Advances in UV induced polymerization

Sara Dalle Vacche

Science and Technology of UV-induced polymerization (2022)

1. Photoresponsive/photoreversible polymers and networks

Reversible networks

Degradability

Recycling

Reshaping

Repairing

Processing

Property tuning

Stimuli responsiveness

Applications

- Photo-degradable linear and crosslinked polymers
- Self-healing polymers
- Photoresists through spatially controlled solubility changes
- Photo-responsive polymers and hydrogels, e.g. for drug delivery or tissue engineering
- Shape-memory polymers

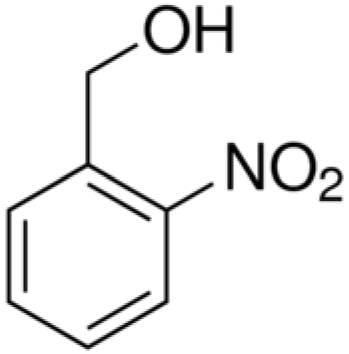
Mechanisms

- Photocleavage
- Photoreversible covalent chemistry
- Photoinduced conformational changes

Photocleavage

Photocleavage

- Photolabile compounds can be introduced in the main chain of a macromolecule; they can then be cleaved on demand by irradiation, resulting in photodegradable materials.
- The photocleavage is not reversible, and usually happens at sites different than crosslinks.
- The most used photocleavable group is *o*-nitrobenzyl



o-nitrobenzyl alcohol

Macromolecular
Rapid Communications

Macromolecular Journals

Communication

Macromol. Rapid Commun.2013, 34, 1446

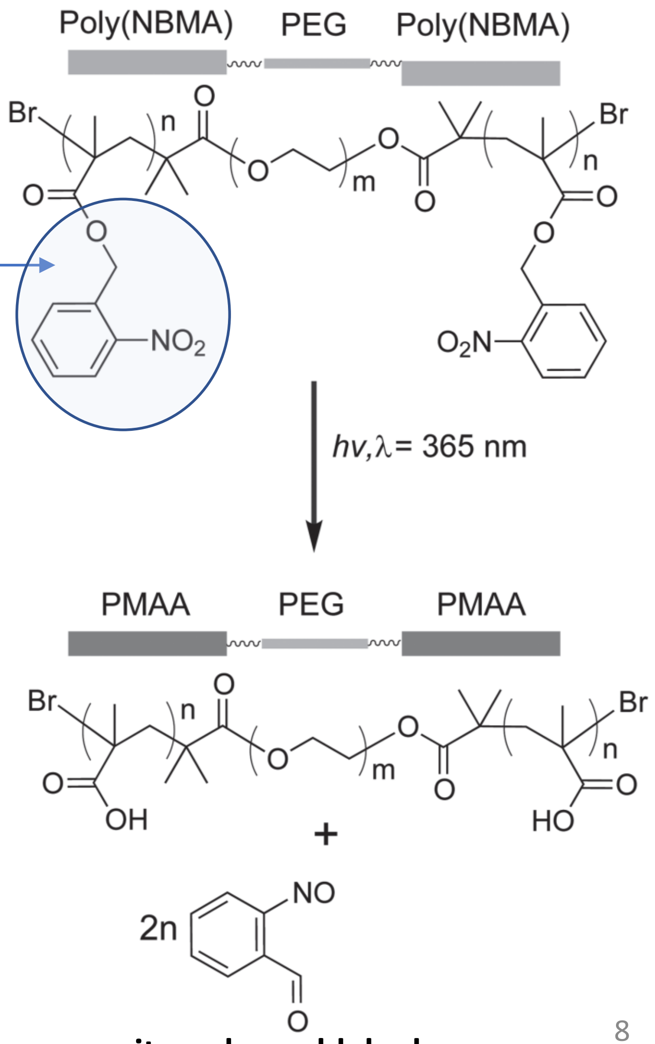
Light-Induced Disintegration of Robust Physically Cross-Linked Polymer Networks

Congcong Zhu, Christopher J. Bettinger*

Poly(*o* -NitroBenzyl MethAcrylate)- *b* -PEG- *b* -poly(NBMA) triblock polymers form physically cross-linked networks in hydrated environments by self-assembly

Light-induced photolysis of poly(NBMA) segments yields water-soluble poly(methacrylic acid)- *b* -PEG- *b* -poly(methacrylic acid) copolymer

o-nitrobenzyl group



***o* -nitrosobenzaldehyde**

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Journals

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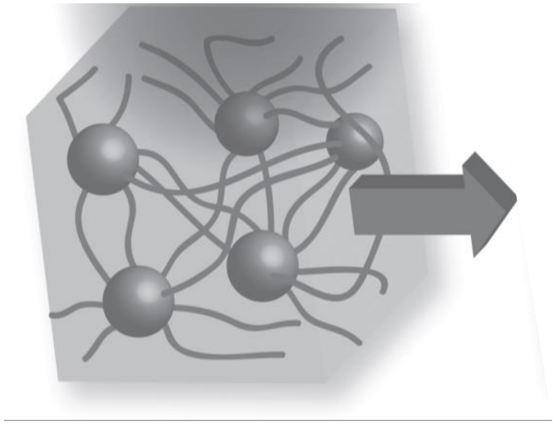
Macromol. Rapid Commun.2013, 34, 1446

Light-Induced Disintegration of Robust Physically Cross-Linked Polymer Networks

Congcong Zhu, Christopher J. Bettinger*

■ Photolabile physical crosslinks
■ Uncaged poly(methacrylic acid)
■ Poly(ethylene glycol) segments



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Light-Induced Disintegration of Robust Physically Cross-Linked Polymer Networks

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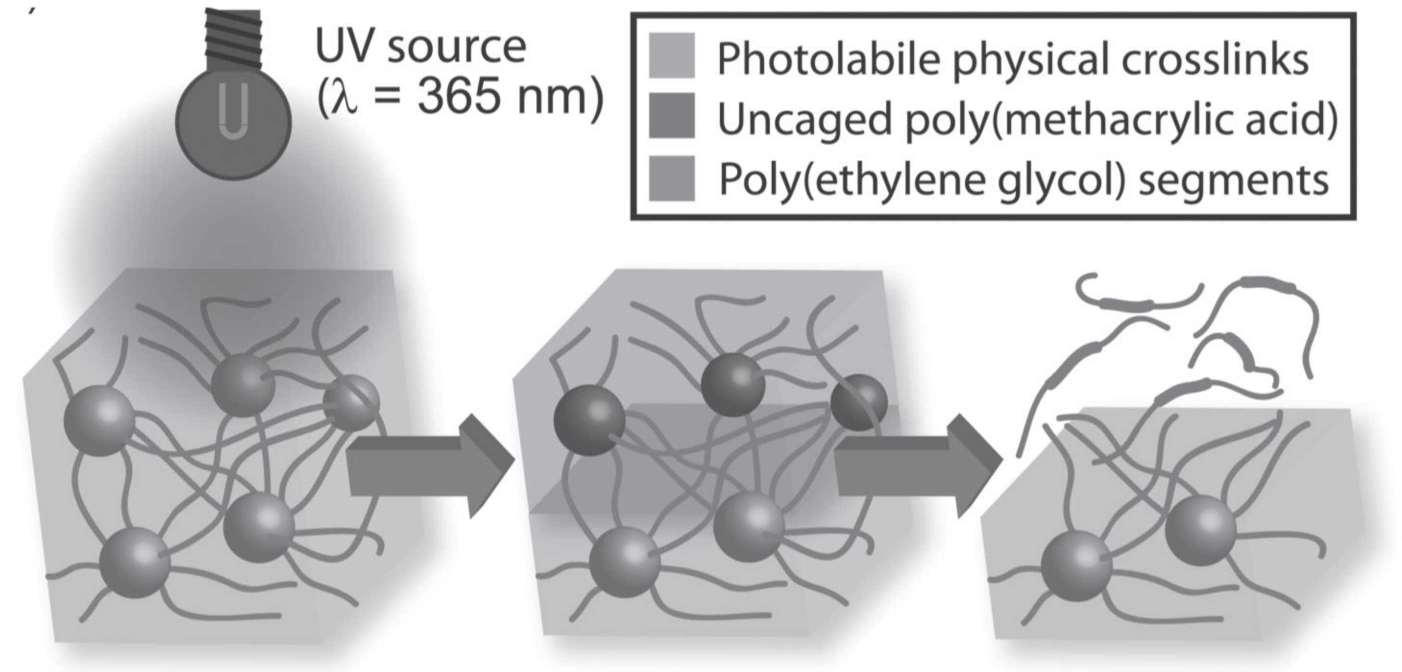
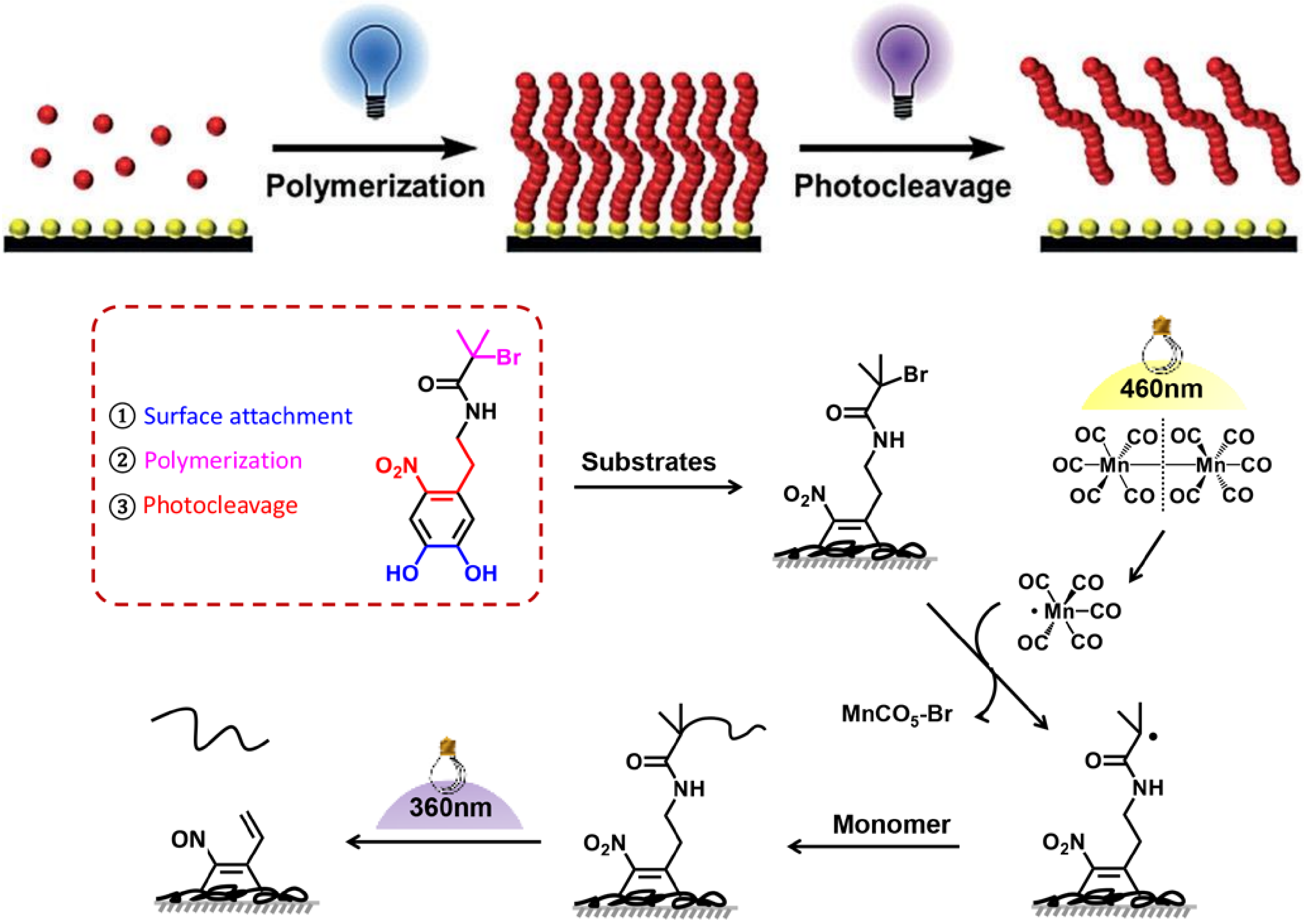


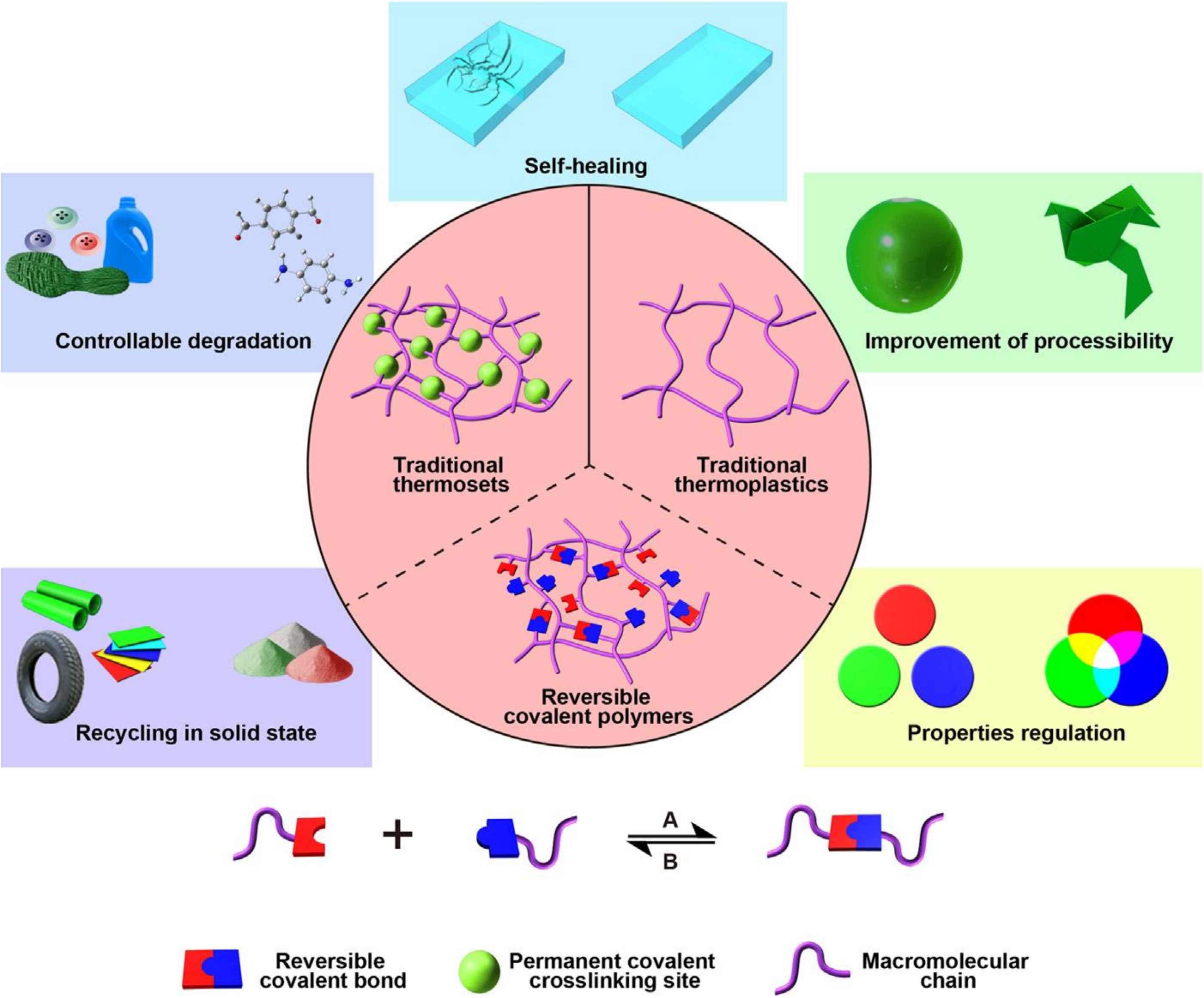
Grafting-from and subsequent photocleavage using multiple wavelengths



X. Xiong, L. Xue, J. Cui, ACS Macro Lett. 2018, 7, 239–243.

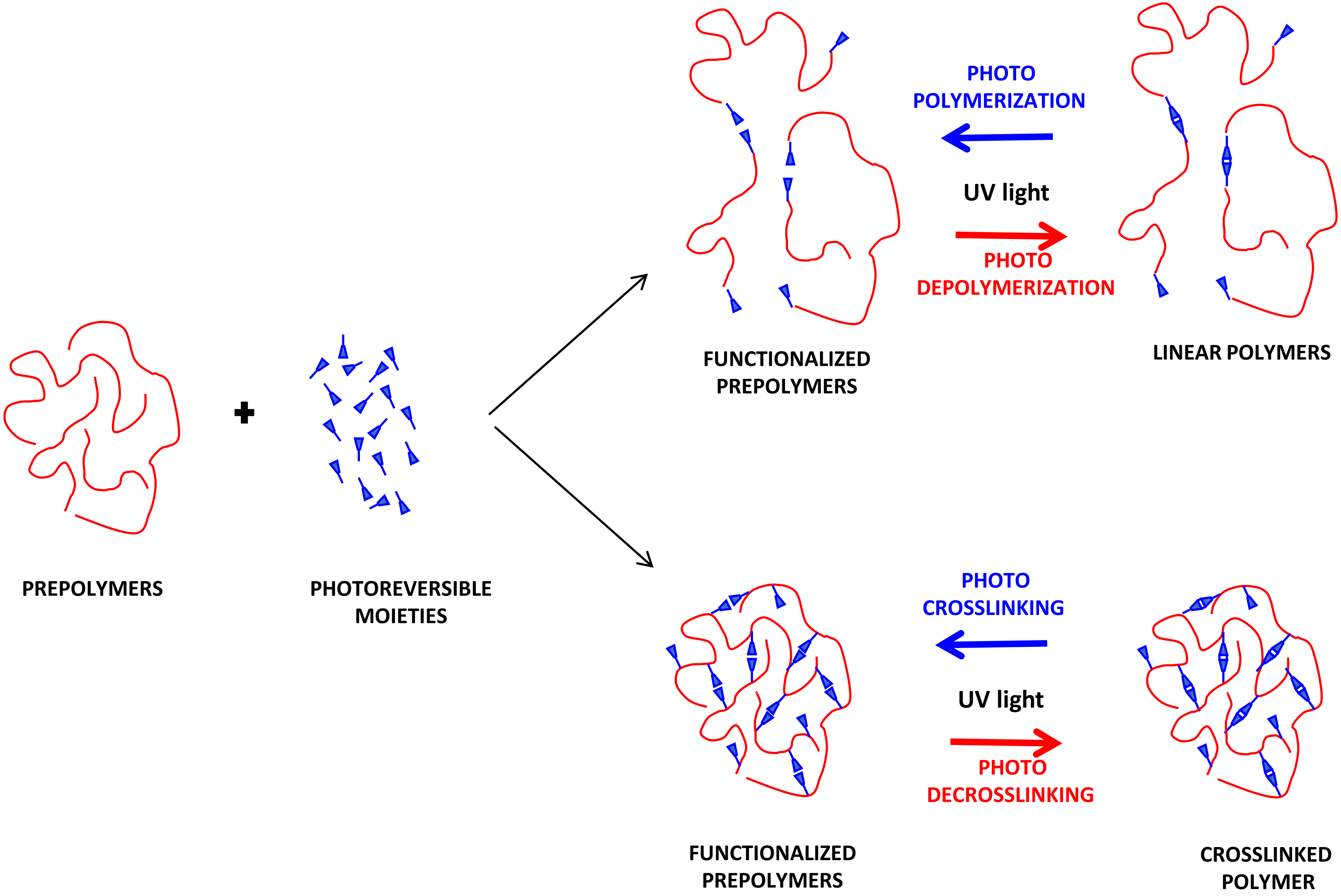
Photo-reversible covalent chemistry

Polymer engineering enabled by reversible covalent chemistry



Z.P. Zhang et al. / Progress in Polymer Science 80 (2018) 39–93

Photo-reversible polymers and networks



PREPOLYMERS

PHOTOREVERSIBLE MOIETIES

FUNCTIONALIZED PREPOLYMERS

PHOTO POLYMERIZATION

UV light

PHOTO DEPOLYMERIZATION

LINEAR POLYMERS

FUNCTIONALIZED PREPOLYMERS

PHOTO CROSSLINKING

UV light

PHOTO DECROSSLINKING

CROSSLINKED POLYMER

Cycloaddition reactions

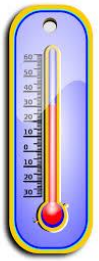
In cycloaddition reactions, two or more **unsaturated molecules** combine with the formation of a **cyclic adduct**. In order for the cycloaddition to be possible, an extended conjugation system is needed.

Cycloaddition can occur via thermal or photochemical activation. The number of electrons involved in the formation of the cyclic adduct is indicated in brackets.

