, 12H, CH_2), 1.87-1.99 (m, 6H, CH_2), 2.15-2.20 (m, 7H, CH and CH_2), 2.49 (dt, J=1.8; 3.6H_2, 9H, CH and CH_2), 3.26-3.41 (m, 7H, CH and CH_2), 3.78 (s, 6H, (CH_2)$_3$), 5.36 (s, 6H, (CH_2)$_3$), 7.15-7.24 (m, 3H, aryl-H), 7.51-7.62 (m, 6H, aryl-H), 7.76-7.84 (m, 6H, aryl-H), 8.36-8.47 (m, 6H, aryl-H)

UV-Vis Studies

UV-Vis studies for PICO I

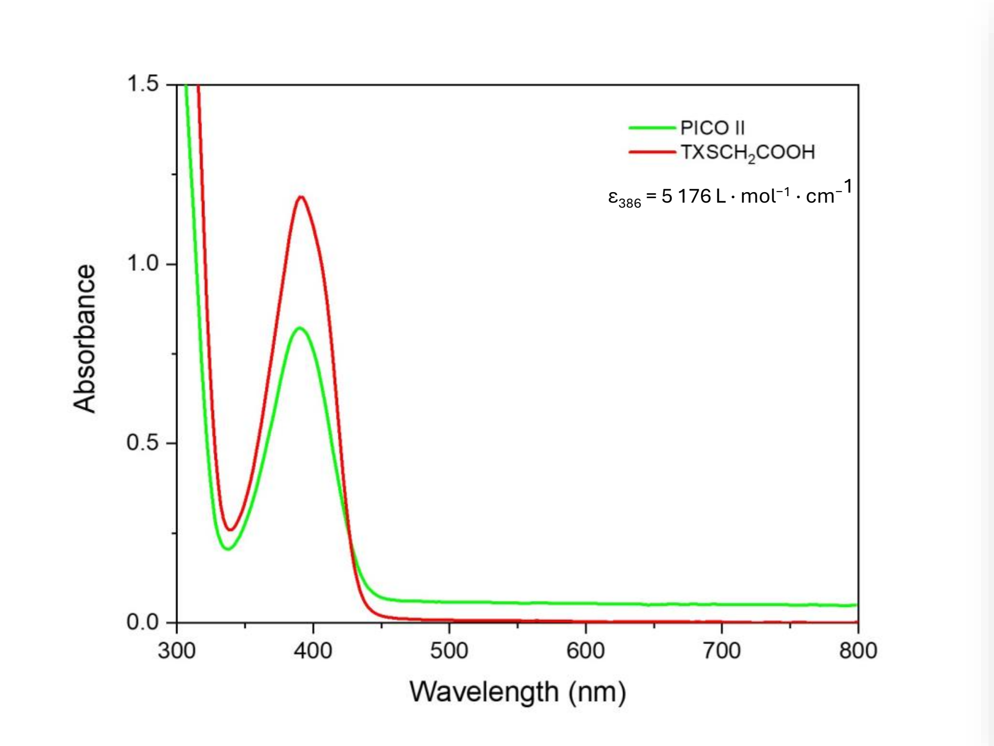


Photolysis in EtOH