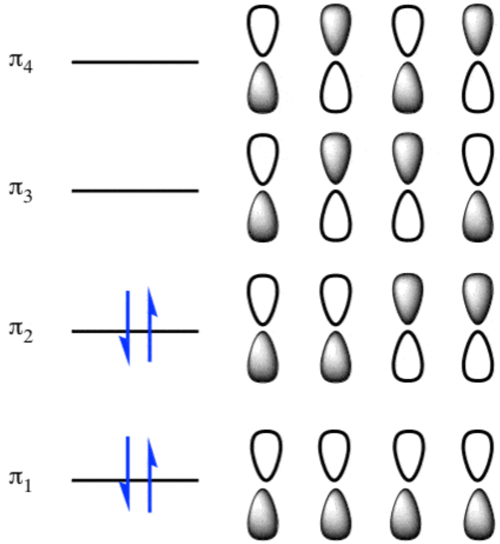
For **thermally** activated cycloadditions the reactants are in the ground electronic state, and usually [**4n + 2]** π electrons are involved.

When [**4n]** π electrons are involved, one electron can be excited from the HOMO (highest occupied molecular orbital, π bonding) to the LUMO (lowest unoccupied molecular orbital, π antibonding) by absorption of light and the cycloaddition is **photochemically** activated .

Thermally activated cycloaddition

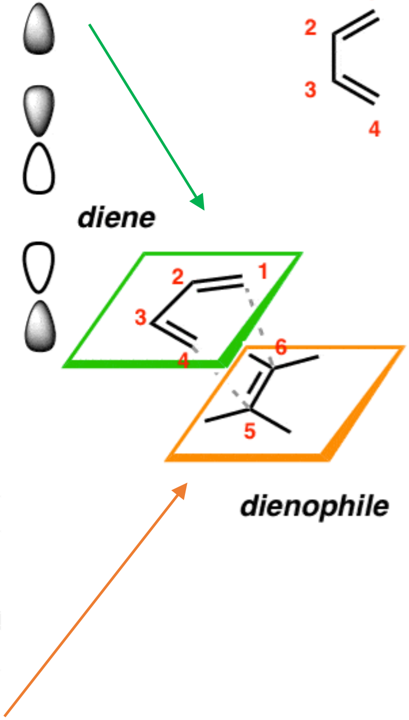


Here are the molecular orbitals of butadiene:

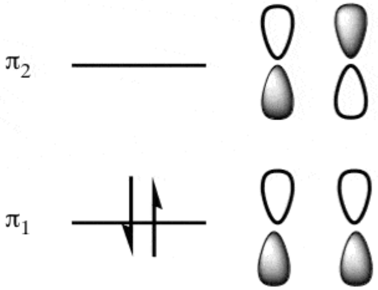


LUMO
lowest unoccupied molecular orbital

HOMO
highest occupied molecular orbital



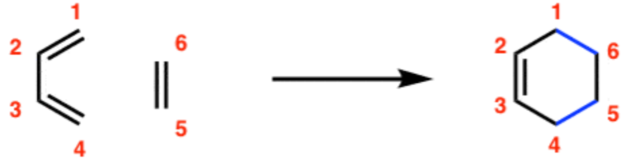
Here are the molecular orbitals of ethene:



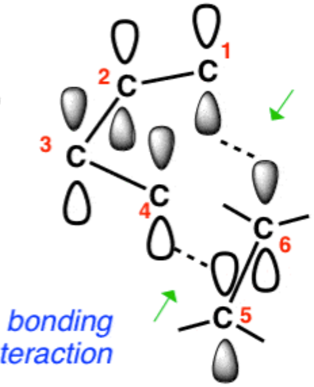
LUMO
lowest unoccupied molecular orbital

HOMO
highest occupied molecular orbital

Molecular Orbital Interactions In The Diels-Alder Reaction



HOMO of diene



bonding interaction

bonding interaction

LUMO of dienophile

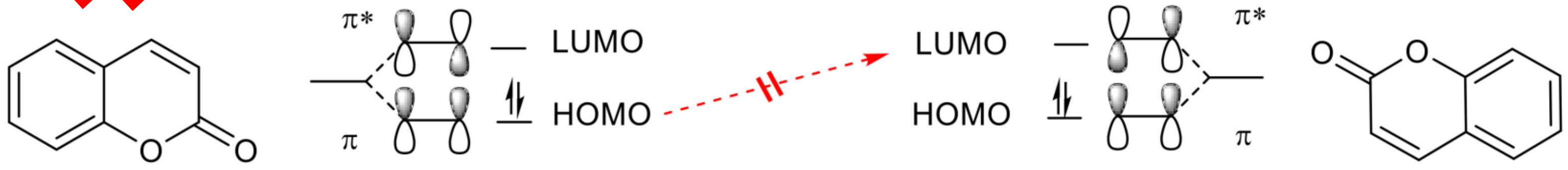
Both reactive sites have constructive orbital overlap between the lobes

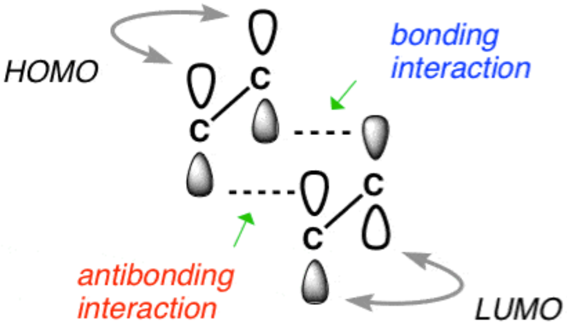
This helps to explain why the Diels-Alder reaction is favorable

https://www.masterorganicchemistry.com/2018/03/23/molecular-orbitals-in-the-diels-alder-reaction/

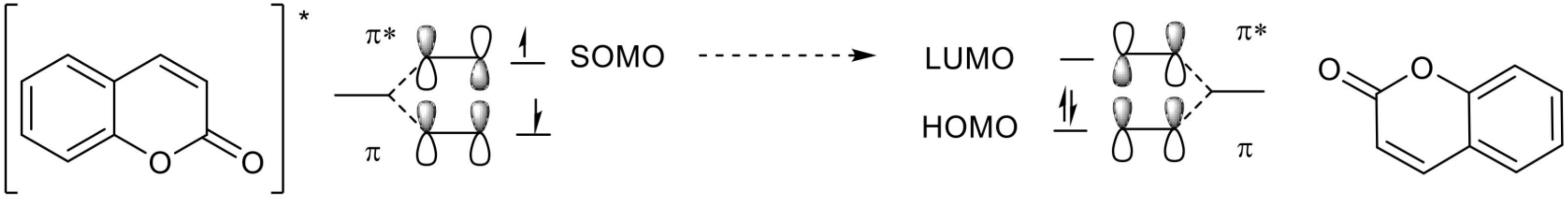
Photochemically activated cycloaddition

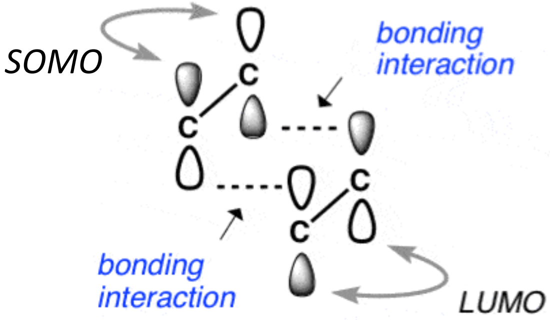
Therm reaction





Photochemical reaction

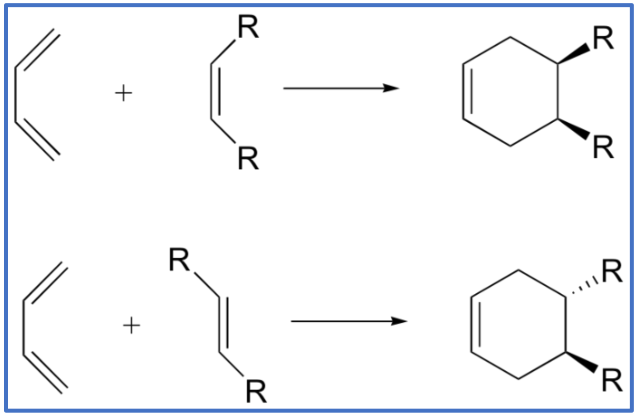




HOMO: Highest Occupied Molecular Orbital
LUMO: Lowest Unoccupied Molecular Orbital
SOMO: (Highest) Semioccupied Molecular Orbital

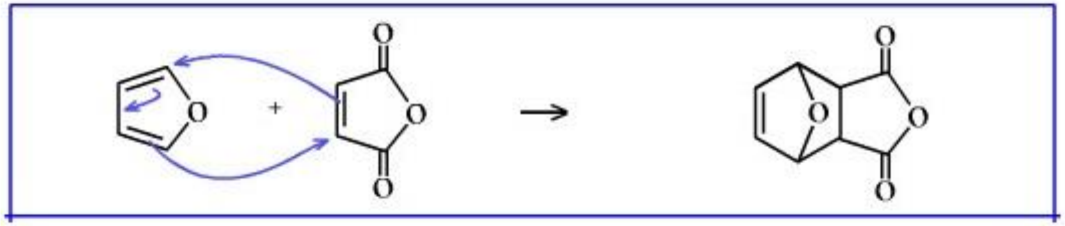
Common cycloadditions: [4+2]

The Diels-Alder (DA) reaction, a **[4+2] cyclization**, is the most common cycloaddition reaction: the two reactants, a conjugated diene and a substituted diene, are referred to as **diene** and **dienophile.** It is **thermally activated** , but some photochemically activated retro-DA reactions have been recently demonstrated.



diene dienophile (with electron-attracting groups)

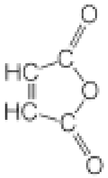
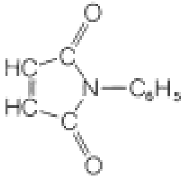
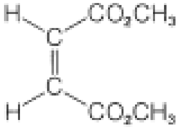
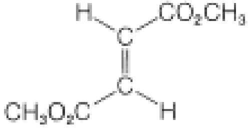
furan/maleic anhydride Diels-Alder reaction



diene Dienophile (with electron-attracting groups)

Gandini A. Prog Polym Sci2013;38:1–29.
Froidevaux V, et al. RSC Adv 2015;5:37742–54

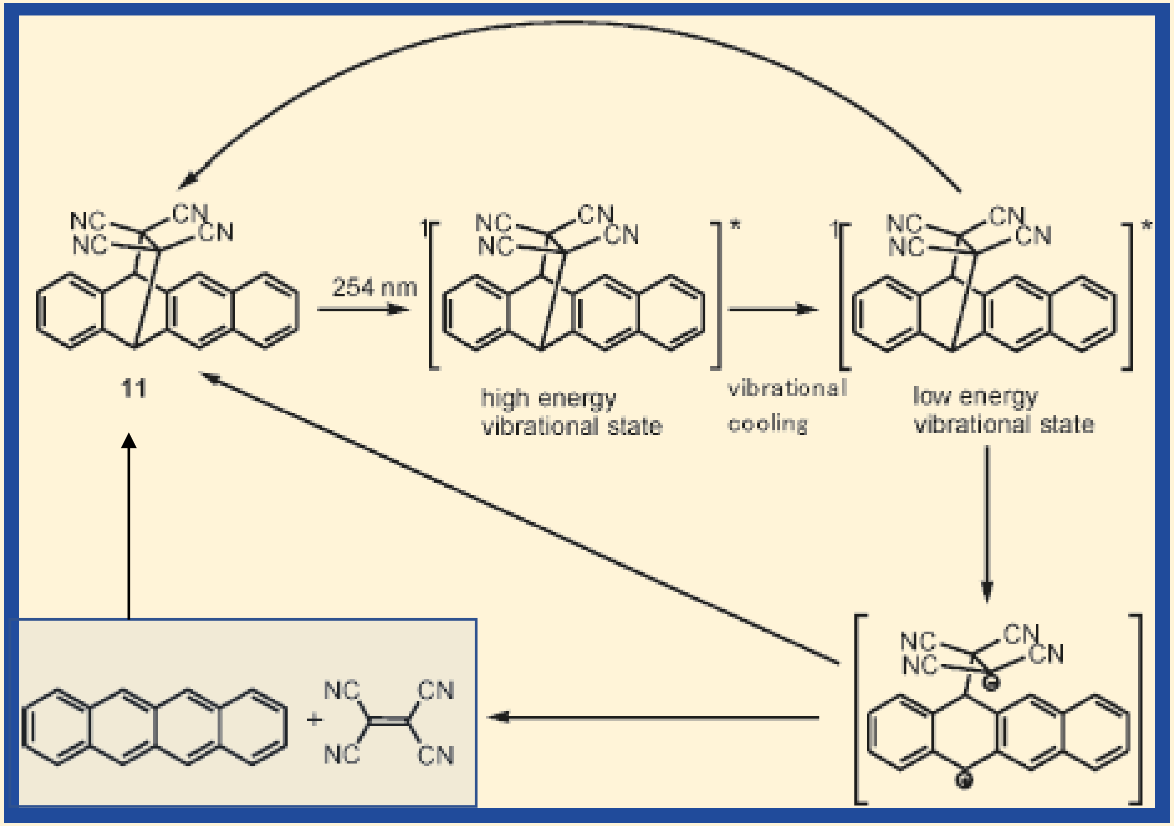
Examples of dienophiles

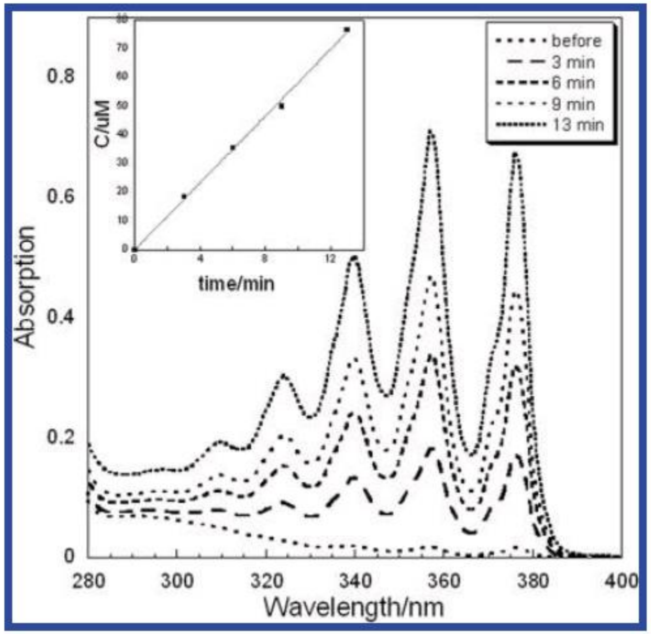
Name	Formula	Name	Formula
tetracyanoethene	$(NC)_2C{=}C(CN)_2$	propenenitrile (acrylonitrile)	$CH_2{=}CH{-}CN$
2-butenal (crotonaldehyde)	$CH_3CH{=}CH{-}CHO$	propenal (acrolein)	$CH_2{=}CH{-}CHO$
3-phenylpropenoic acid (cinnamic acid, cis and trans)	$C_6H_5CH{=}CH{-}CO_2H$	ethyl propenoate (ethyl acrylate)	$CH_2{=}CH{-}CO_2C_2H_5$
cis-butenedioic anhydride (maleic anhydride)		*N*-phenyl-*cis*-butenimide (*N*-phenylmaleimide)	
dimethyl *cis*-butenedioate (dimethyl maleate)		dimethyl *trans*-butenedioate (dimethyl fumarate)	
1-nitropropene	$CH_3CH{=}CH{-}NO_2$	2-nitro-1-phenylethene	$C_6H_5CH{=}CH{-}NO_2$

https://chem.libretexts.org/

Photochemically activated retro Diels-Alder

DA adducts of tetracyanoethylene (TCNE) dienophile with unsubstituted anthracene or naphthacene as the diene.



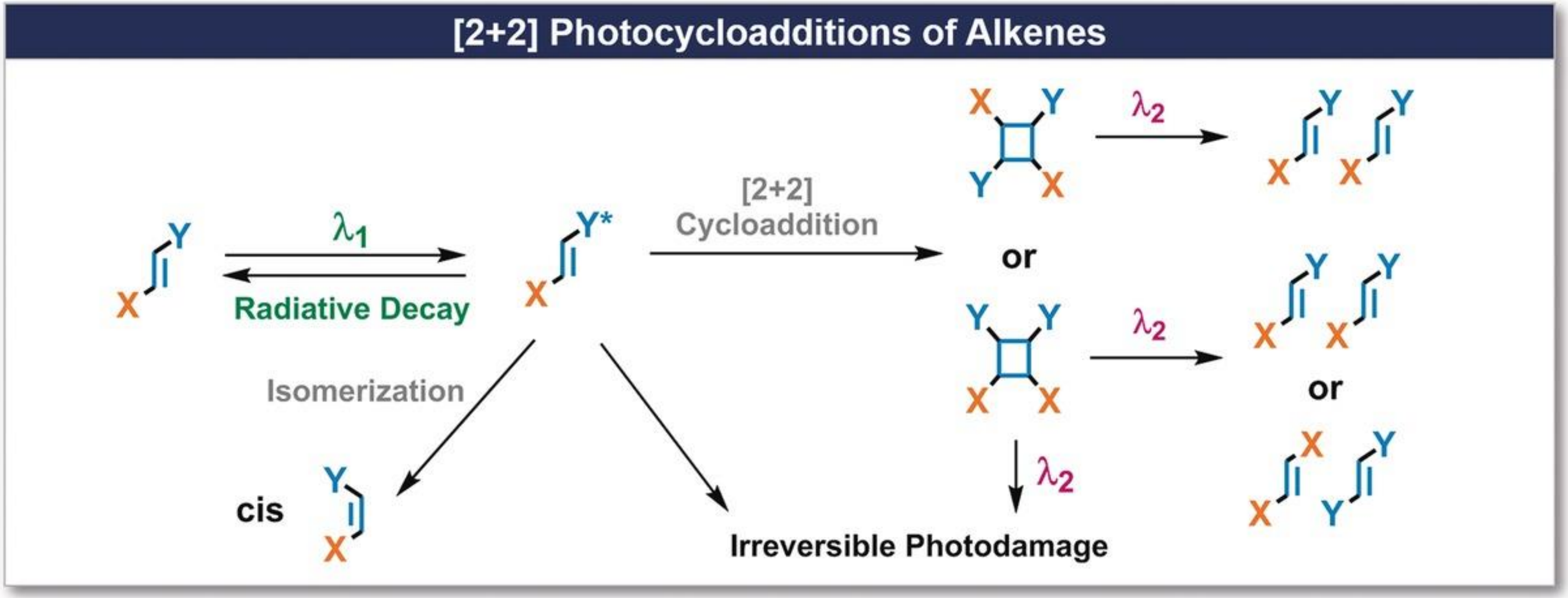


Millimolar solutions of the adducts in acetonitrile or acetontrile/methanol mixture were irradiated under 254 nm UV light (8W) in an inert atmosphere at room temperature.