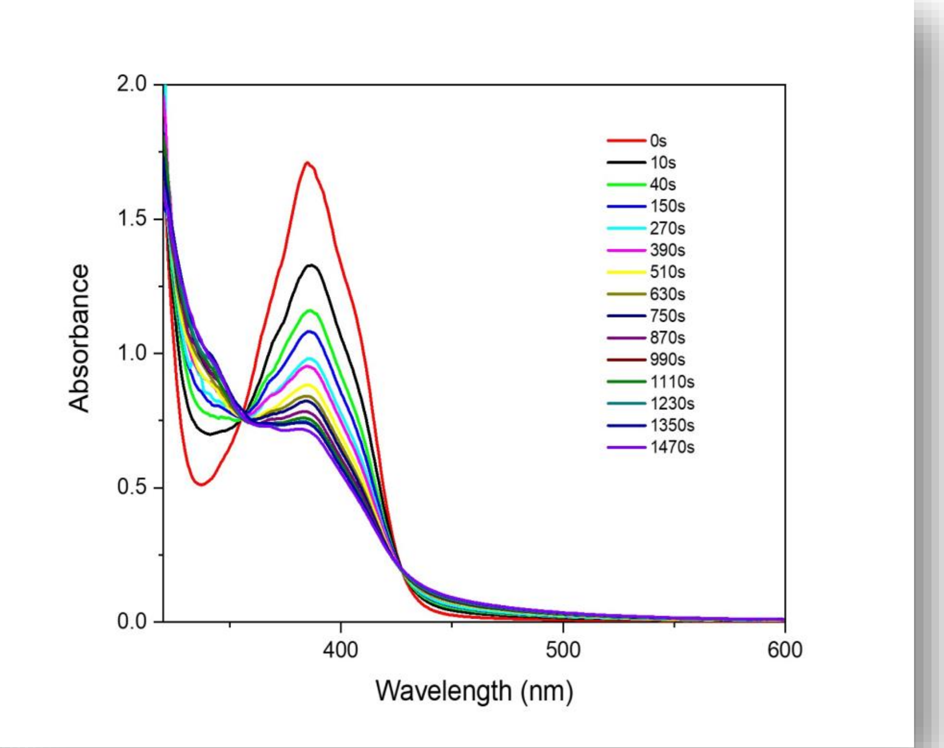


UV-Vis Studies

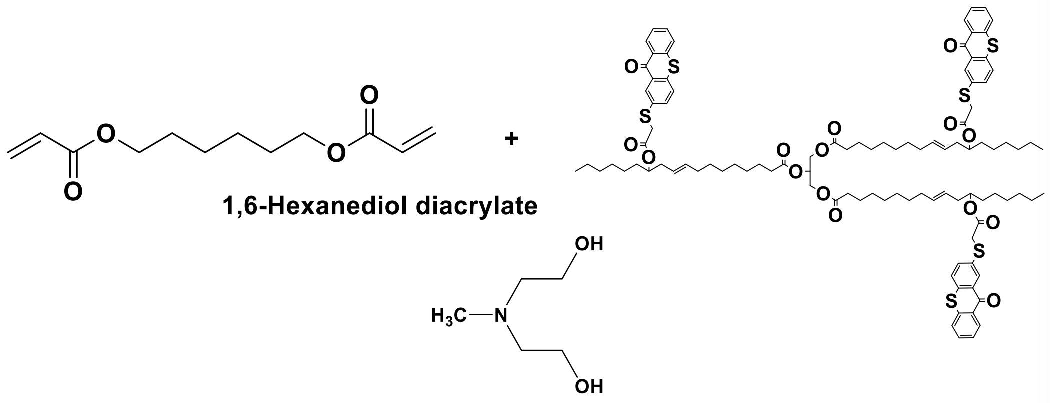
UV-Vis Studies for PICO II

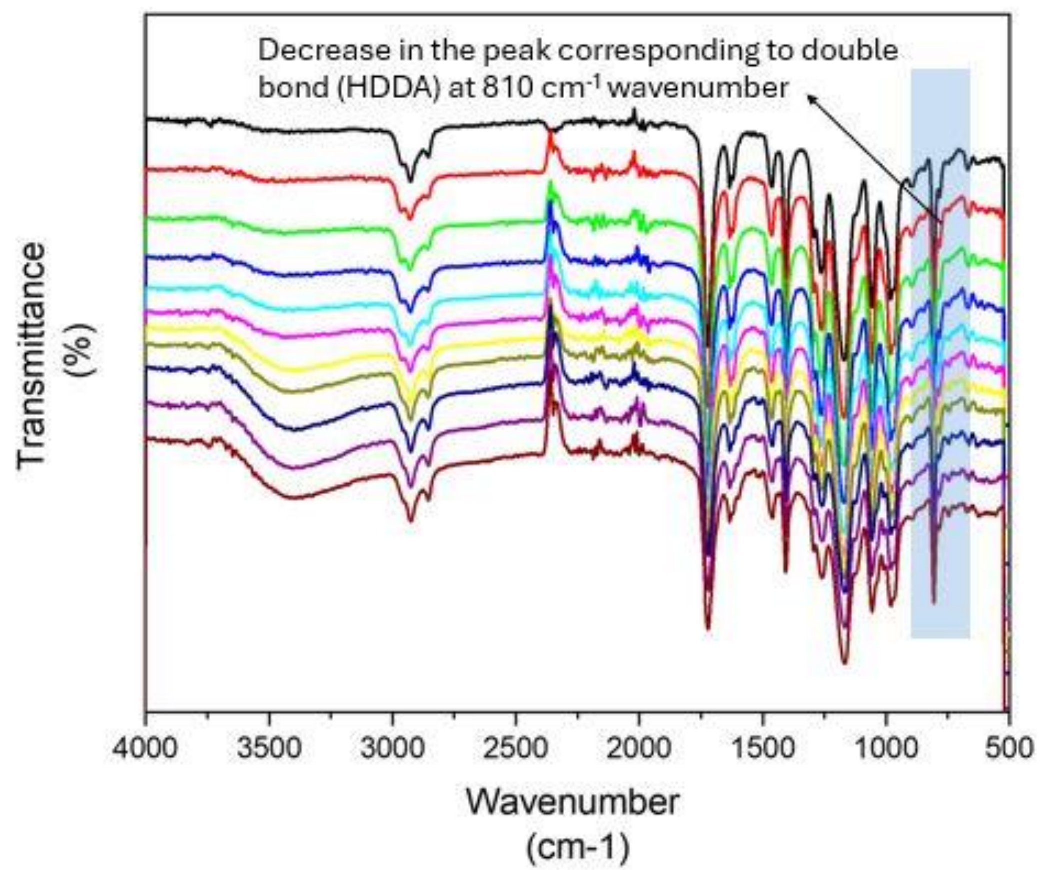


Photolysis in DCM



Real-time FTIR studies(RT-FTIR)