J. Phys. Chem. A 2011, 115, 8093–8099

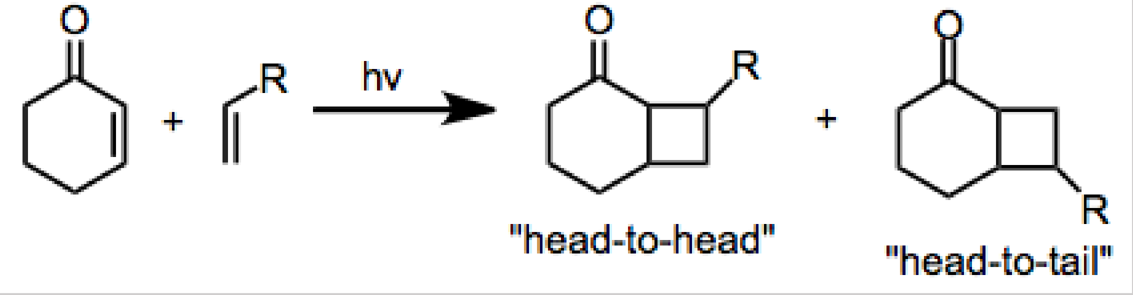
Common cycloadditions: [2+2]

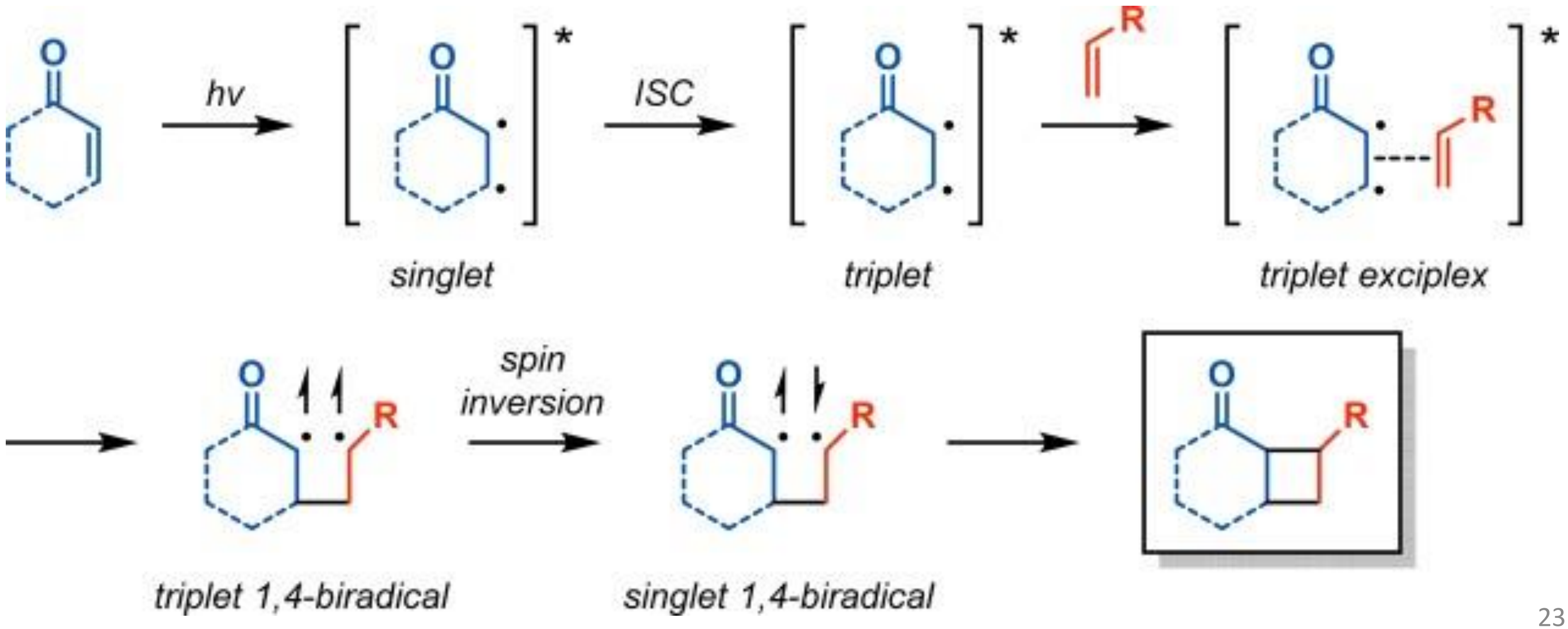
[2+2] Photocycloaddition is the combination of an excited state **enone** (conjugated alkene-chetone) with an **alkene,** or between **two alkenes,** to produce a **cyclobutane**



Common cycloadditions: [2+2]

[2+2] Photocycloaddition of an enone with an alkene





Common cycloadditions: [4+4]

The **[4+4] photocycloaddition** is a reaction in which **two unsaturated molecules** connect via four electrons from each molecule to create a **cyclooctane** ring

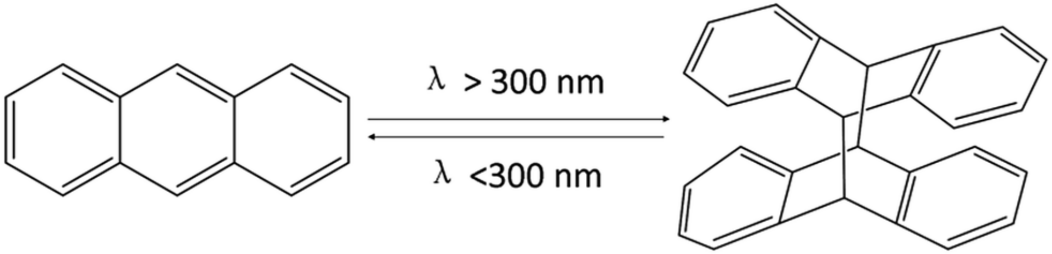


Photo-reversible dimerization reactions

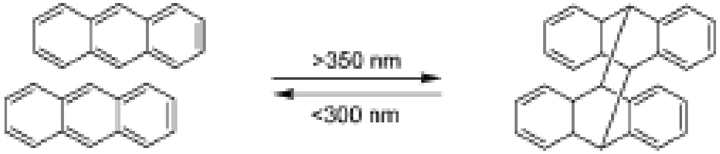
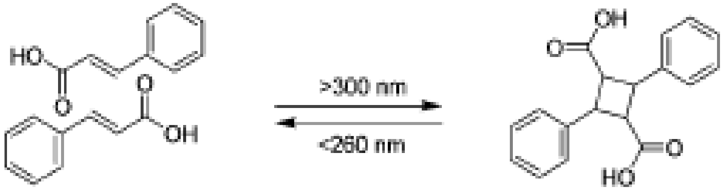
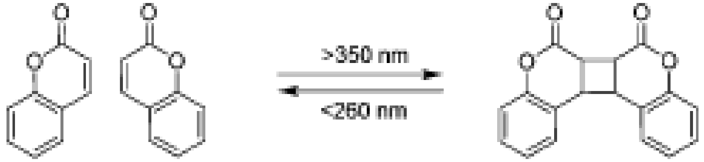
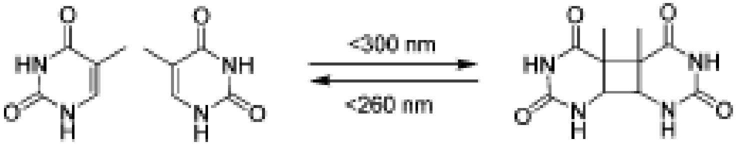
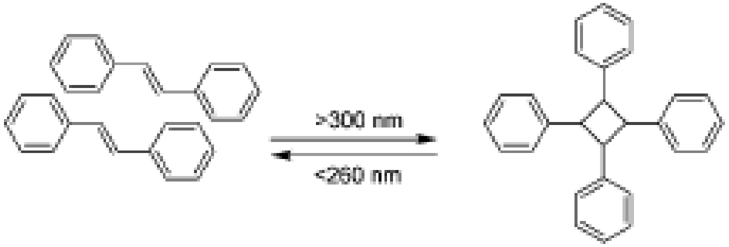
Most commonly **photo-reversible dimerisation** reactions proceed with a **[4+4] or [2+2] cycloaddition** mechanism.

The **[4+4] dimerization of anthracene** upon exposure to sunlight was described in 1867.

Thirty-five years later, the light-induced dimerization of **cinnamic acid, stilbene, and coumarin** in the solid state and solution, was demonstrated via a **[2+2] mechanism**.

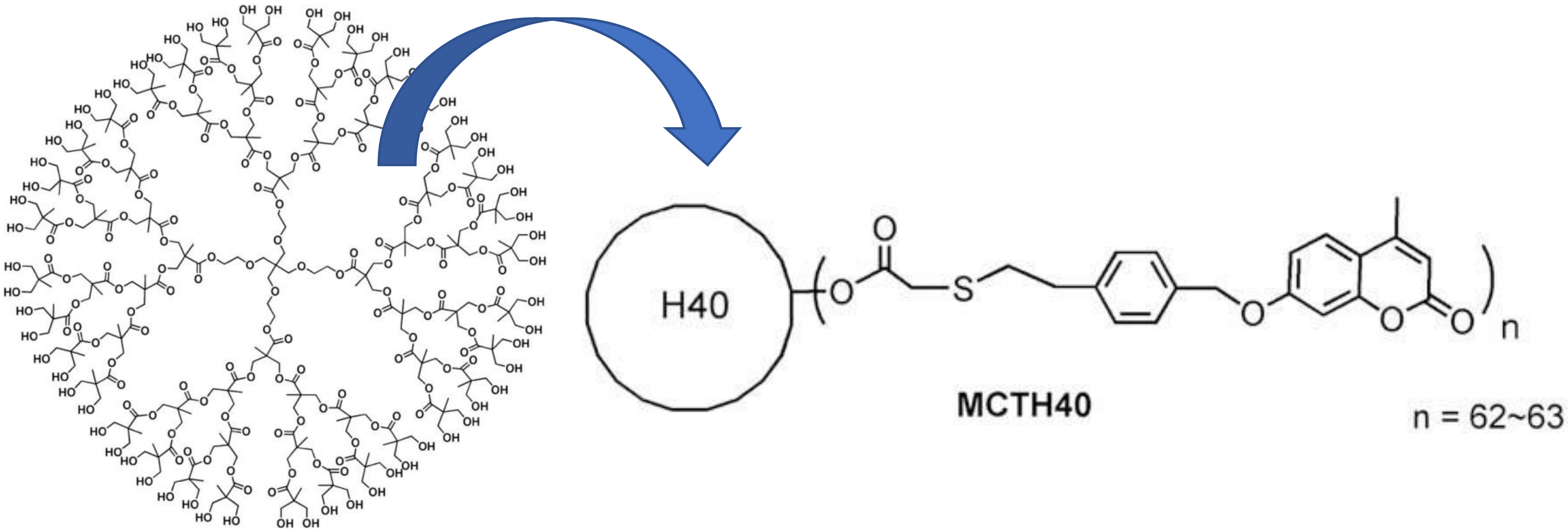
Further research in the **1960s** revealed the **reversibility** of [2+2] and [4+4] photocycloadditions, upon irradiation with shorter wavelengths

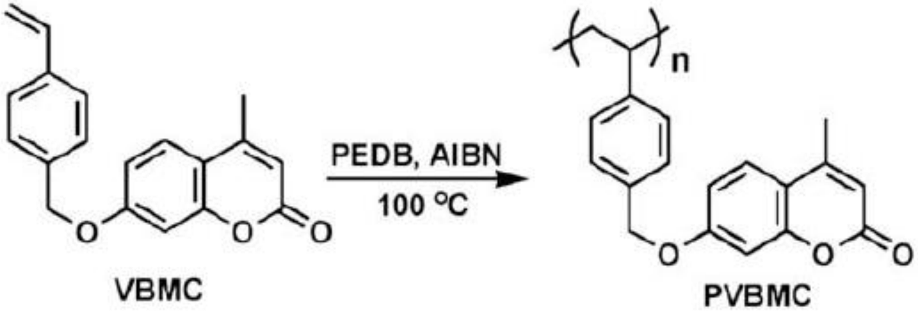
Photo-reversible dimerization reactions

Compound	Reaction
Anthracene[a]	 >350 nm <300 nm
Cinnamic acid[b]	 >300 nm <260 nm
Coumarin[b]	 >350 nm <260 nm
Thymine[b]	 <300 nm <260 nm
Stilbene	 >300 nm <260 nm

G.Kaur et al. Polym Chem 2014, 5 , 2171

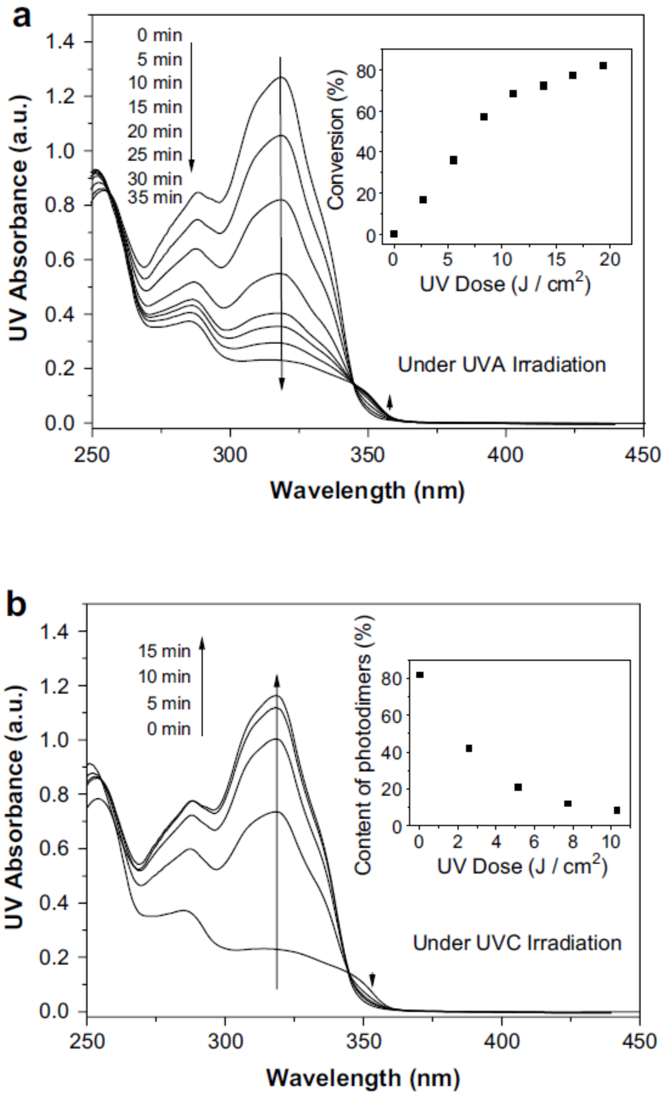
Examples: [2+2] dimerisation of coumarin moieties





Examples: [2+2] dimerisation of coumarin moieties

MCTH40 in chloroform solution



MCTH40 and PVBMC in chloroform solution

UVA cycle : 35 min
UVC cycle : 15 min

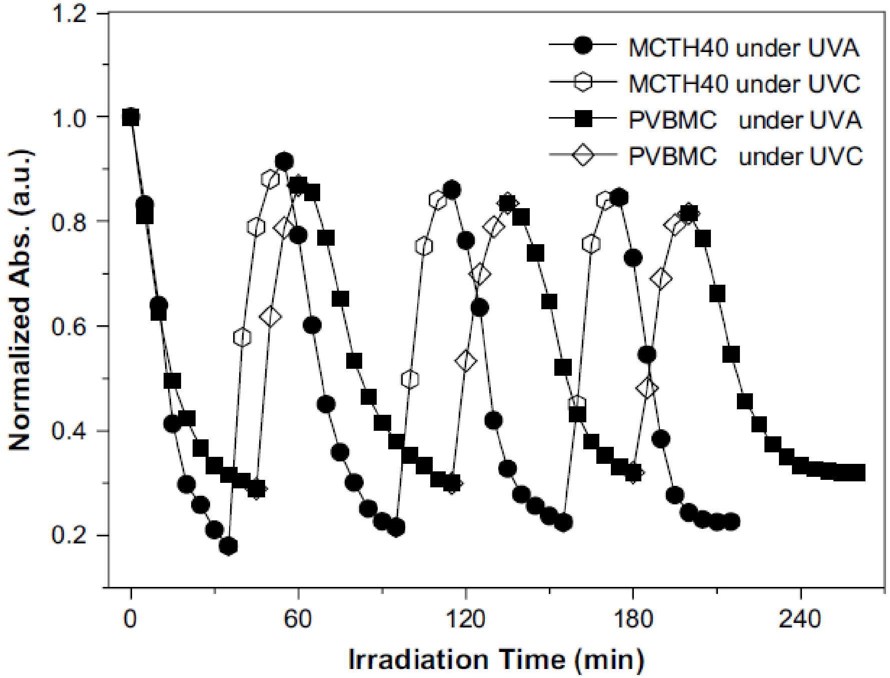
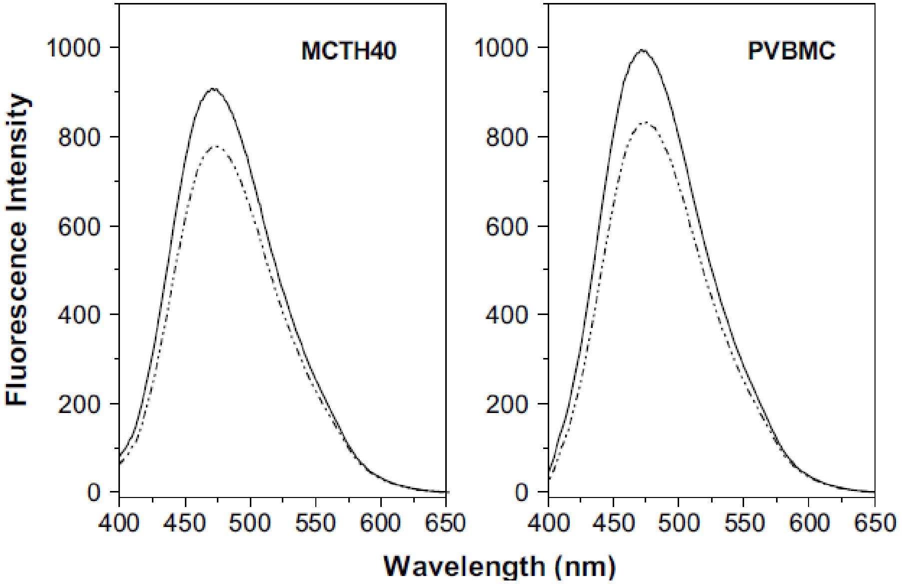


Fig. 5. UV absorbance changes of MCTH40 and PVBMC at 319 nm with irradiation of UVA light ($\lambda_{max} = 365$ nm, decrease in absorbance) and UVC light ($\lambda_{max} = 254$ nm, increase in absorbance) for three cycles.

Examples: [2+2] dimerisation of coumarin moieties

Assessing the reversibility of the reaction: fluorescence; GPC



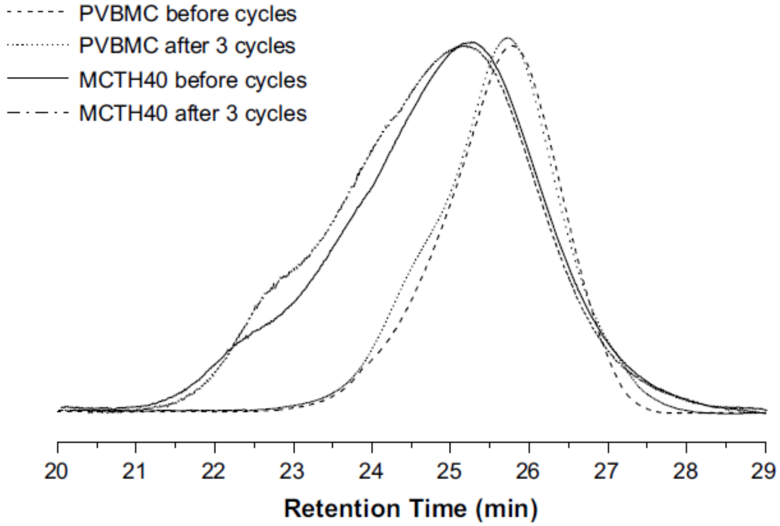
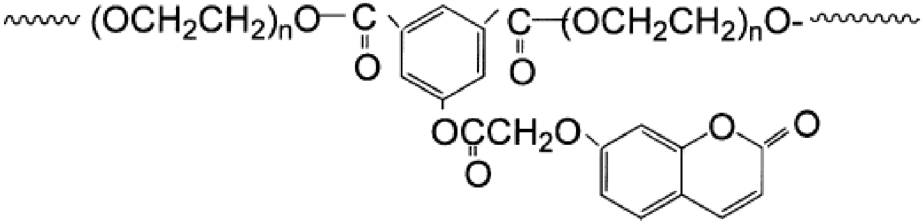


Fig. 7. GPC traces of MCTH40 and PVBMC before UV irradiation and after three photo-reversible cycles.

Examples: [2+2] dimerisation of coumarin moieties

Poly(ethylene glycol) hydrogel with pendant coumarin group (ICME3000)



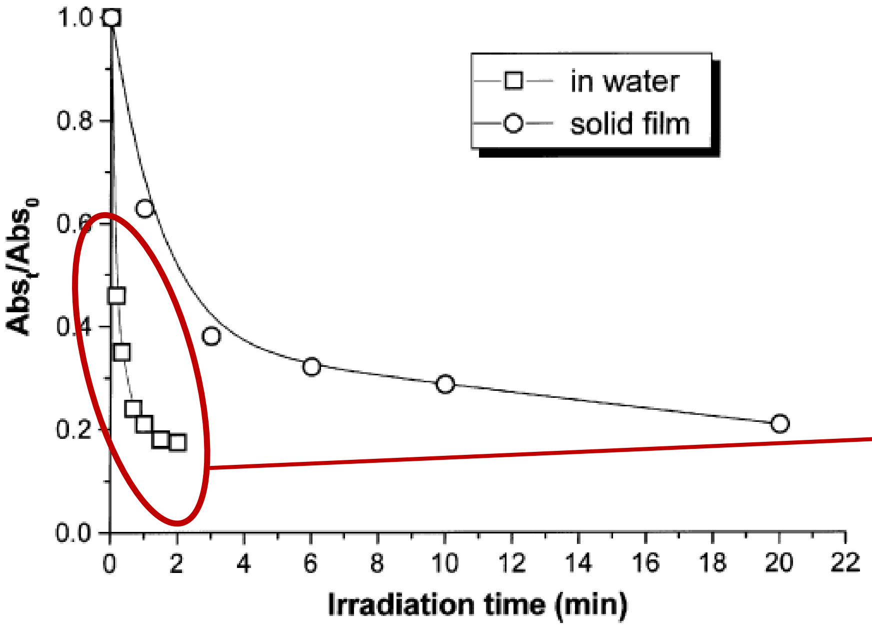


Fig. 2. Comparison of cross-linking rate of ICME3000 in water and in the form of thin film.