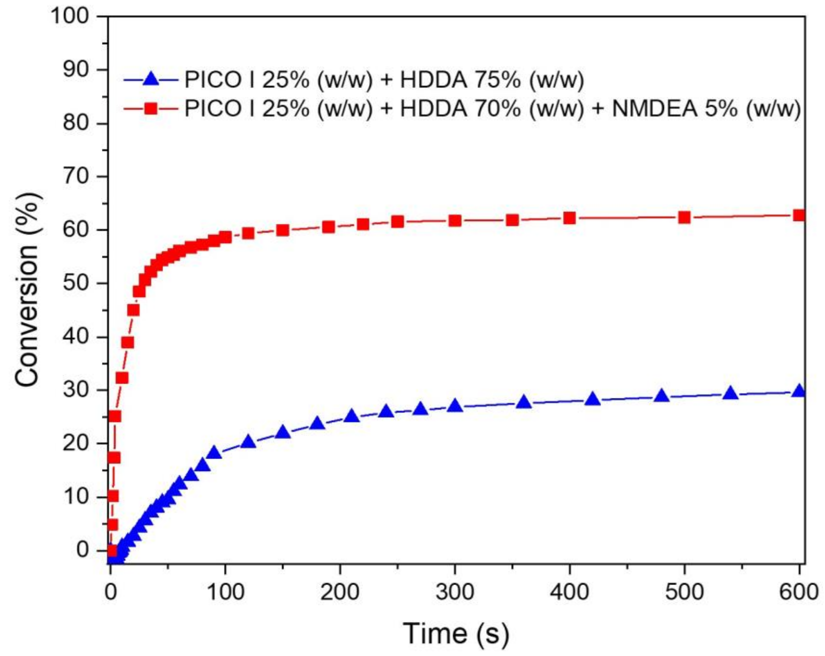


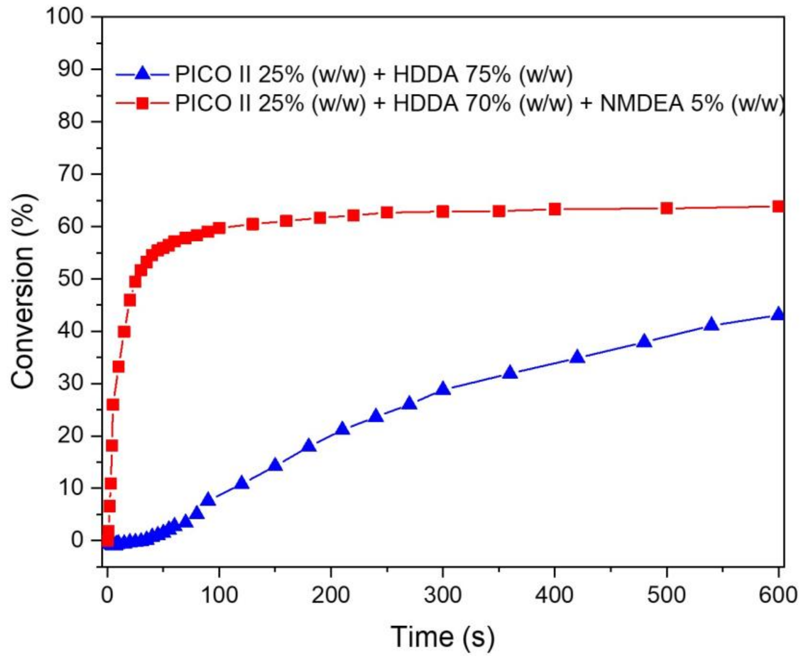


HDDA 70% (w/w) + PICO2 25% (w/w) + NMDEA 5% (w/w)
Conversion degree formula is reported below:

$$Conversion\% = \frac{A_0 - A_t}{A_0} \times 100$$

Real-time FTIR studies (RT-FTIR)





Photoinitiated polymerization of methyl methacrylate (MMA) by PICO I in DCM

Run	CO	MMA	[PICO I] 10mg/10ml	$TXCH_2COOH$	NMDEA	DCM	AIR	N_2	Conversion %
1	-	+	+	-	-	-	+	-	2.12
2	-	+	+	-	-	-	-	+	4.44
3	-	+	+	-	+	+	+	-	3.11
4	-	+	+	-	+	+	-	+	4.54
5	-	+	-	-	-	+	-	-	-
6	+	+	-	+	-	+	+	-	2.99
7	+	+	-	+	-	+	-	+	2.31
8	+	+	-	+	+	-	+	-	1.54
9	+	+	-	+	+	-	-	+	1.50
10	+	+	-	-	-	+	-	-	-

$[MMA] = 4.68\ mol \cdot L^{-1}$

$[CO] = 1x10^{-3}$ M

$[TXCH_2COOH] = 1x10^{-3}$ M

$[NMDEA] = 1x10^{-2}$M

Irradiation time = 60 minutes

Photoinitiated polymerization of methyl methacrylate (MMA) by PICO II in DCM

Run	CO	MMA	[PICO II] 10mg/10ml	$TXSCH_2COOH$	NMDEA	DCM	AIR	N_2	Conversion %
1	-	+	+	-	-	-	+	-	2.16
2	-	+	+	-	-	-	-	+	2.80
3	-	+	+	-	+	+	+	-	3.18
4	-	+	+	-	+	+	-	+	2.00
5	-	+	-	-	-	+	-	-	-
6	+	+	-	+	-	+	+	-	3.15
7	+	+	-	+	-	+	-	+	2.24
8	+	+	-	+	+	-	+	-	3.20
9	+	+	-	+	+	-	-	+	3.22
10	+	+	-	-	-	+	-	-	-