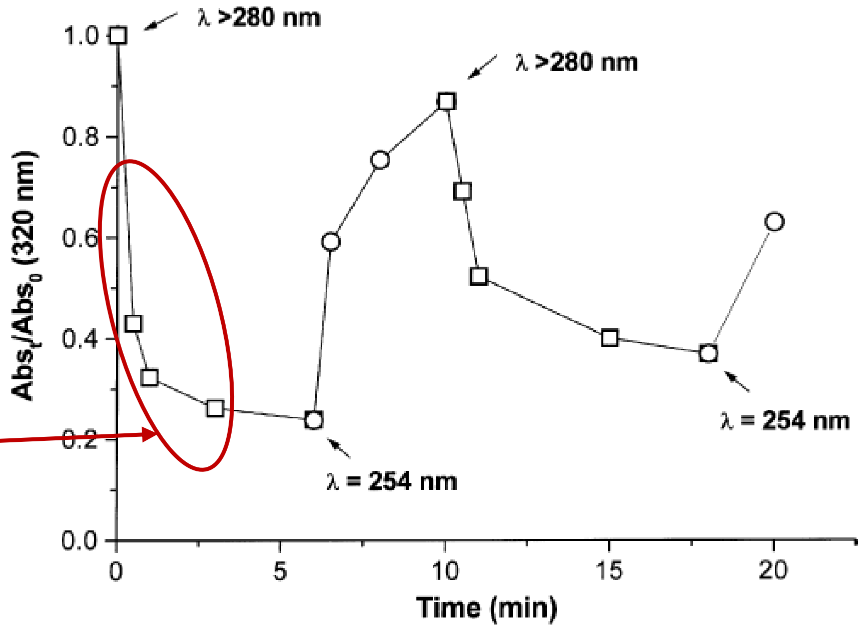
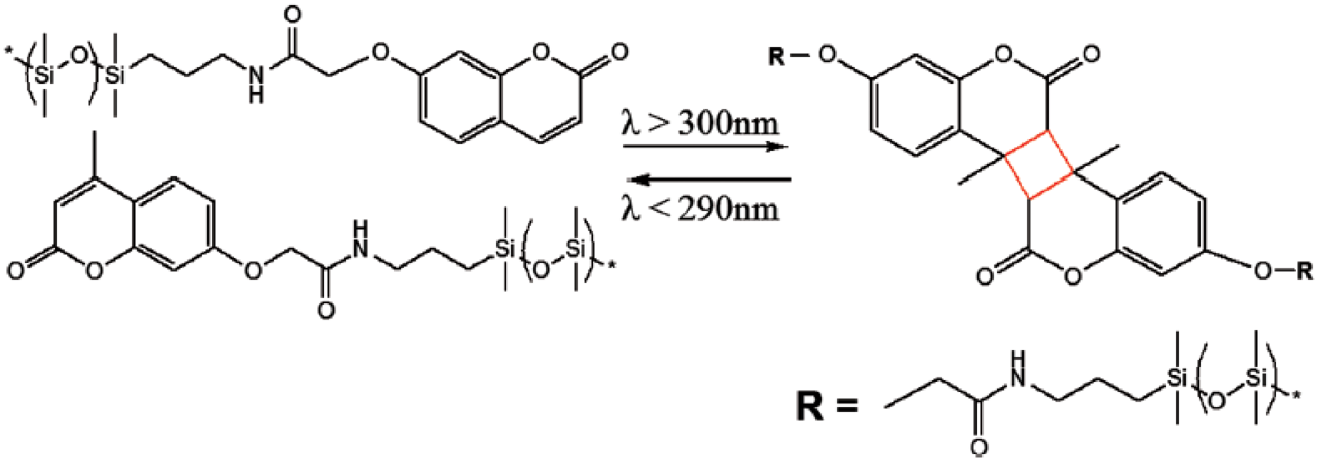


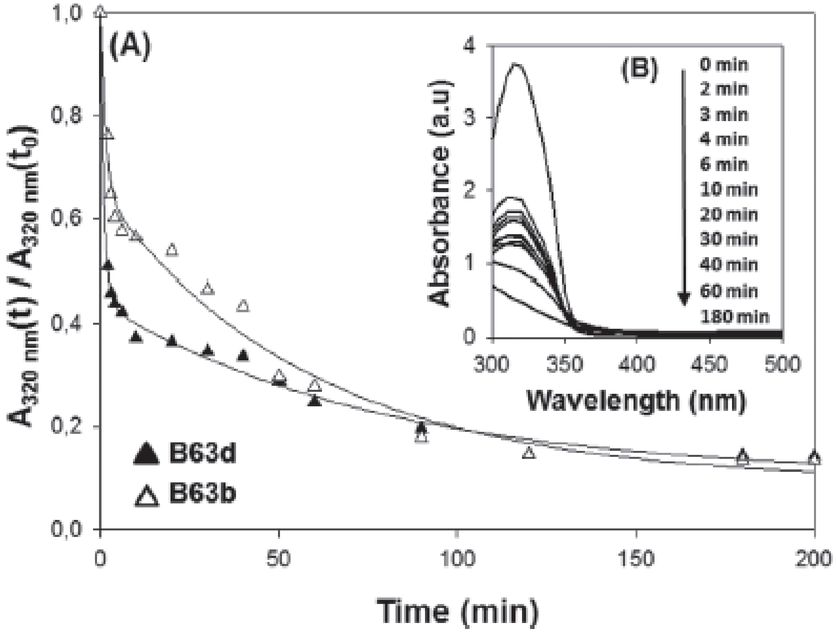
Fig. 3. Effect of light on absorption at 320 nm for ICME3000 in water.

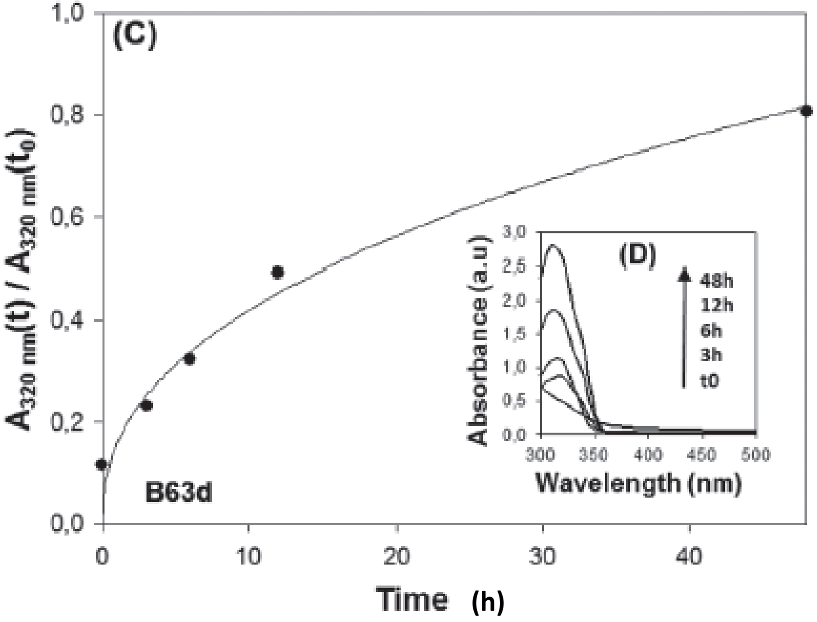
M. Nagata, Y. Yamamoto / Reactive & Functional Polymers 68 (2008) 915–921

Examples: [2+2] dimerisation of coumarin moieties

Photoreversible crosslinking of PDMS- coumarin polymer.

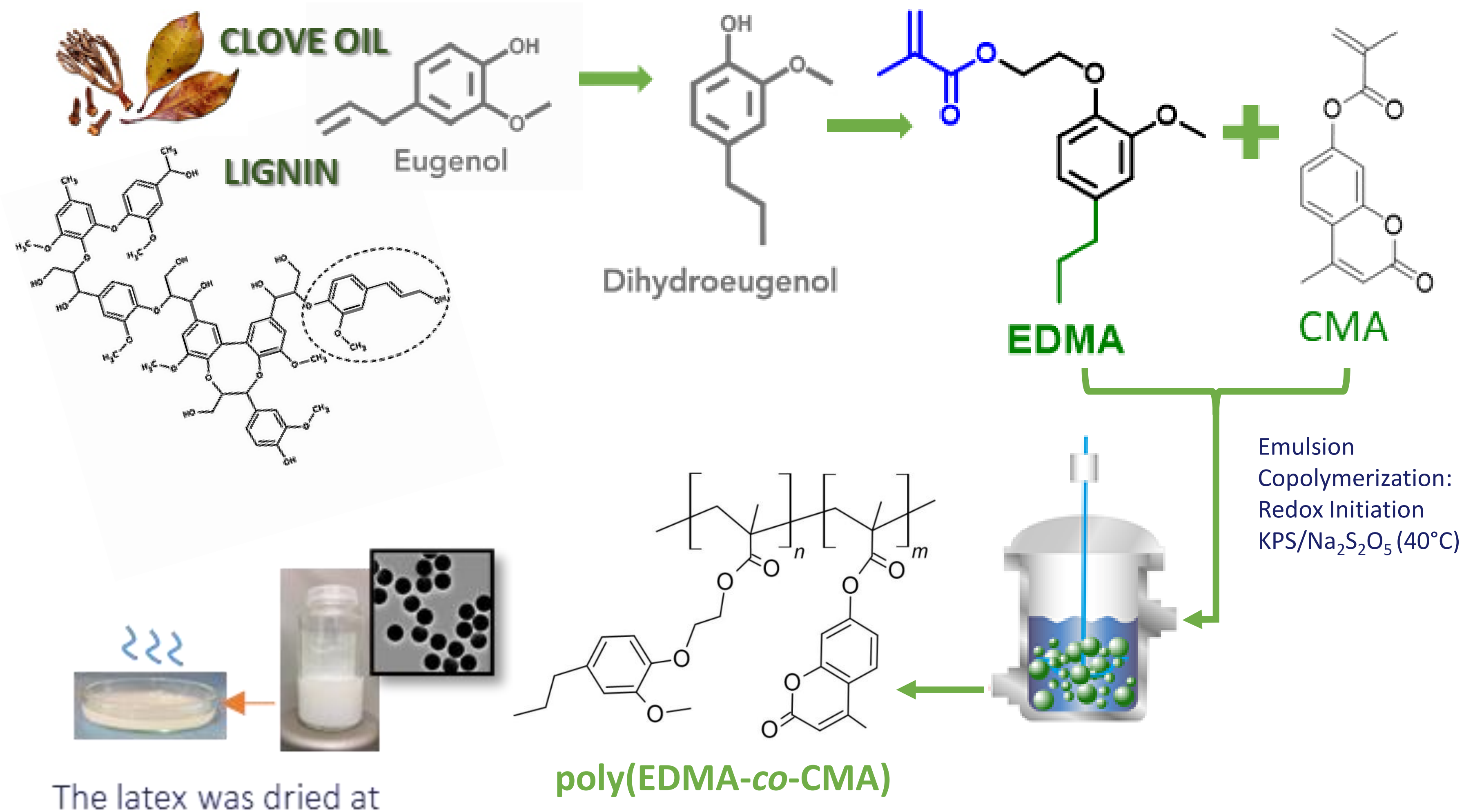






Rachid Jellali et al. *Macromol. Biosci.* **2017**, *17,* 1600495

[2+2] Photocycloaddition in biobased polymers

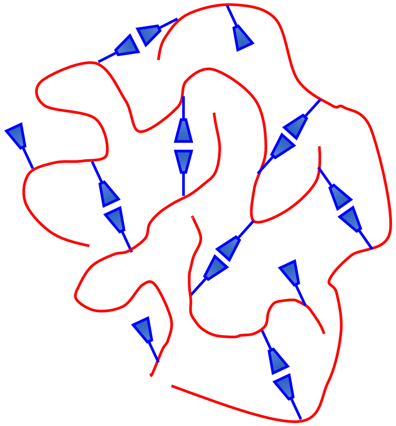


Emulsion Copolymerization:
Redox Initiation
KPS/$Na_2S_2O_5$ (40°C)

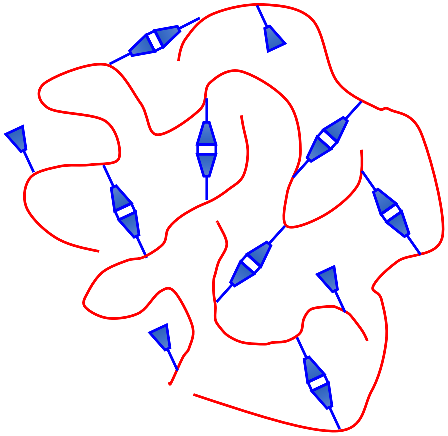
The latex was dried at room T to obtain a film.

T_g = 30 °C

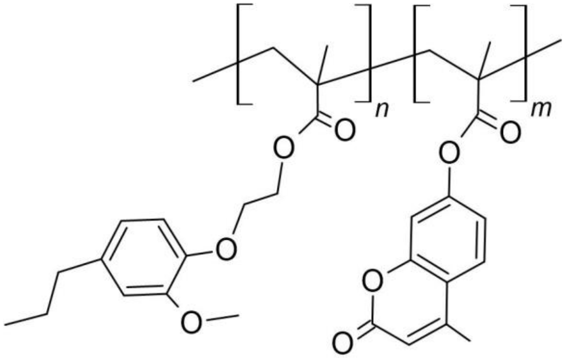
[2+2] Photocycloaddition in biobased polymers

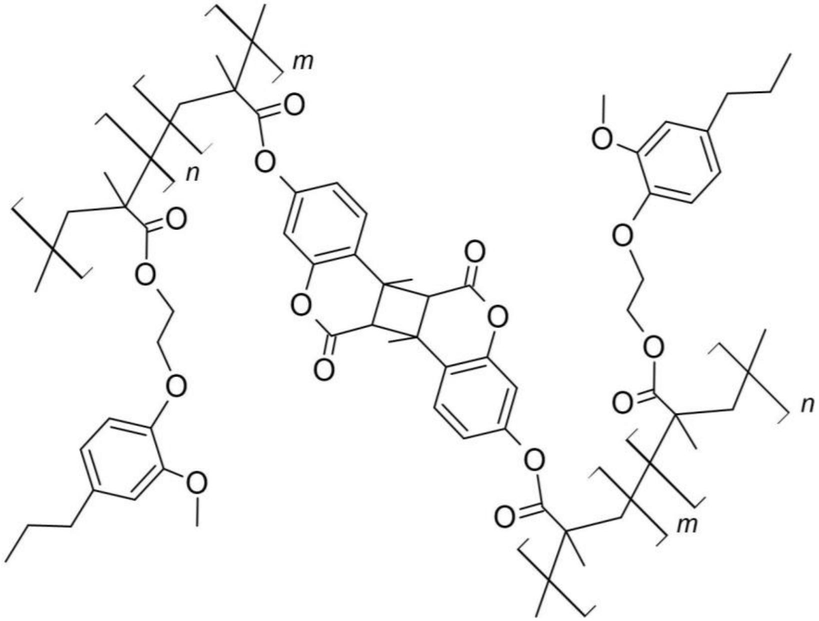


UV 365 nm



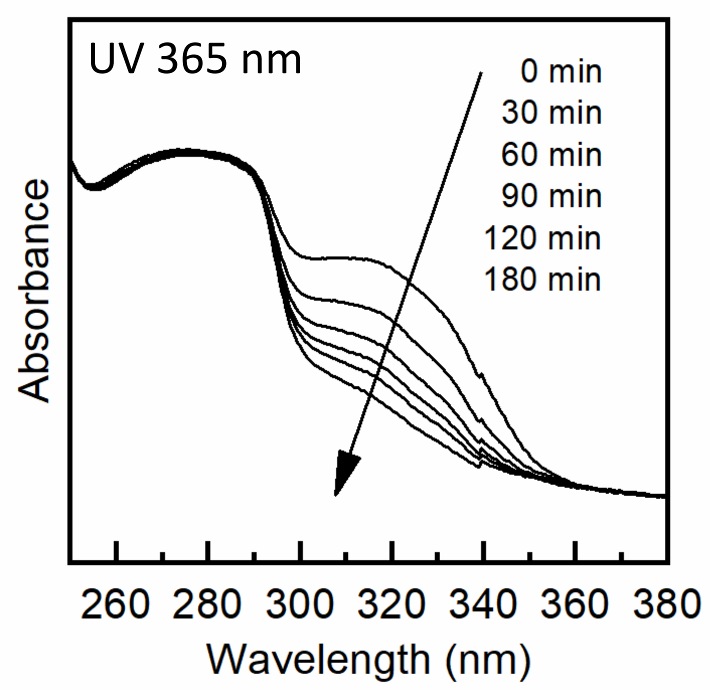
In acetone



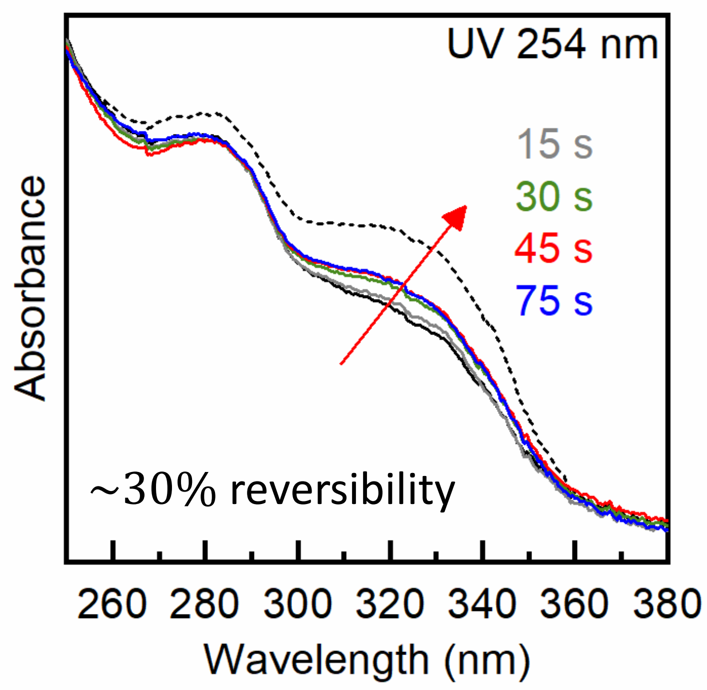


[2+2] Photocycloaddition in biobased polymers

Irradiation with UV 365 nm



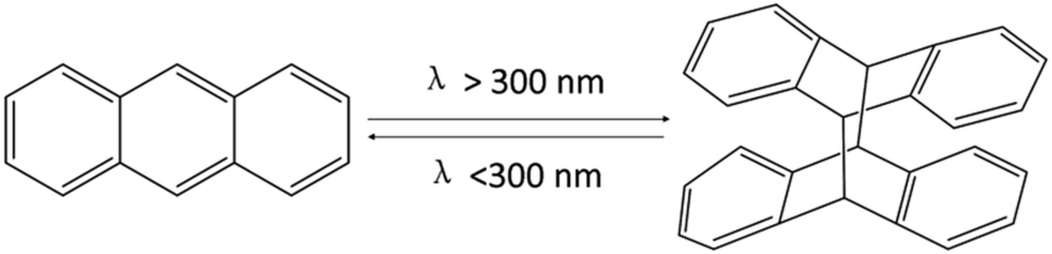
Irradiation with UV 254 nm
after 20 min @ UV 365 nm



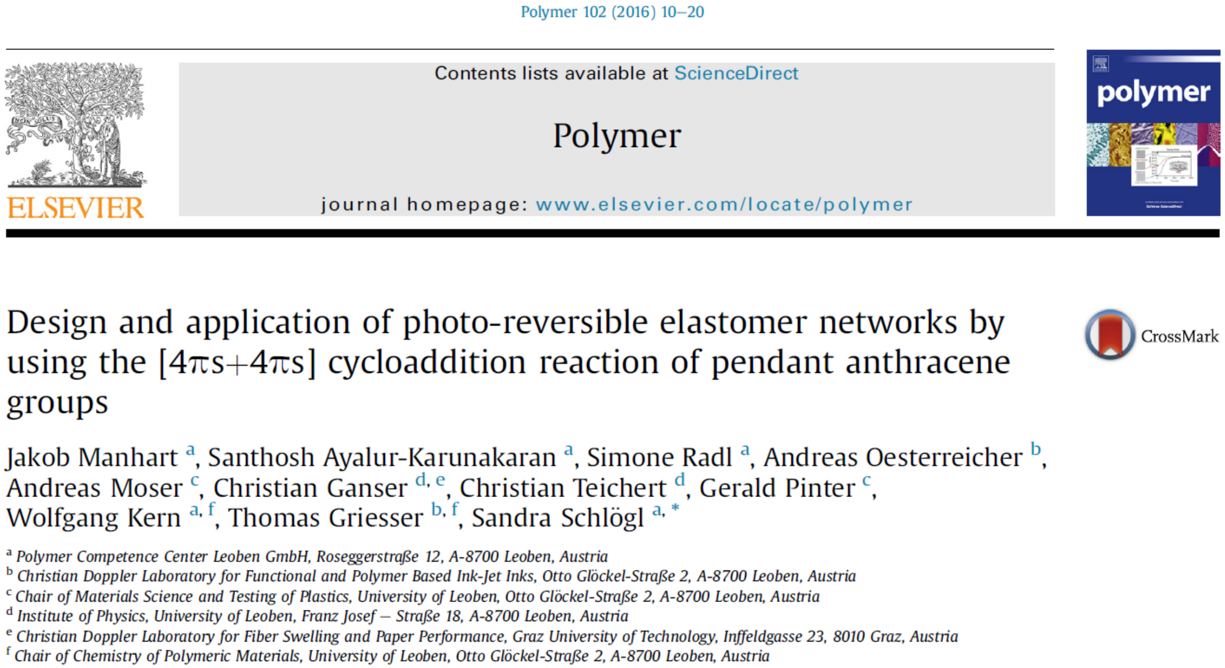
Poly(EDMa-co-CMA) with 5wt% CMA moieties