$[MMA] = 4.68\ mol \cdot L^{-1}$

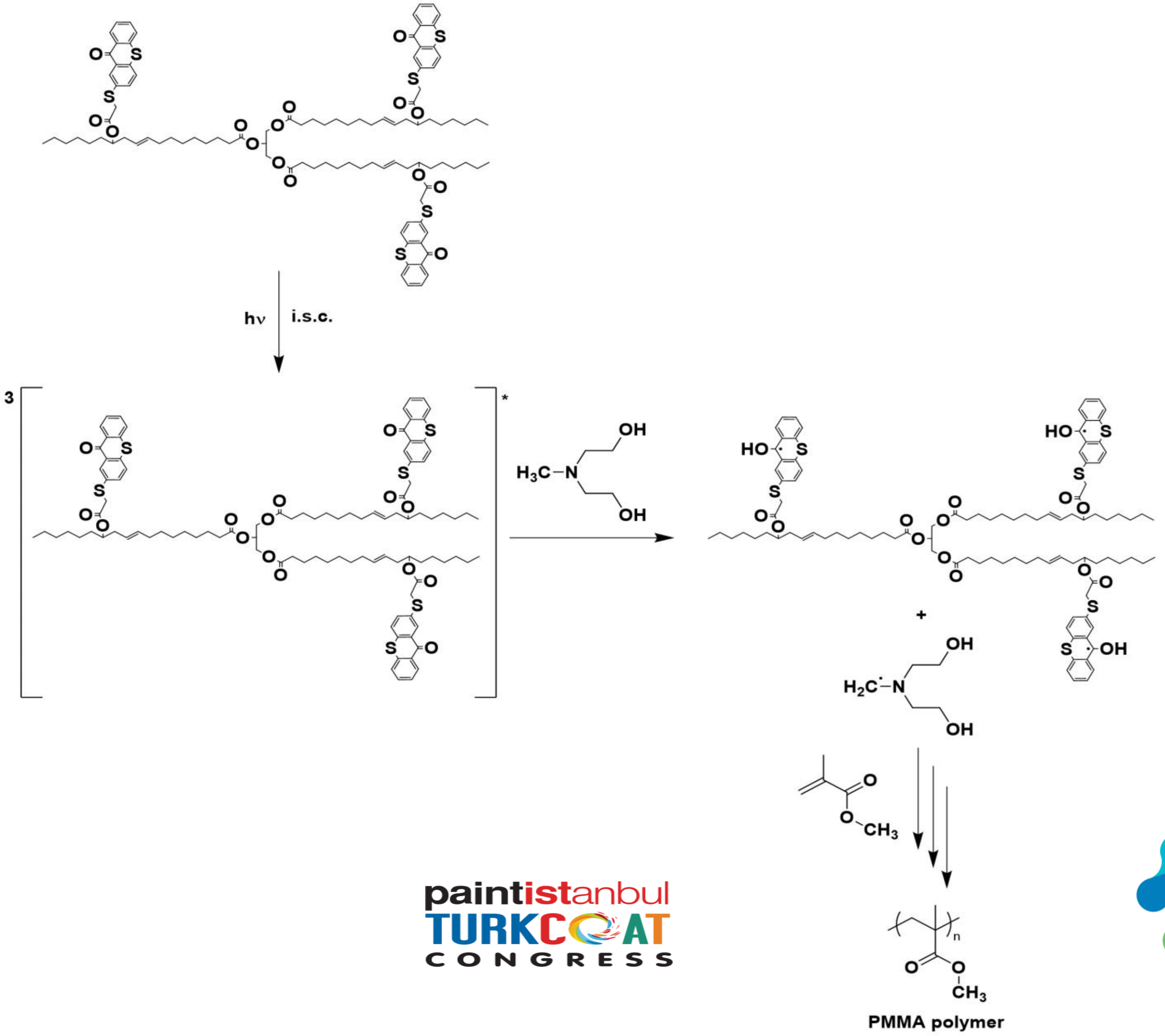
$[CO] = 1x10^{-3}$ M

$[TXSCH_2COOH] = 1x10^{-3}$ M

$[NMDEA] = 1x10^{-2}$ M

Irradiation time = 60 minutes

Possible Initiation Mechanism of Thioxanthonated Castor Oil



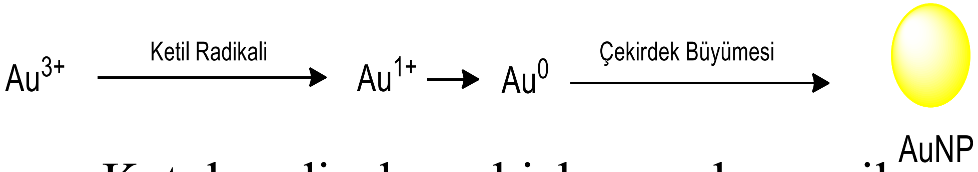
UV-Curing Applications

PICO I (25% w/w) + HDDA (75% w/w) formulation in absence (above) and in presence of NMDEA 5% w/w (below)