Examples: [4+4] dimerisation of anthracene moieties

- Initiating window for photo-dimerization of anthracenes extends up to 400 nm
- Reverse reaction can proceed photochemically or termally or mechanically



Example: photoreversible elastomer



Polymer 102 (2016) 10–20

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Polymer

journal homepage: www.elsevier.com/locate/polymer

Design and application of photo-reversible elastomer networks by using the $[4\pi s+4\pi s]$ cycloaddition reaction of pendant anthracene groups

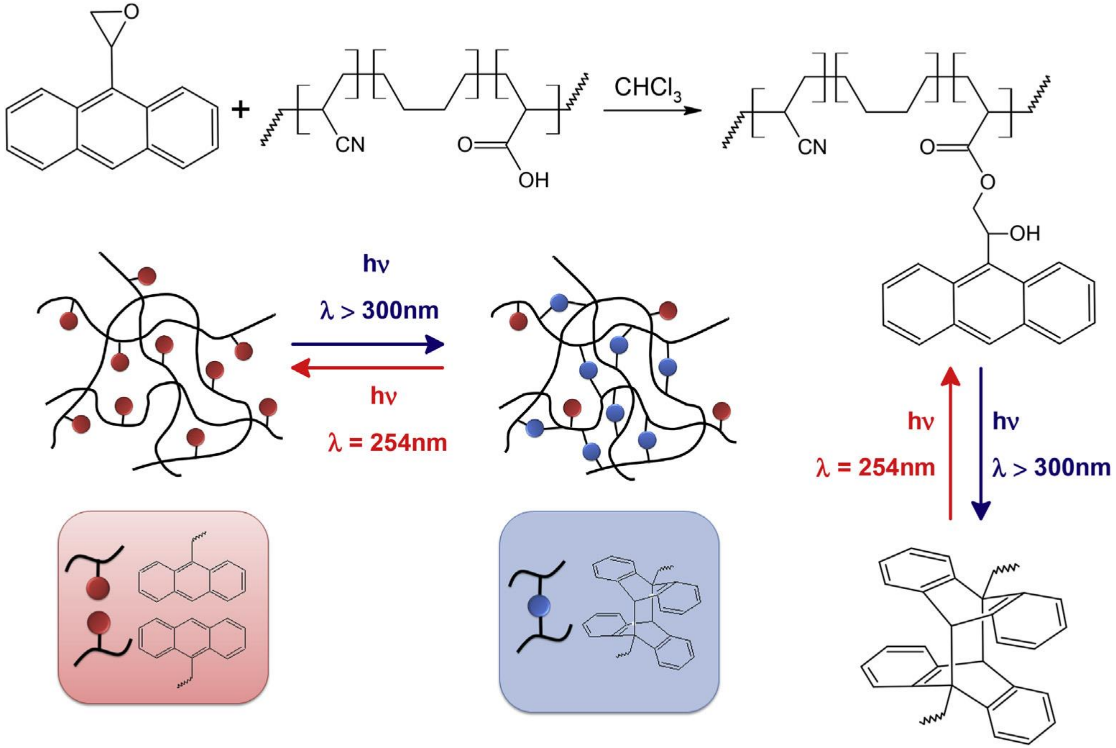
Jakob Manhart [a], Santhosh Ayalur-Karunakaran [a], Simone Radl [a], Andreas Oesterreicher [b], Andreas Moser [c], Christian Ganser [d, e], Christian Teichert [d], Gerald Pinter [c], Wolfgang Kern [a, f], Thomas Griesser [b, f], Sandra Schlögl [a, *]

[a] *Polymer Competence Center Leoben GmbH, Roseggerstraße 12, A-8700 Leoben, Austria*
[b] *Christian Doppler Laboratory for Functional and Polymer Based Ink-Jet Inks, Otto Glöckel-Straße 2, A-8700 Leoben, Austria*
[c] *Chair of Materials Science and Testing of Plastics, University of Leoben, Otto Glöckel-Straße 2, A-8700 Leoben, Austria*
[d] *Institute of Physics, University of Leoben, Franz Josef – Straße 18, A-8700 Leoben, Austria*
[e] *Christian Doppler Laboratory for Fiber Swelling and Paper Performance, Graz University of Technology, Inffeldgasse 23, 8010 Graz, Austria*
[f] *Chair of Chemistry of Polymeric Materials, University of Leoben, Otto Glöckel-Straße 2, A-8700 Leoben, Austria*

- Photo-reversible cycloaddition reaction of anthracene moieties is used to obtain carboxylated nitrile butadiene rubber networks with wavelength dependent properties.
- In thin films, the wavelength dependent changes in solubility are employed for the preparation of reversible photoresists enabling the preparation of 2D microstructures and a switching between negative- and positive-type patterns.
- Along with thin films, the wavelength dependent modulation of thermo-mechanical properties is also demonstrated for macroscopic samples, which shows the versatility of these optically stimuli-responsive networks.

Example: photoreversible elastomer

Anthracene derivatives with reactive epoxy groups are covalently attached to the polymer side chain of a commercially available rubber via ring opening reaction between the epoxy and the carboxylic groups.

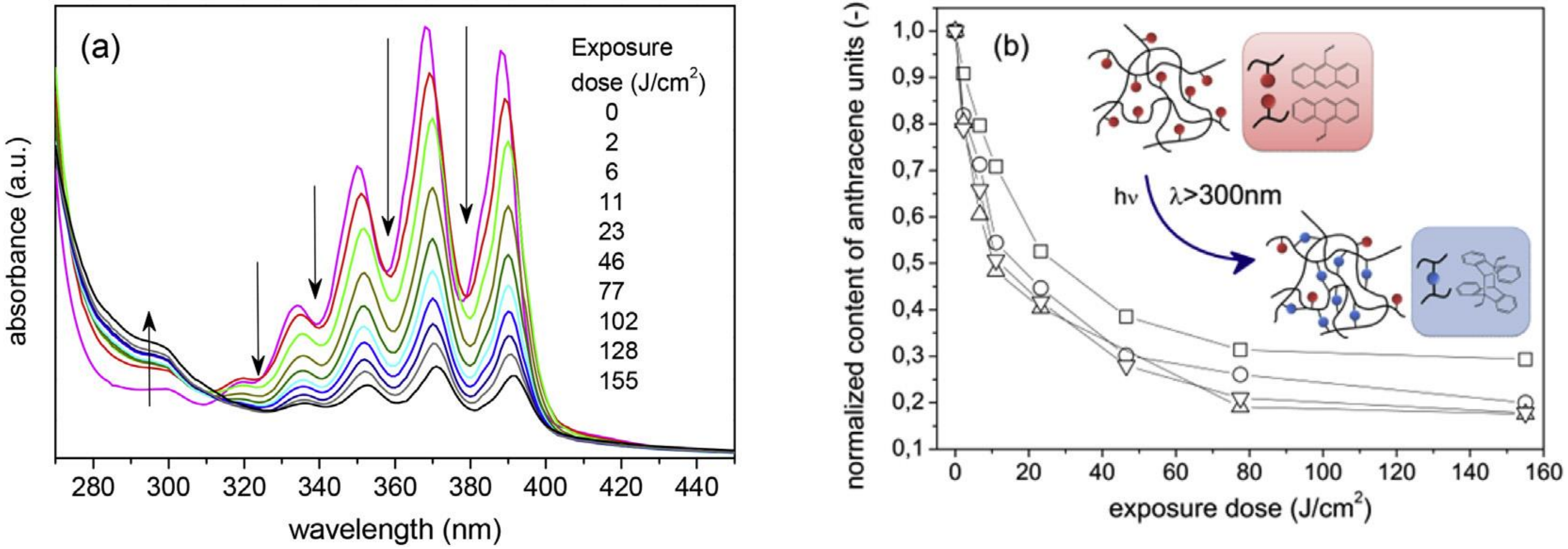


Rubber crosslinking: UV exposure at **λ > 300 nm** at room temperature.

Photo-cleavage of the photodimers: UV illumination at **254 nm**

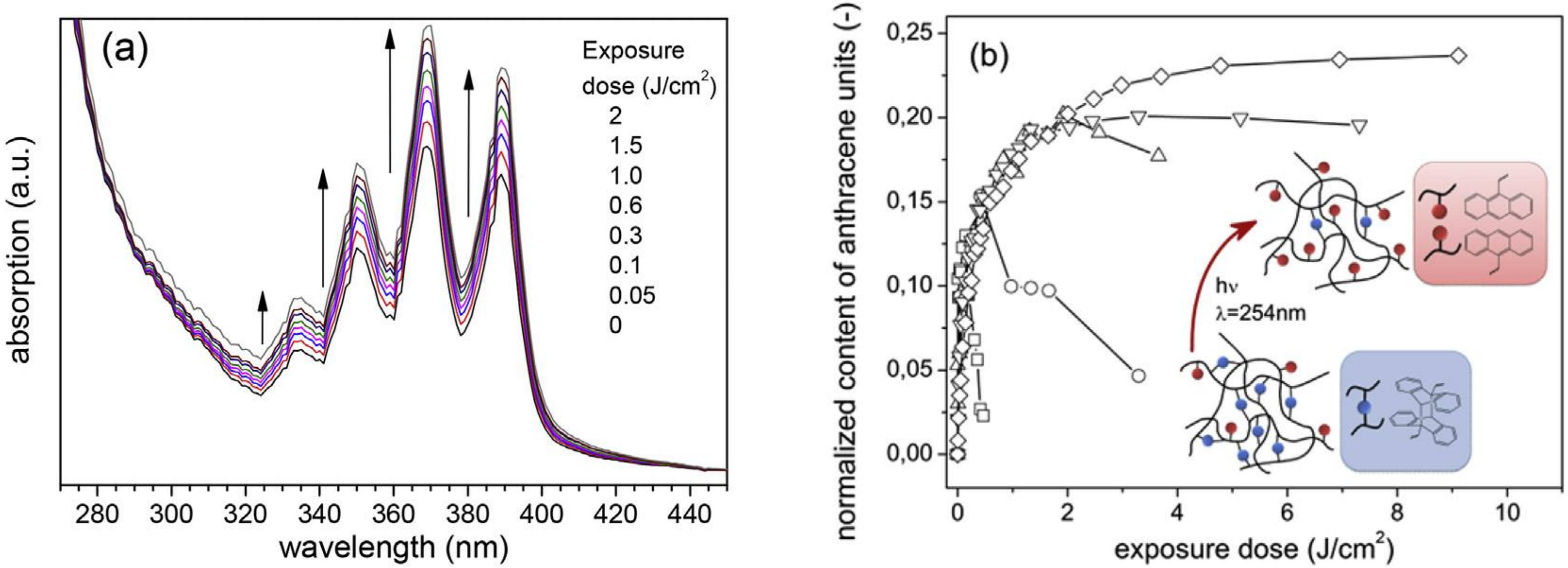
Example: photoreversible elastomer

- T_g of the rubber changes from -19 °C (unmodified) to -7 °C (1.3 mol% modification yield) : photo-dimerization occurs in the rubbery state ensuring a high mobility of the pendant groups as the UV illumination is carried out at room temperature.
- Decrease of anthracene bands at 336, 350, 370, 390 nm



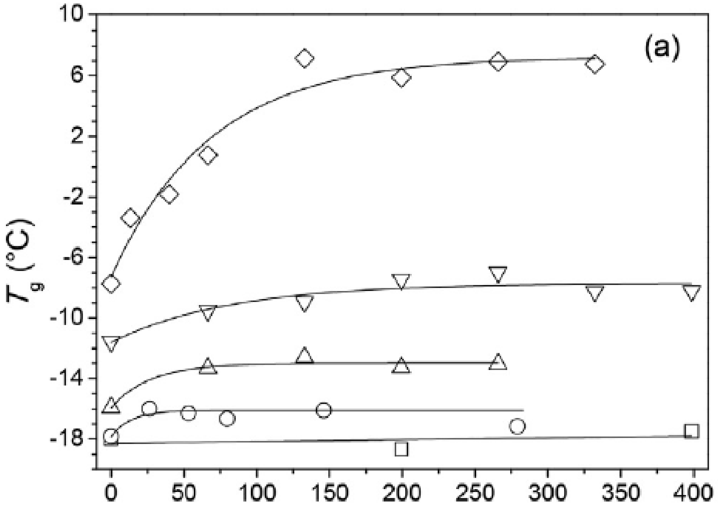
Example: photoreversible elastomer

- Photo-cleavage of crosslink sites: regeneration of free anthracene moieties by deep UV exposure (254 nm) under inert atmosphere.



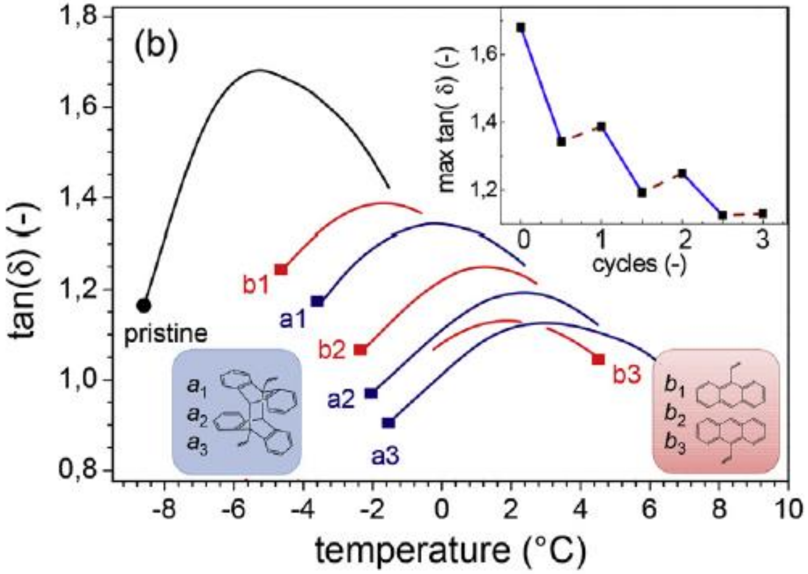
- A distinctive increase of the characteristic anthracene absorption bands is observed due to the regeneration of free anthracene units.
- The cleavage yield is strongly influenced by the exposure dose employed in the photocrosslinking step which determines the number of crosslink sites in the modified XNBR films

Example: photoreversible elastomer

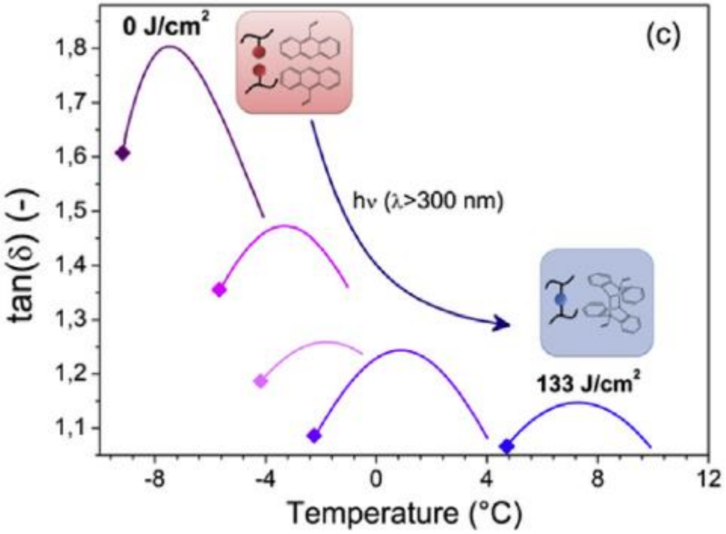


(□) rubber-0, (○) rubber-1, (△) rubber-2, (▽) rubber-3, and (◇) rubber-4

Increasing degree of functionalization



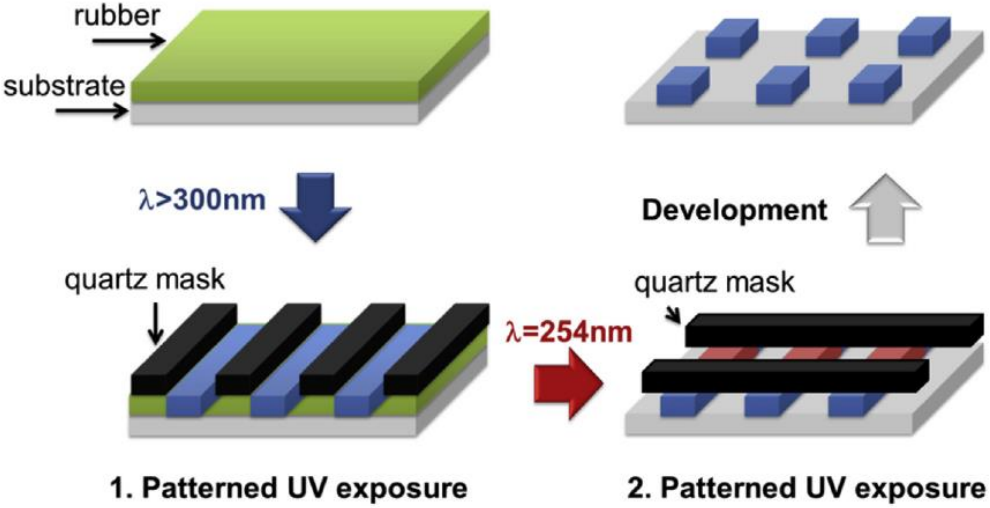
DMA curves of rubber-4 over repeated cycles of UV induced crosslinking (a1, a2, a3) with 46 J/cm2 (l > 300 nm, N2) and UV induced cleavage (b1, b2, b3) with 9.72 J/cm2 (254 nm, N2). The insert depicts the max. tand values over three cycles



DMA curves of rubber-4 as a function of exposure dose (300 nm)

Example: patterning of photoreversible elastomer

Patterning of photoreversible elastomer (photoresist)



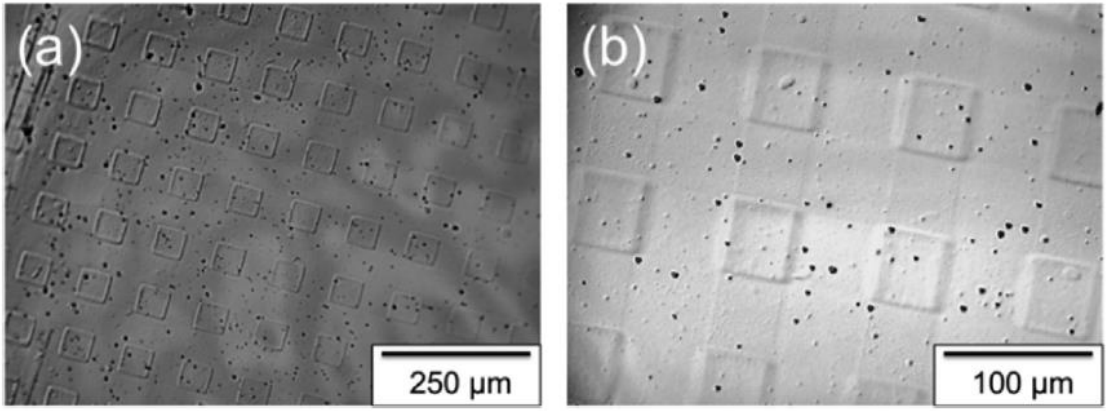
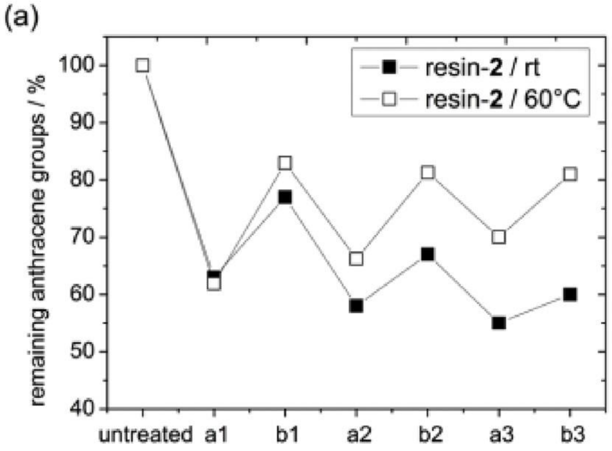
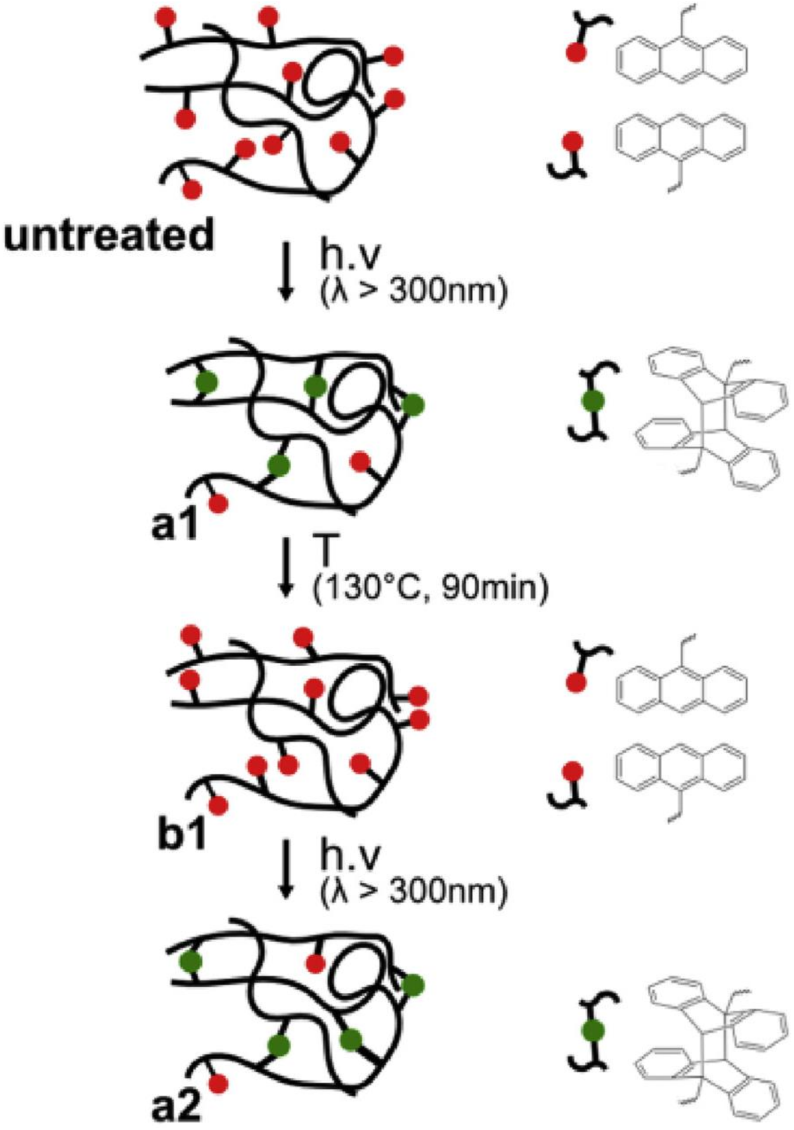


Fig. 9. Optical micrographs of reversibly patterned thin rubber-**4** films after development in acetonitrile.

Example : mendable epoxy

The [4+4] cycloaddition reaction of anthracene derivatives can be also exploited in solid films to prepare reversible and mendable epoxy based materials.
However, irradiation with 254 nm UV-light did not lead to a significant regeneration of the consumed anthracene moieties.
Thus, a **thermally controlled de-crosslinking route** was pursued involving a thermal annealing step at 130 C for 90 min.



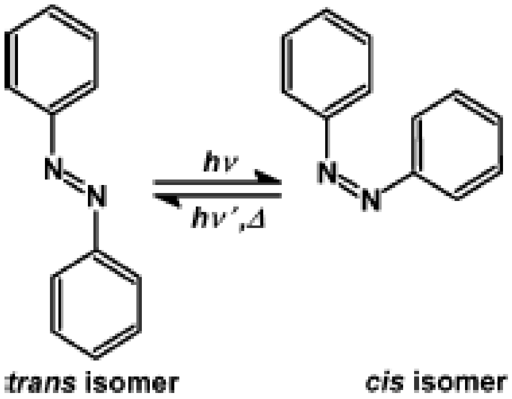


Limitations of photocycloadditions

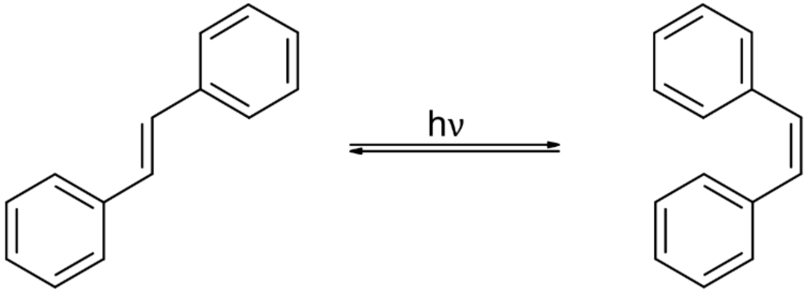
- Low yields for the dimerization as well as incomplete cycloreversions.
- Kinetic effects caused by the matrix are critical for the efficiency of the cycloreversion:
    - to obtain full cycloreversion where diffusion after the photoscission does not separate the photoreactive groups as well as in highly multivalent systems, the photoreversion efficiency must be assessed as a function of the wavelength to minimize the overlap of the cyclization and cycloreversion efficiencies.

Conformational changes

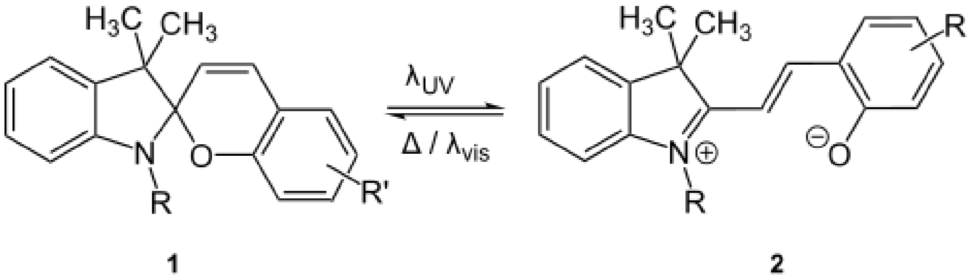
Conformational changes



Azobenzene



Stilbene



Spiropyrans

Conformational changes: example

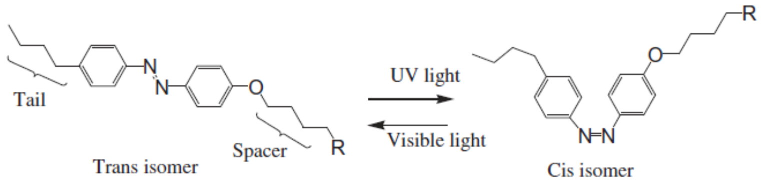


Figure 1. Isomerisation of azobenzene with an alkyl tail and a spacer, where R represents a main chain.

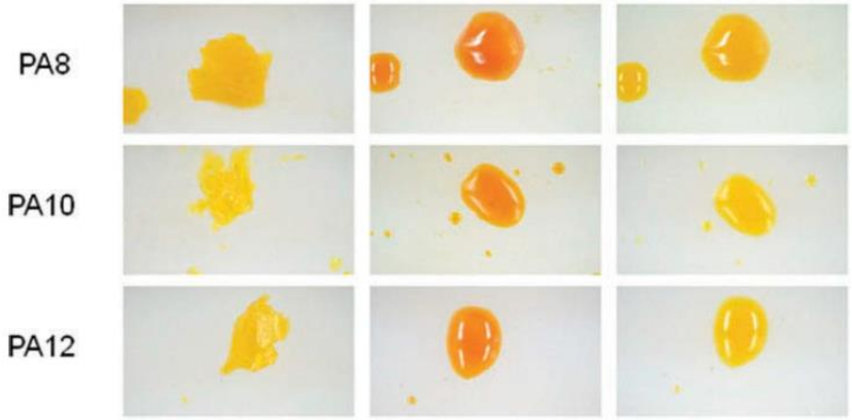
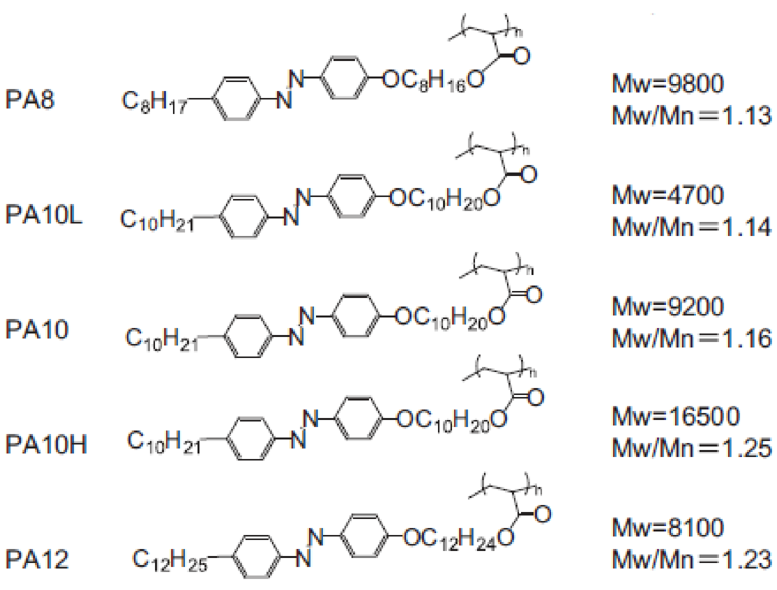


Figure 3. Morphological observation of polymers without irradiation (left) and with UV light irradiation (λ = 365 nm, 20 mW·cm^{-2}) for 2 h (centre) and with subsequent visible light irradiation for 20 min (λ = 520 nm, 15 mW·cm^{-2}).

Table 1. Photoliquefaction speed of polymers.

	Disbonding time (s)	
Samples	Thermosetting	Photosetting
SA	18	20
PA12	27	38
PA10	93	171
PA8	72	98



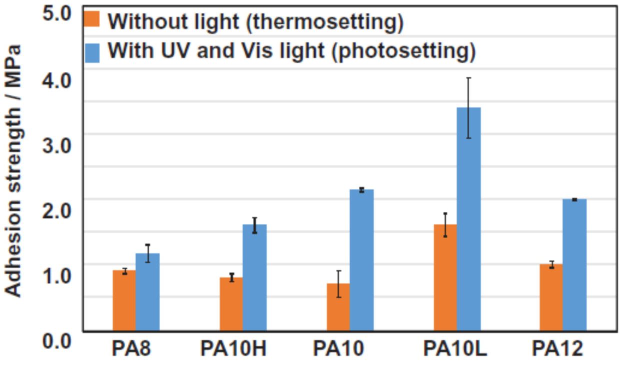
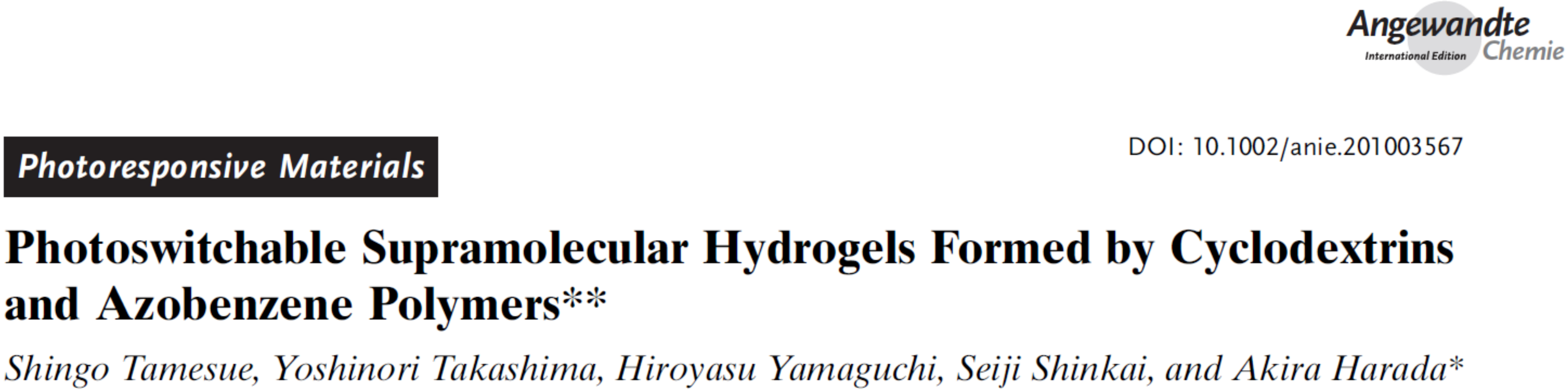


Figure 4. Adhesion strengths of polymeric compounds to glass substrates, prepared by thermal process (thermosetting) and photochemical process (photosettting).

Haruhisa Akiyama, Tamaki Fukata, Aishi Yamashita, Masaru Yoshida & Hideyuki Kihara (2017) Reworkable adhesives composed of photoresponsive azobenzene polymer for glass substrates, The Journal of Adhesion, 93:10, 823-830, DOI: 10.1080/00218464.2016.1219255



Angewandte Chemie International Edition

Photoresponsive Materials

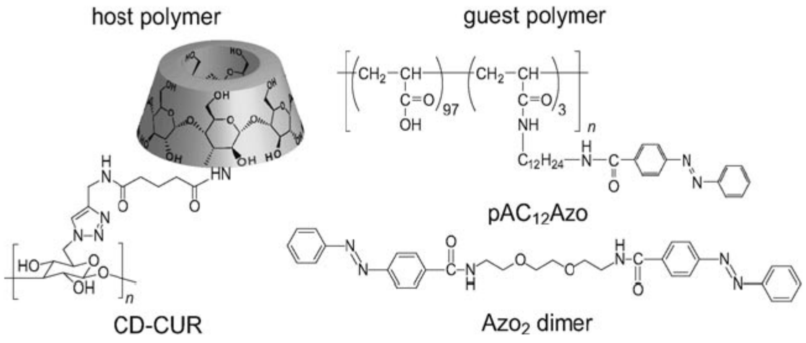
DOI: 10.1002/anie.201003567

Photoswitchable Supramolecular Hydrogels Formed by Cyclodextrins and Azobenzene Polymers**

*Shingo Tamesue, Yoshinori Takashima, Hiroyasu Yamaguchi, Seiji Shinkai, and Akira Harada**

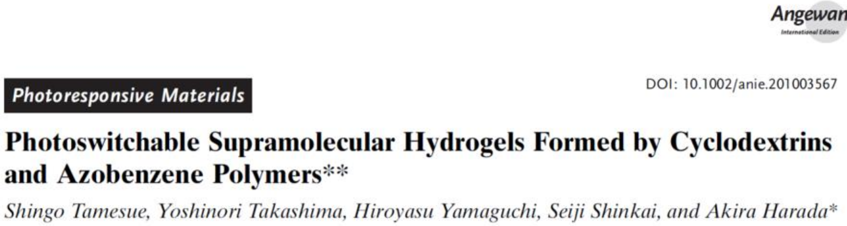
To obtain a hydrogel, curdlan (b-1,3 glucan, CUR) was used as a backbone because it has a rather rigid structure and Cyclodextrins (CD) can be attached to each monomer unit in the polymer chain.

A supramolecular hydrogel was obtained by mixing CUR functionalized with CDs (CD-CUR) and a guest polymer with Azobenzene moieties attached to it (Scheme 1).



Scheme 1. Structures of the compounds used.

Angew. Chem. Int. Ed. 2010, 49, 7461



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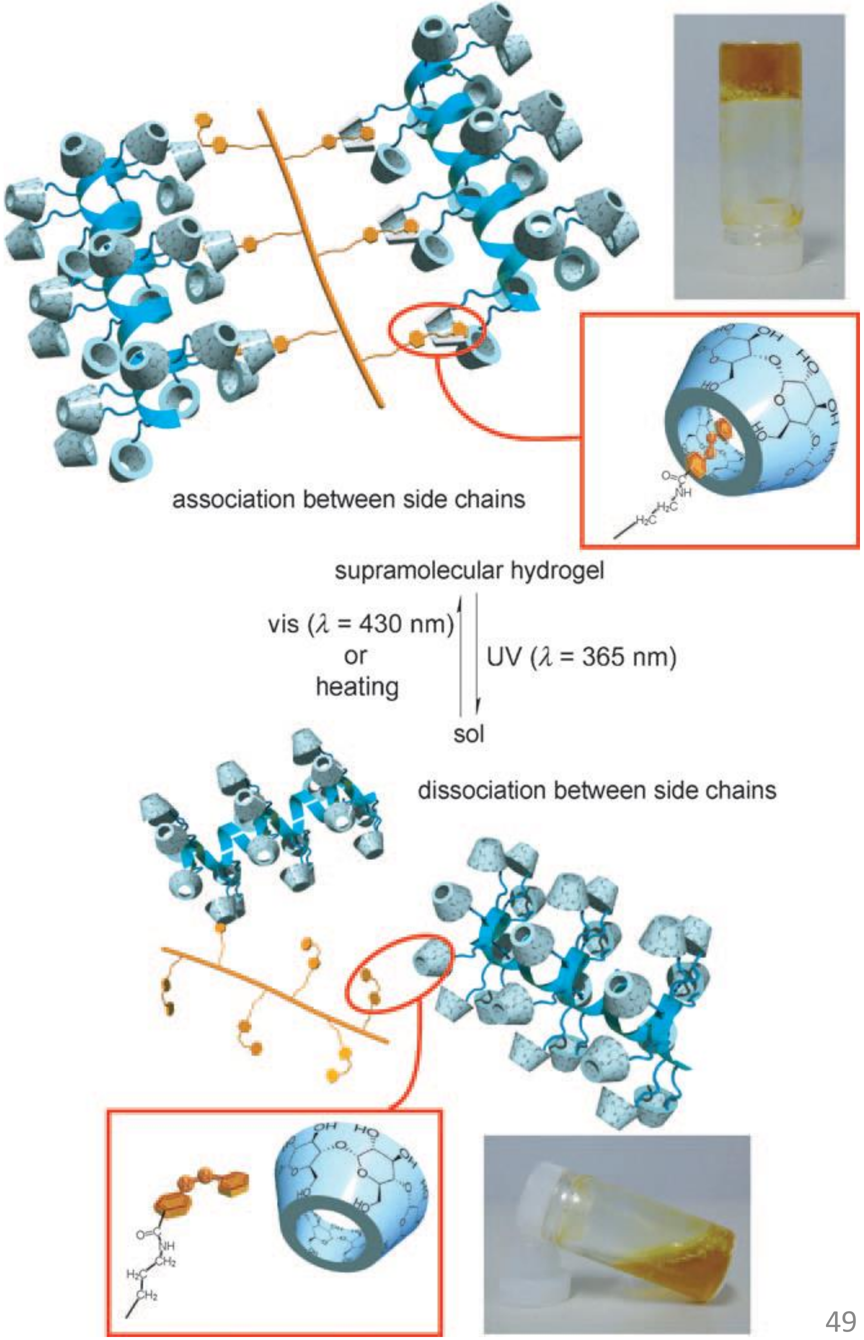
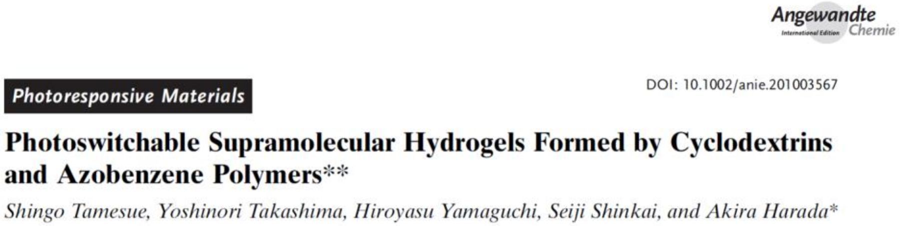
Photoirradiation with UV light (365 nm) caused an isomerization of the trans-azo group in $pAC_{12}Azo$ to the cis-azo group (trans/cis=12:88).

Visible light (430 nm) or heating (60 °C) caused the isomerization of the azo group from cis to trans (trans/cis=75:25).





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UV irradiation at 365 nm of the supramolecular hydrogel caused a decrease in the viscosity of the hydrogel to give the sol.

UV irradiation at 430 nm (or heating) of the sol state recovered the viscosity of the system to give the hydrogel within two minutes (red line).