UV-Curing Applications

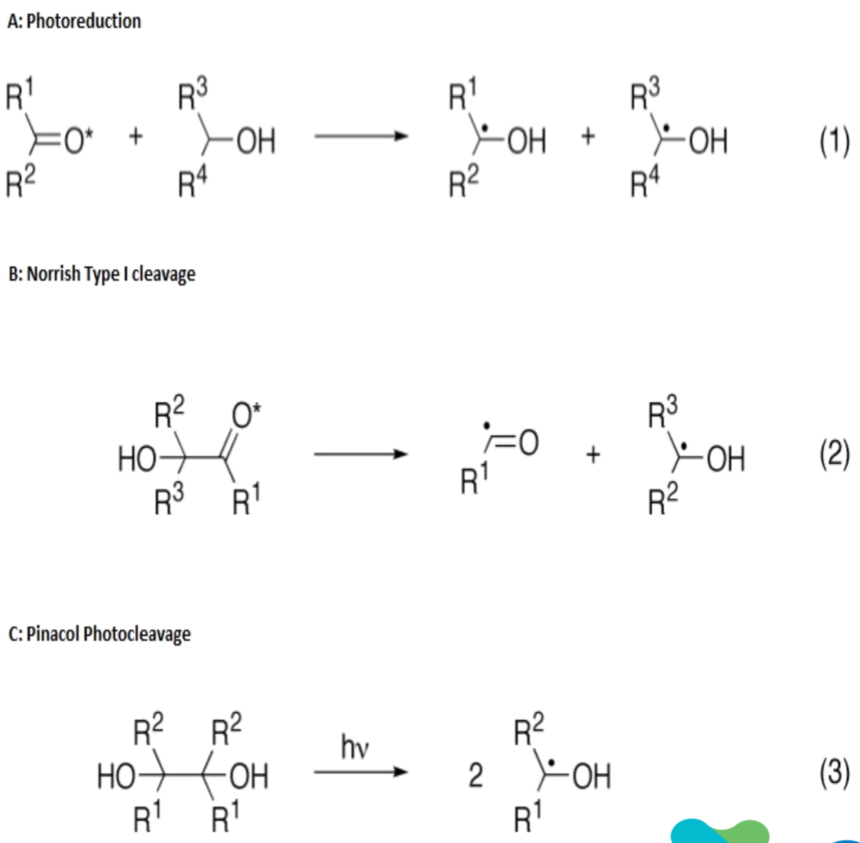
PICO II (25% w/w) + HDDA (75% w/w) formulation in absence (above) and in presence of NMDEA 5% w/w (below)

Photoinduced reduction of Metallic salts



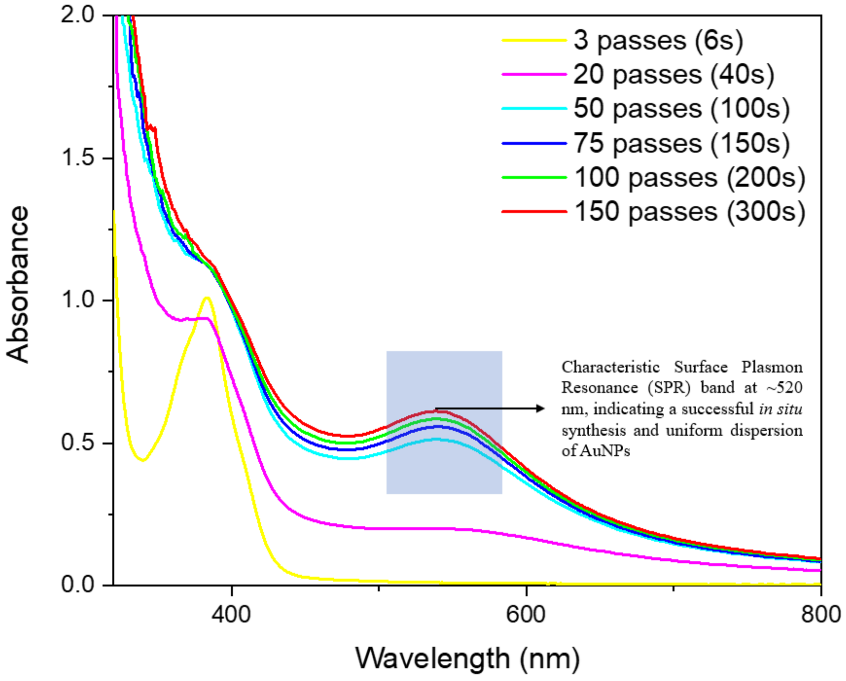
Ketyl radicals, which can be easily produced photochemically, are generally used to reduce metal salts.

Although ketyl radical is obtained effectively by Pinocol cleavage, they are not preferred because they are in competition for absorption with metal-containing substances (Low λ).