The viscosity changes could be repeatedly induced by using both UV and visible light

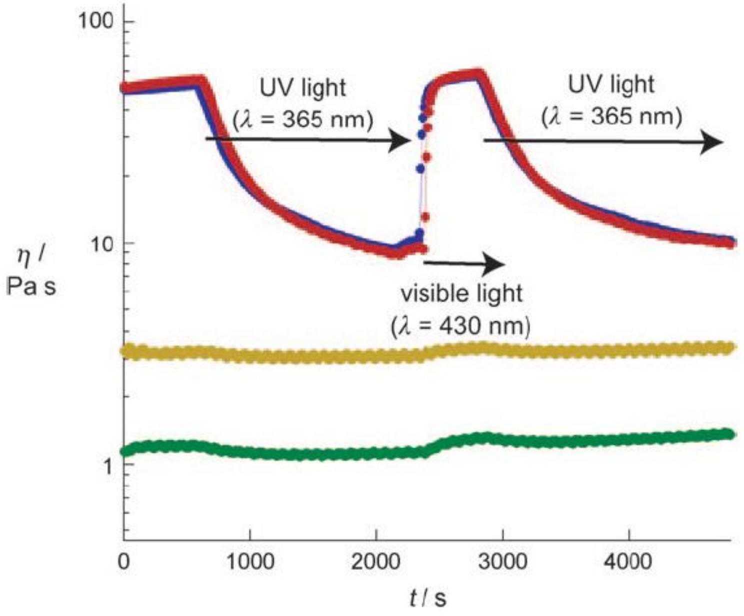
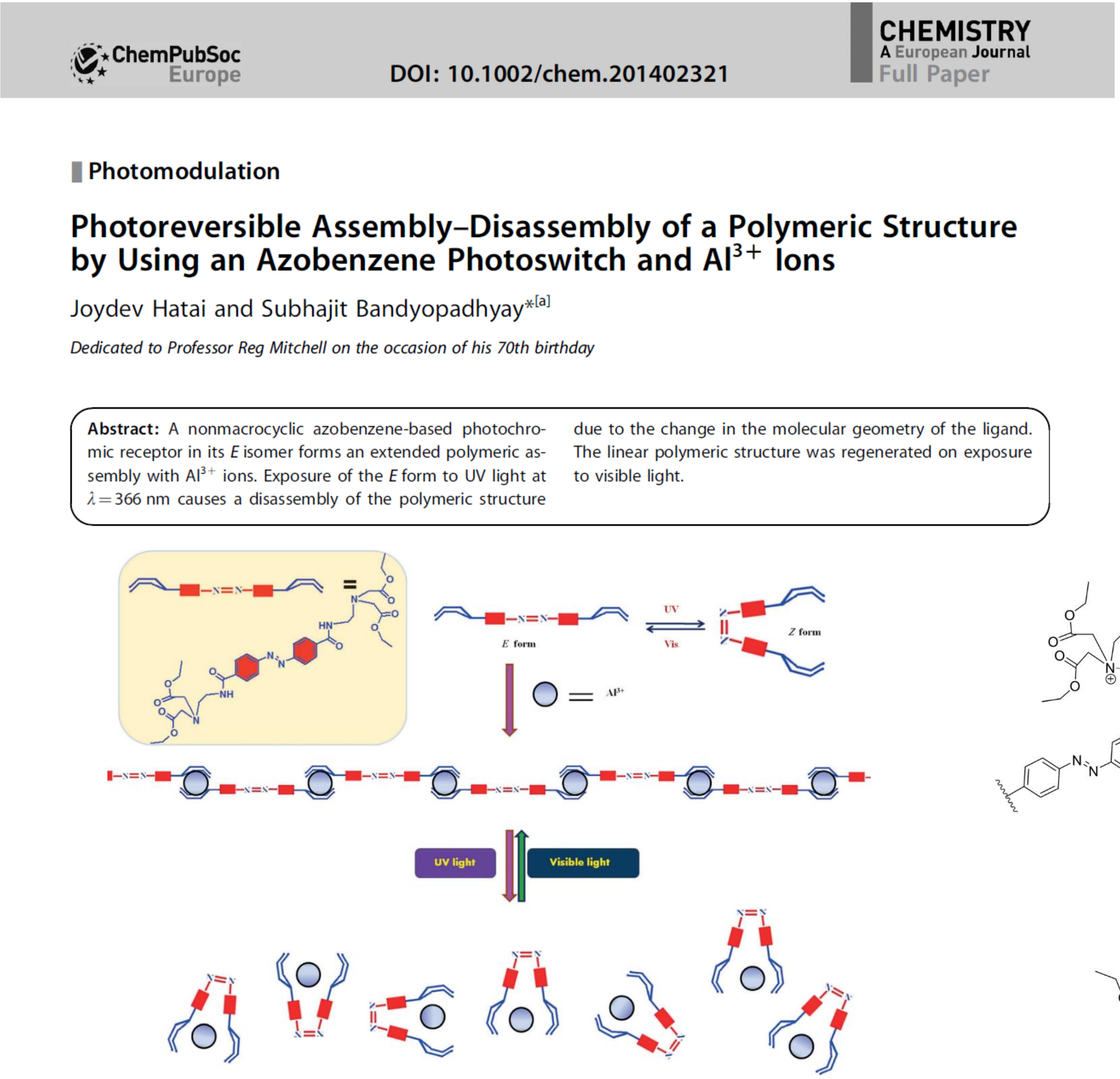


Figure 4. Zero-shear viscosity change for CD-CUR/pAC$_{12}$Azo after repeated photoirradiation with UV ($\lambda = 365$ nm) and visible light ($\lambda = 430$ nm, red line). Photoisomerization behavior of CD-CUR/pAC$_{12}$Azo in the presence of 4 equiv of $C_{12}CA_2Na_2$ (green line), TEG (blue line), and α-CD (yellow line), respectively.



ChemPubSoc Europe

DOI: 10.1002/chem.201402321

CHEMISTRY
A European Journal
Full Paper

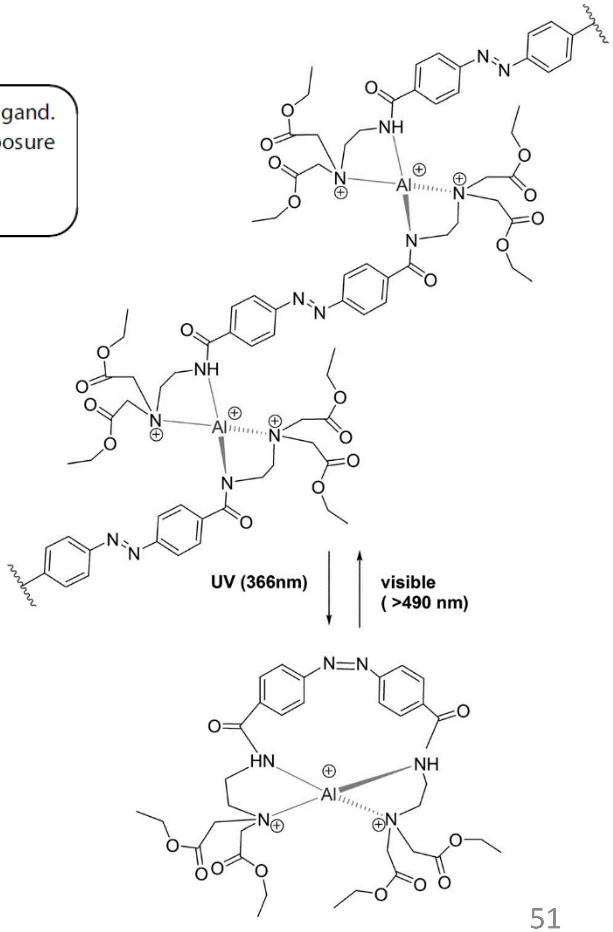
Photomodulation

Photoreversible Assembly–Disassembly of a Polymeric Structure by Using an Azobenzene Photoswitch and Al^{3+} Ions

Joydev Hatai and Subhajit Bandyopadhyay*[a]

Dedicated to Professor Reg Mitchell on the occasion of his 70th birthday

Abstract: A nonmacrocyclic azobenzene-based photochromic receptor in its *E* isomer forms an extended polymeric assembly with Al^{3+} ions. Exposure of the *E* form to UV light at $\lambda = 366$ nm causes a disassembly of the polymeric structure due to the change in the molecular geometry of the ligand. The linear polymeric structure was regenerated on exposure to visible light.



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to visible

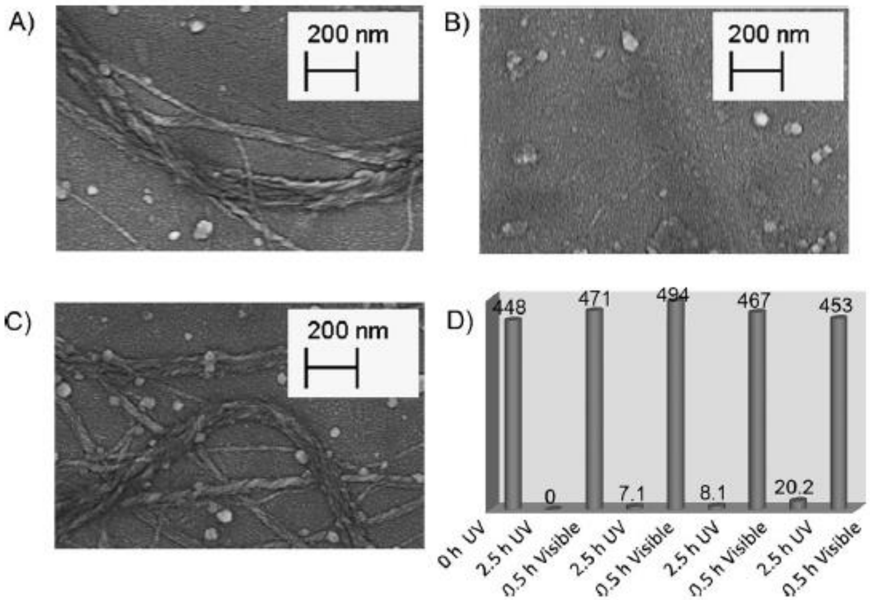

Figure 4. SEM images: A) a dried of sample *E*-**1** and Al^{3+} ions (10 μM each) in MeOH and B) a dried sample of the same solution irradiated with 8 W of UV light at $\lambda = 366$ nm for 2.5 h at 25 °C. C) The spaghetti-like structures were regenerated on irradiation with visible light ($\lambda = > 490$ nm) for 0.5 h. This change did not occur on photoirradiation of the solid samples. D) DLS studies on alternately UV- and visible-light-exposed samples containing a solution of **1** with Al^{3+} ions (10 μM each) in methanol at 25 °C. The numbers on the top of the bars indicate the hydrodynamic diameter of the samples in nanometers.

COMMUNICATION

Polymer Actuators

ADVANCED MATERIALS

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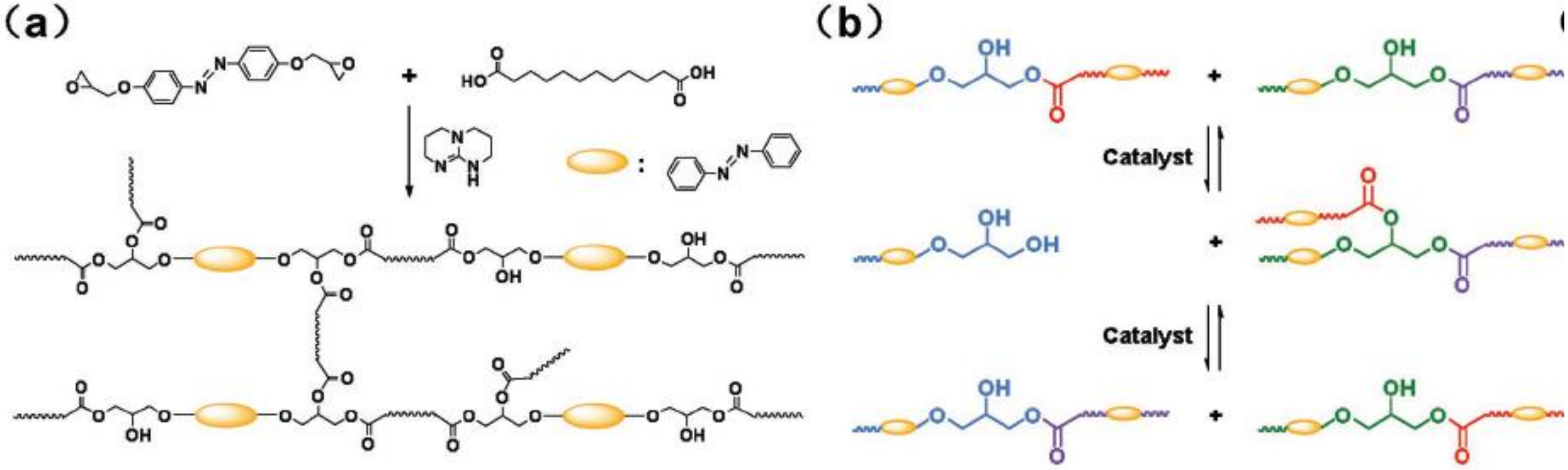
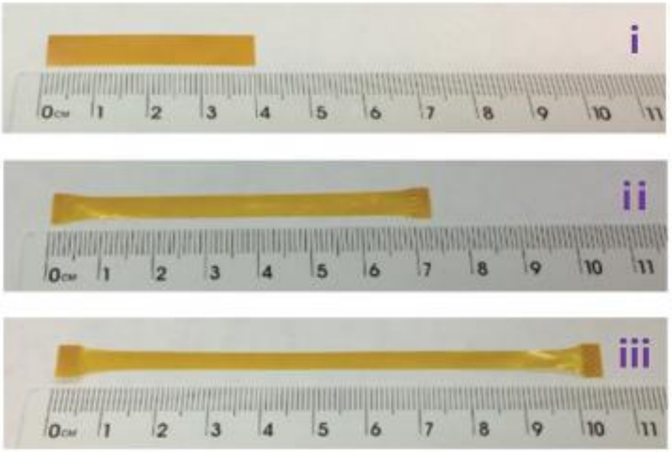
Tunable Photocontrolled Motions Using Stored Strain Energy in Malleable Azobenzene Liquid Crystalline Polymer Actuators

Xili Lu, Shengwei Guo, Xia Tong, Hesheng Xia, and Yue Zhao**





The **ligh-induced stress** is **proportional** to the pre-imposed **strain and to** the **light intensity**

COMMUNICATION

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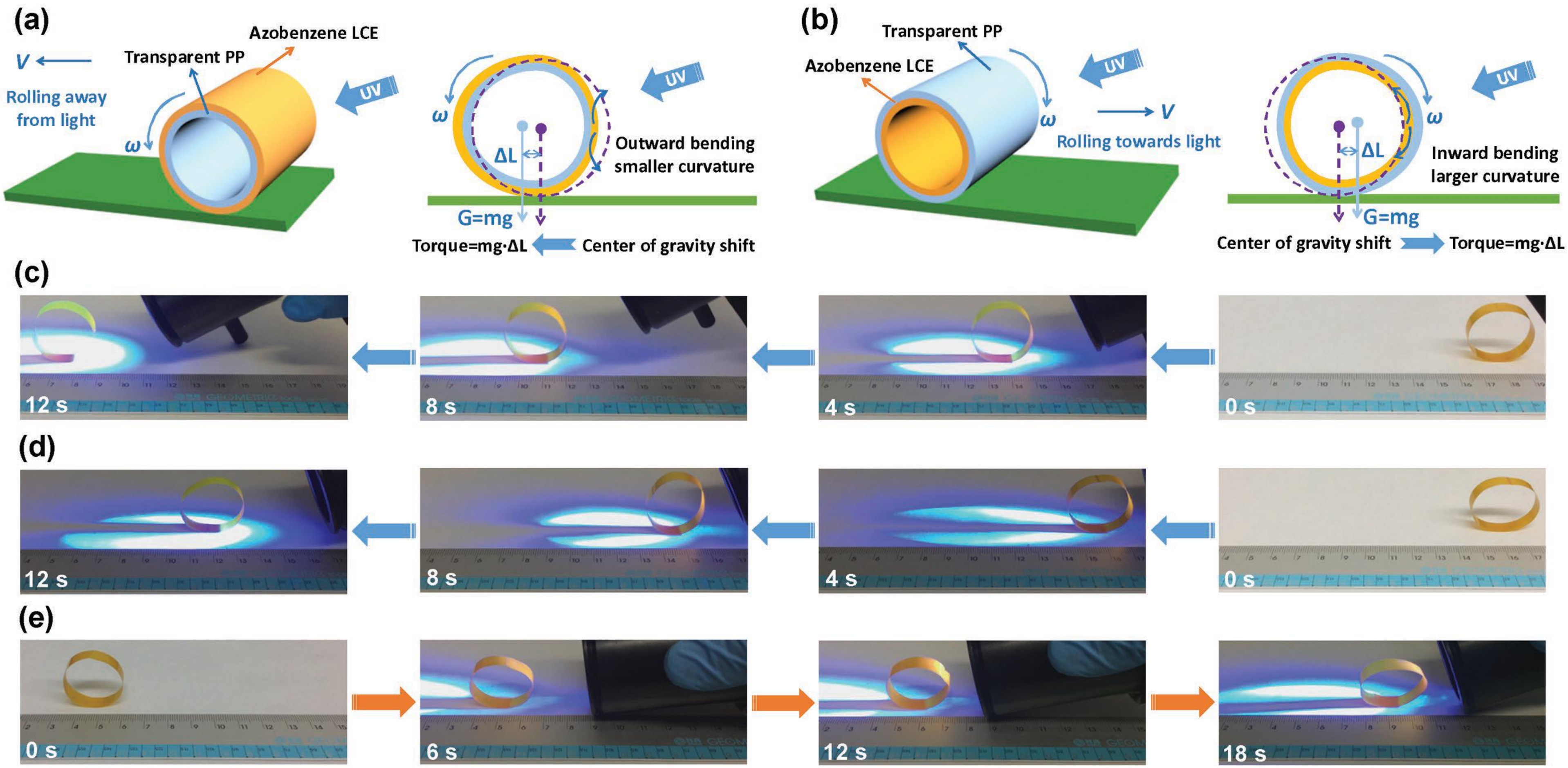
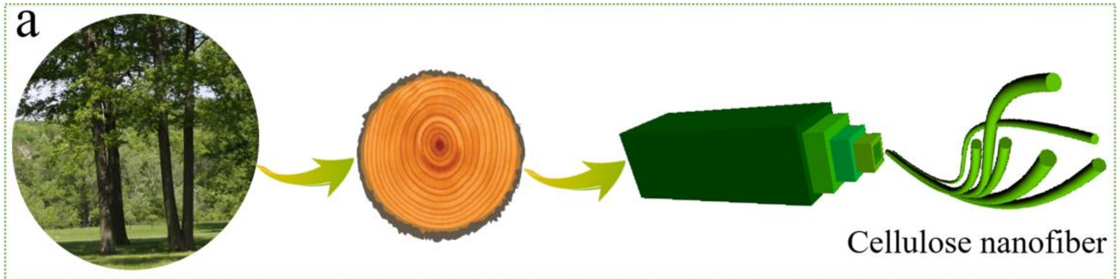


2. Photocured composites from biobased resins and cellulosic fillers

Microfibrillated Cellulose (MFC)

Cellulose: most abundant biopolymer on earth; renewable, sustainable, biodegradable.



Jiao L, et al. (2016) Natural Cellulose Nanofibers As Sustainable Enhancers in Construction Cement. PLoS ONE 11(12): e0168422.

Destructuration of cellulose sources: cellulose microfibrils (MFC), usually aqueous dispersions.

MFC films: good barrier against gases like O_2, CO_2 and N_2

Klemm, D., et al. Cellulose: Fascinating Biopolymer and Sustainable Raw Material. Angew Chem Int Ed. 44, 3358–3393 (2005)
García, A, et al. Industrial and crop wastes: A new source for nanocellulose biorefinery. Ind. Crops Prod. 93, 26–38 (2016).

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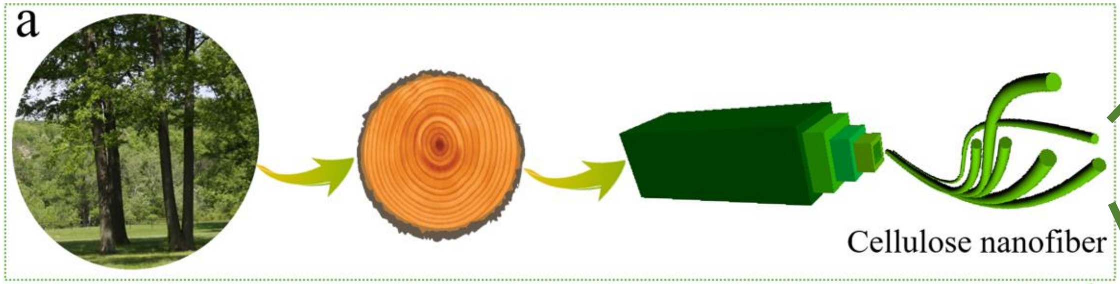
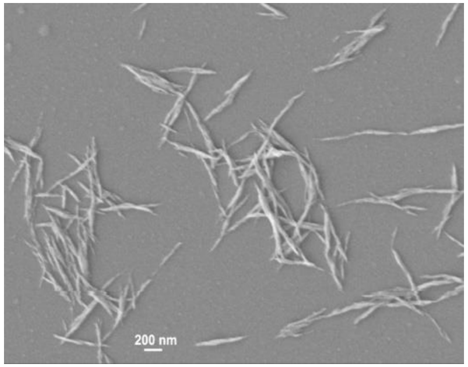
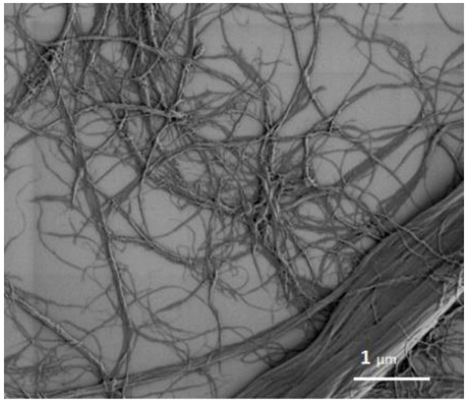


Cellulose nanocrystals (CNC)



Microfibrillated cellulose (MFC)



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García, A, et al. Industrial and crop wastes: A new source for nanocellulose biorefinery. Ind. Crops Prod. 93, 26–38 (2016).