In-situ Photochemical Synthesis of Nanocomposites Containing AuNPs

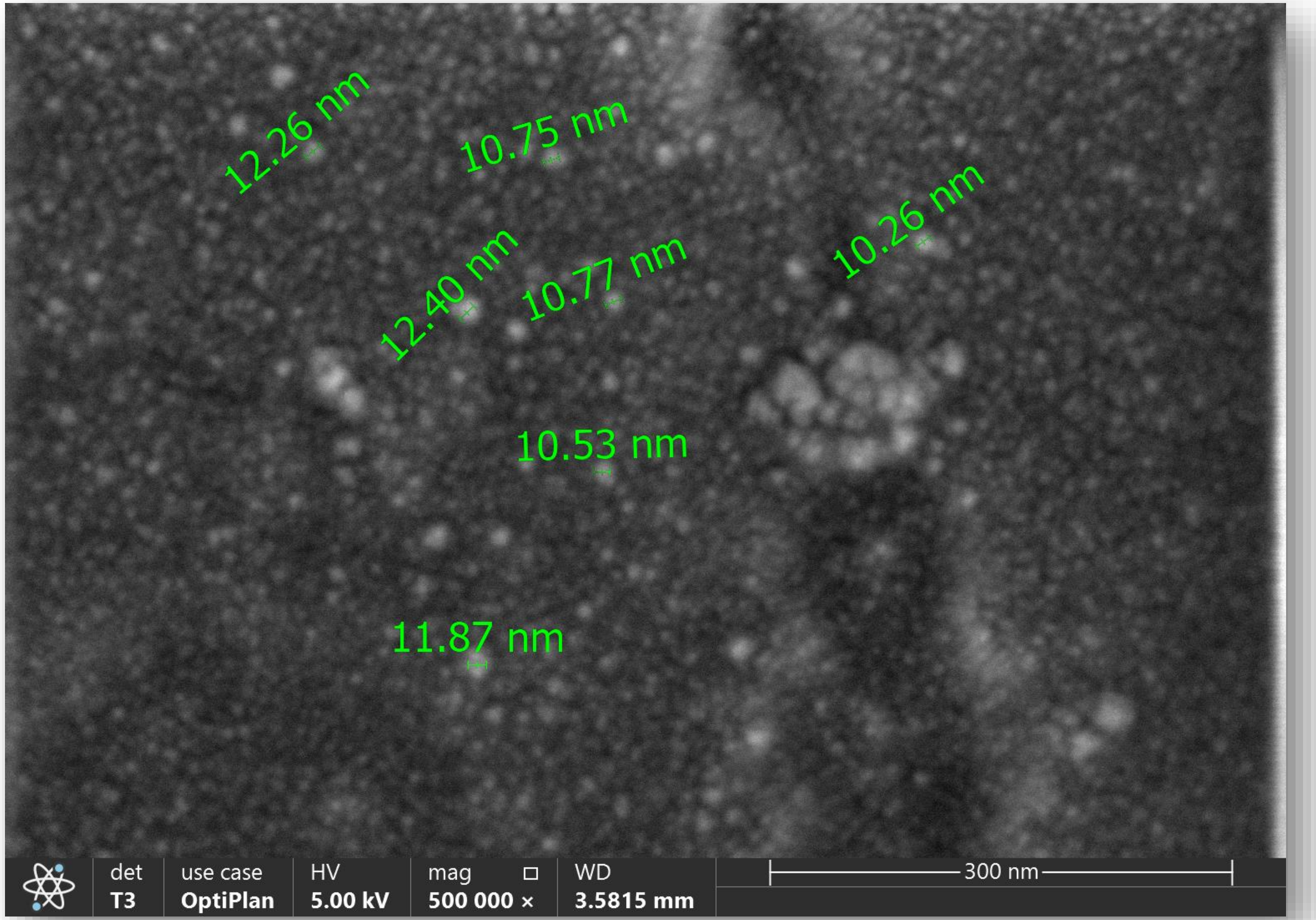
PICO II 50% (w/w) + NMDEA 5% (w/w) + HDDA 41% (w/w) + $HAuCl_4$ 4% (w/w)

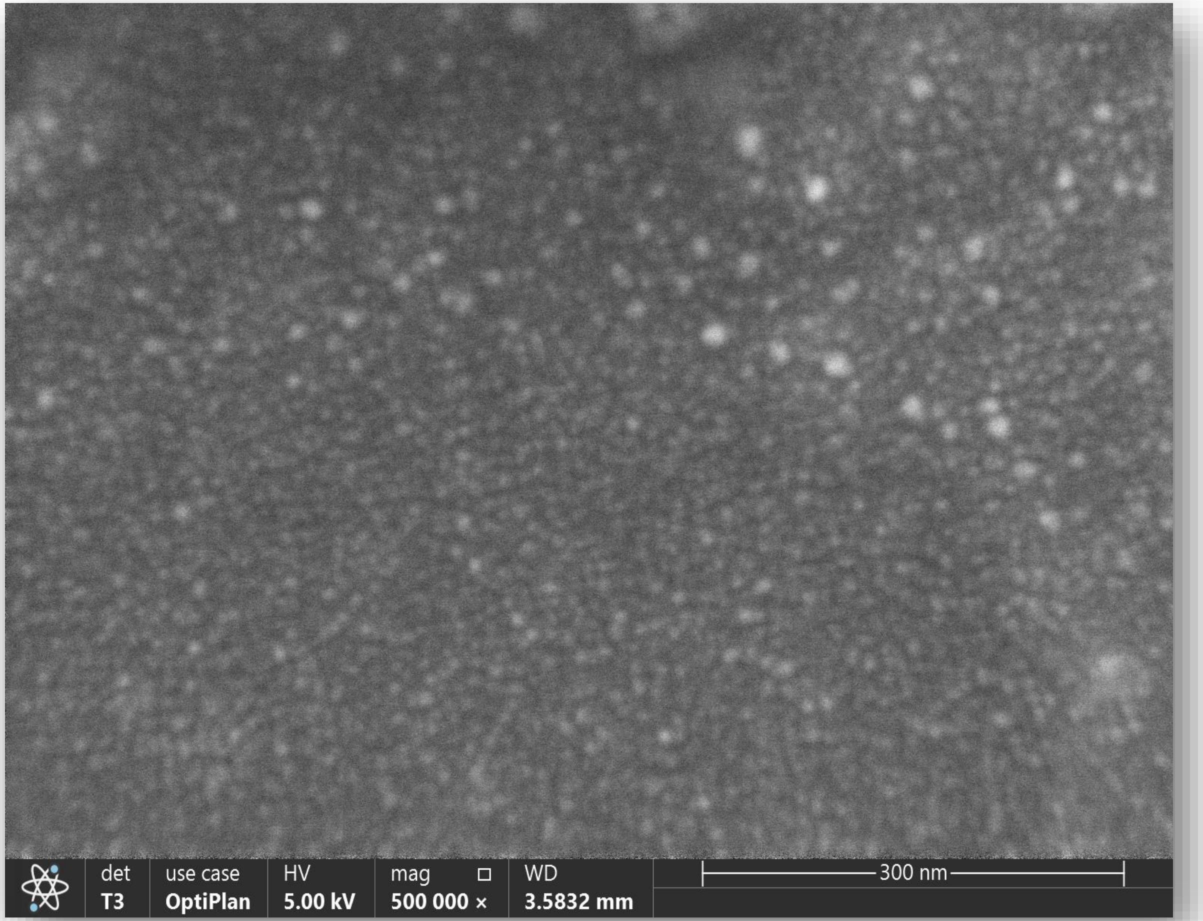


A biobased gold nanocomposite coating

PICO II (25% w/w) + HDDA (70% w/w) + NMDEA (5% w/w) (left)
PICO II 50% (w/w) + NMDEA 5% (w/w) + HDDA 41% (w/w) + $HAuCl_4$ 4% (w/w) (right)

SEM images of biobased nanocomposites





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Conclusion

- ✓ In this work, novel macrophotoinitiators were successfully synthesized by attaching thioxanthone (TX) moieties to a castor oil-derived backbone

- ✓ Combination of the macrophotoinitiator, HDDA, and NMDEA (N-methyldiethanolamine) led to the formation of highly transparent polymer films on glass slides, highlighting the effectiveness of the system in producing uniform and defect-free coatings.

- ✓ Incorporation of gold salt ($HAuCl_4$) into the formulation enabled the *in-situ* generation of gold nanoparticles during the photopolymerization process, resulting in gold nanocomposite materials

Acknowledgement

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