Microfibrillated Cellulose (MFC): challenges

⚠ High hydrophilicity prevents use in highly humid environments

↓

Combine MFC with other (bio)polymers in the form of composites.

<u>water-soluble polymers:</u>

✓ processing in aqueous solution
✓ good filler dispersion
✗ poor water resistance.

<u>non water-soluble polymers</u>

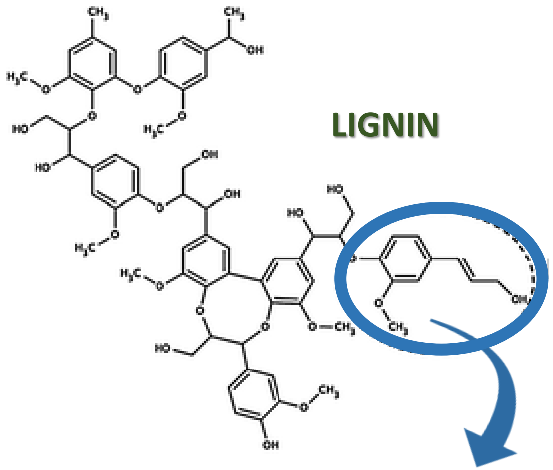
✓ improved water resistance
✗ poor MFC dispersion
✗ complex processing

Processing in organic solvent:
✗ drying / solvent exchange
✗ agglomeration of MFC

Melt compounding:
✗ high T and shear
✗ fiber surface modification

Dufresne, A. Cellulose nanomaterial reinforced polymer nanocomposites. Curr Opin Colloid Interface Sci 29, 1–8 (2017)
Hubbe, M. A. et al. Nanocellulose in Thin Films, Coatings, and Plies for Packaging Applications: A Review. BioResources 12, 2143–2233 (2017).
Oksman, K. et al. Review of the recent developments in cellulose nanocomposite processing. Compos A Appl Sci Manuf 83, 2–18 (2016)

Biobased monomers

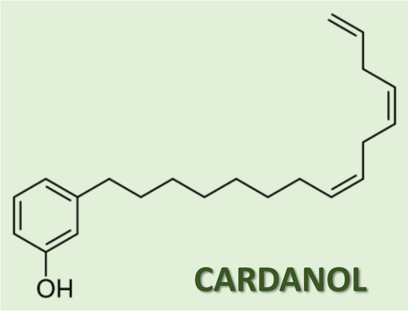


LIGNIN

CASHEW FRUIT

CASHEW SHELLS

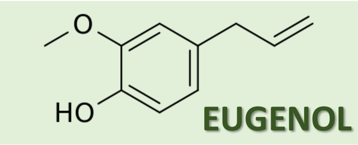
CASHEW NUTS



CARDANOL

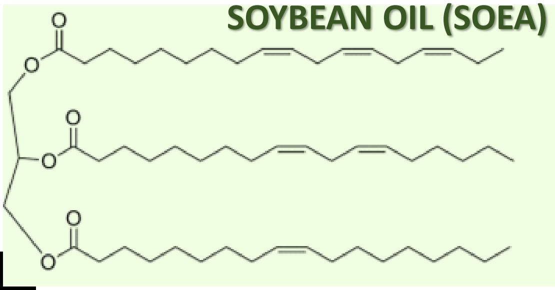
CLOVE
Bud-Leaf-Stem

CLOVE OIL



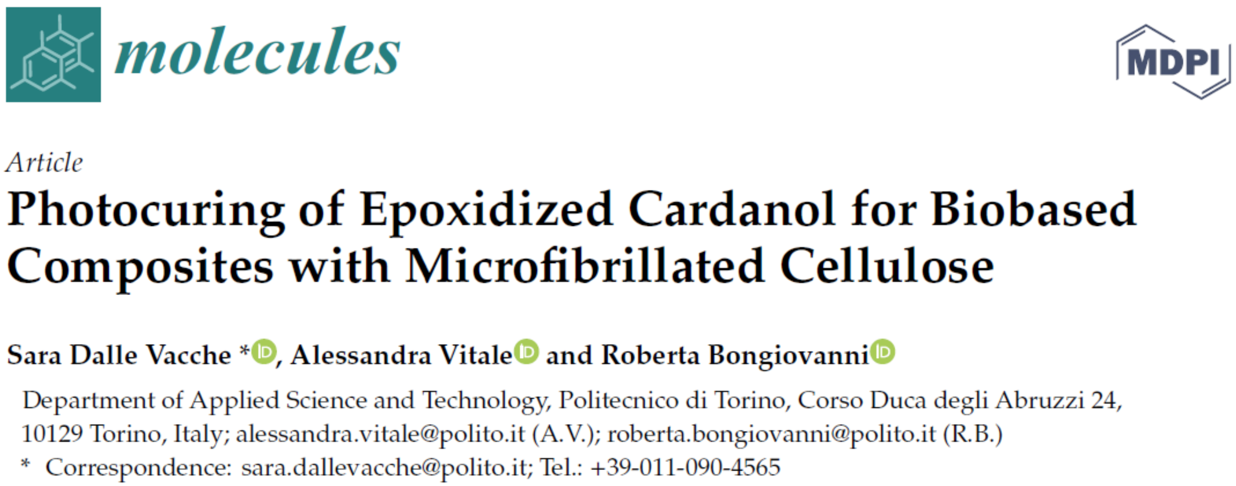
EUGENOL

VEGETABLE OILS
(soybean, linseed…)



SOYBEAN OIL (SOEA)

Composites: solvent-exchange process



molecules

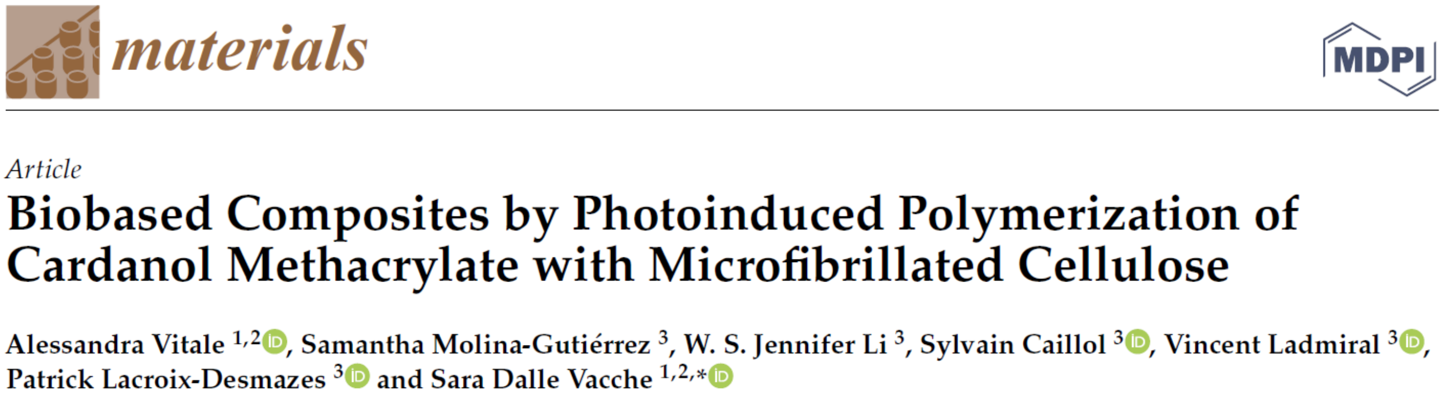
MDPI

Article

Photocuring of Epoxidized Cardanol for Biobased Composites with Microfibrillated Cellulose

Sara Dalle Vacche *, Alessandra Vitale and Roberta Bongiovanni

Department of Applied Science and Technology, Politecnico di Torino, Corso Duca degli Abruzzi 24,
10129 Torino, Italy; alessandra.vitale@polito.it (A.V.); roberta.bongiovanni@polito.it (R.B.)
* Correspondence: sara.dallevacche@polito.it; Tel.: +39-011-090-4565



materials

MDPI

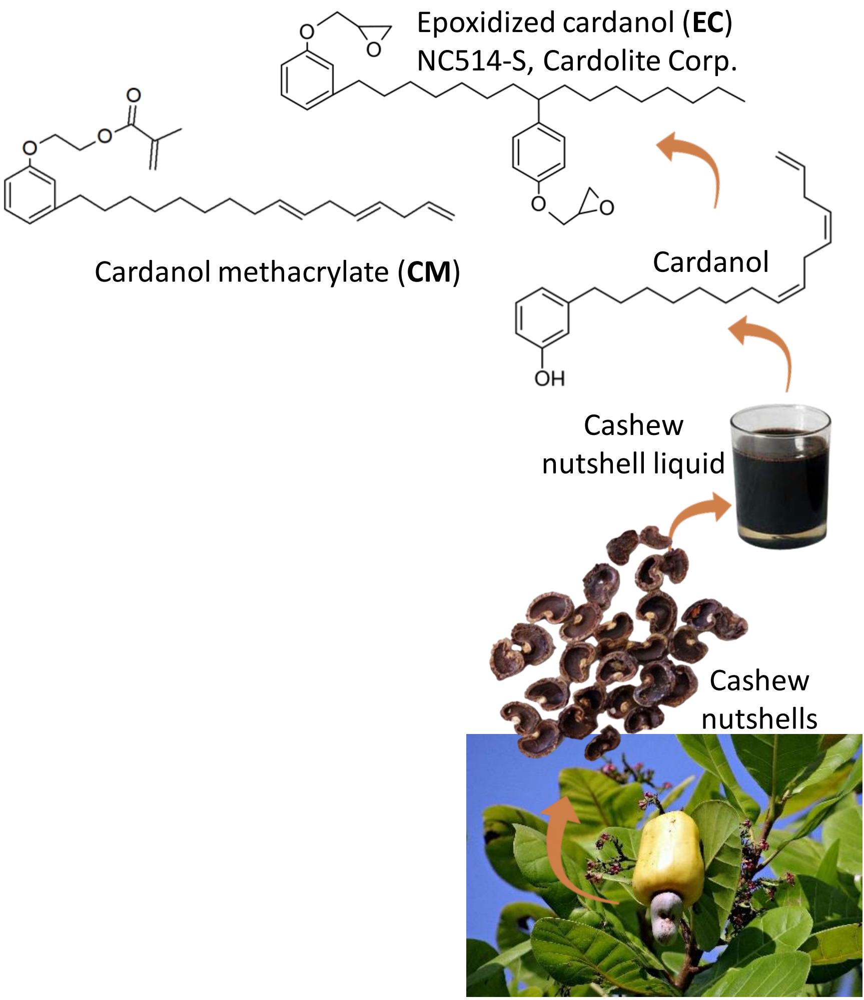
Article

Biobased Composites by Photoinduced Polymerization of Cardanol Methacrylate with Microfibrillated Cellulose

Alessandra Vitale [1,2], Samantha Molina-Gutiérrez [3], W. S. Jennifer Li [3], Sylvain Caillol [3], Vincent Ladmiral [3], Patrick Lacroix-Desmazes [3] and Sara Dalle Vacche [1,2,*]

Molecules **2019**, 24, 3858
Materials **2022**, 15, 339.

Cellulose + cardanol based photocurable resin



Epoxidized cardanol (**EC**)
NC514-S, Cardolite Corp.

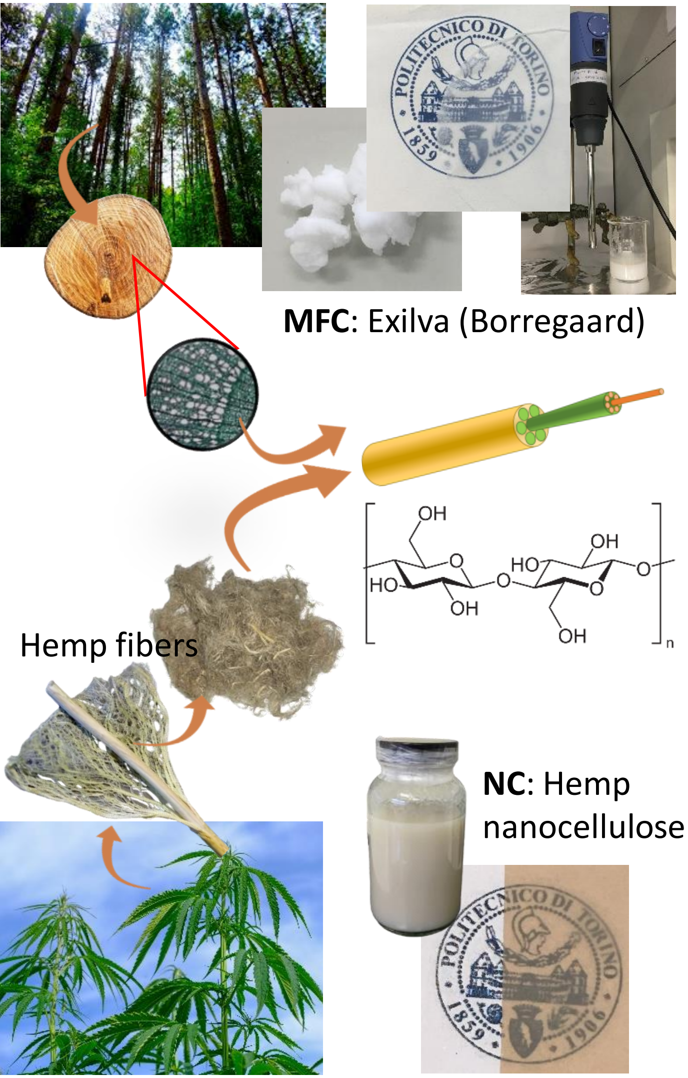
Cardanol methacrylate (**CM**)

Cardanol

Cashew
nutshell liquid

Cashew
nutshells

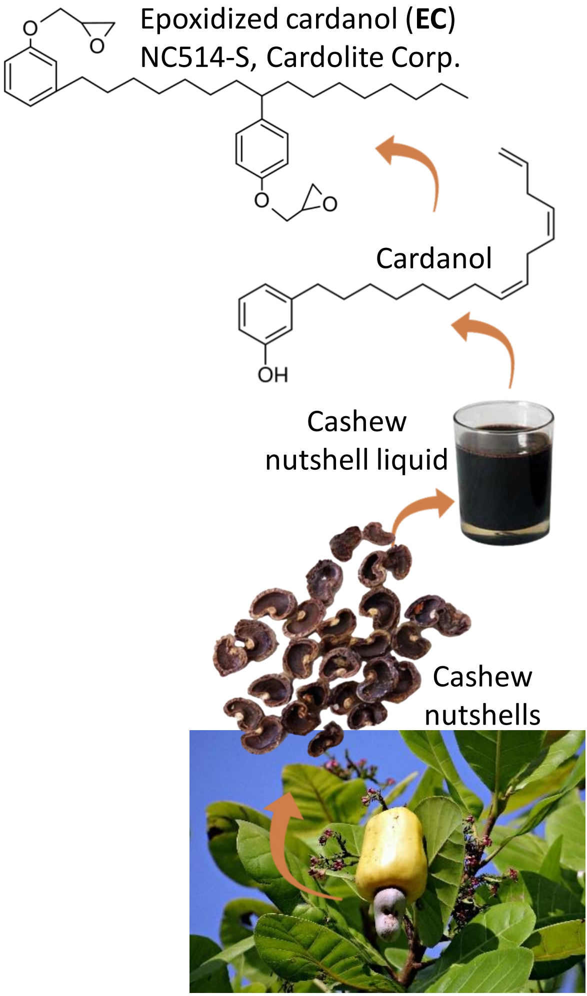
Cellulose + cardanol based photocurable resin



MFC: Exilva (Borregaard)

Hemp fibers

NC: Hemp nanocellulose



Epoxidized cardanol (**EC**)
NC514-S, Cardolite Corp.

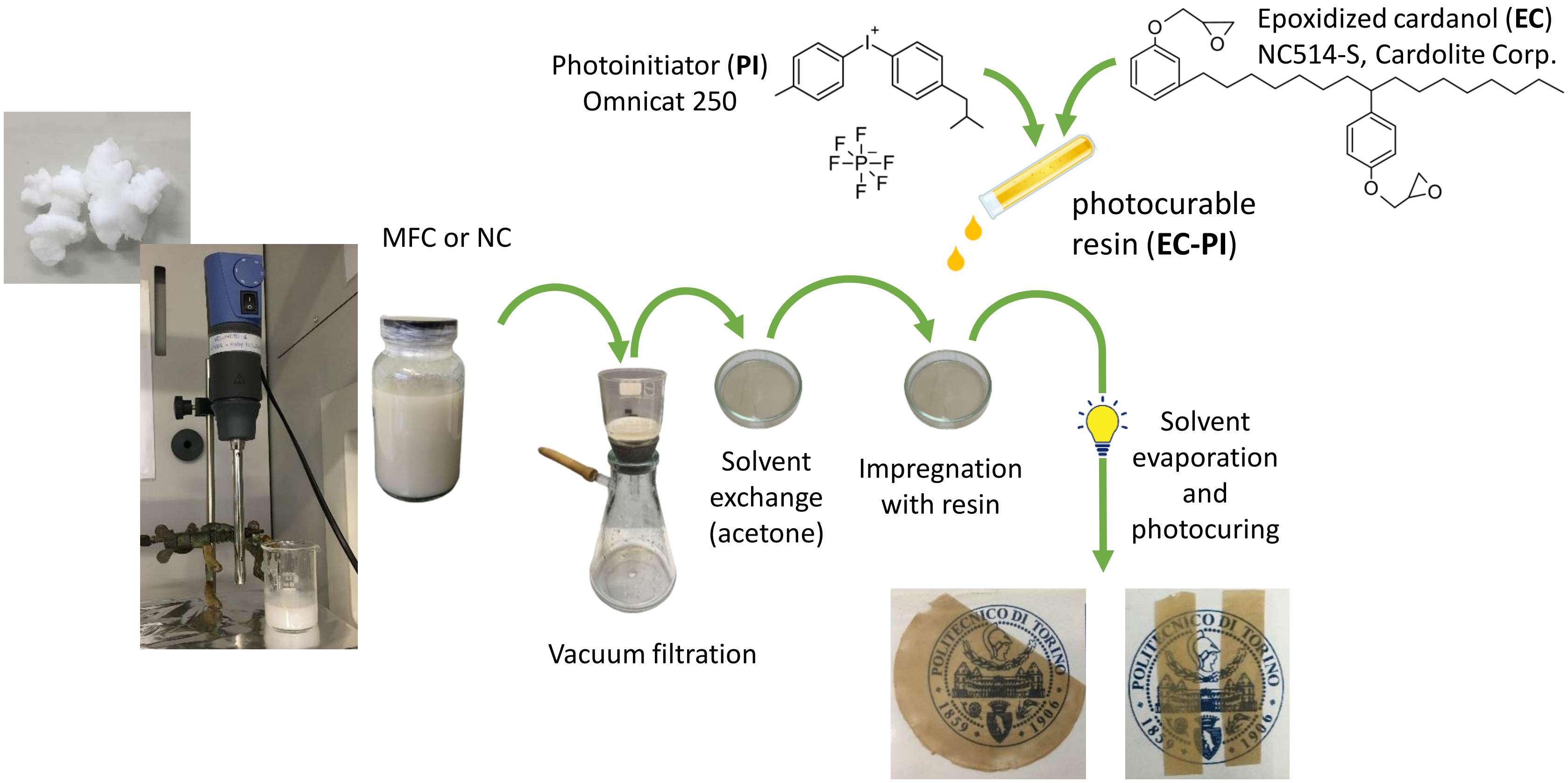
Cardanol

Cashew nutshell liquid

Cashew nutshells

Cellulose + cardanol based photocurable resin

S. Dalle Vacche et al. *Molecules* **2019**, *24*(21), 3858 ; *J. Compos. Sci* **2021**, *5*(1), 11



Photoinitiator (**PI**)
Omnicat 250

Epoxidized cardanol (**EC**)
NC514-S, Cardolite Corp.

photocurable
resin (**EC-PI**)

MFC or NC

Vacuum filtration

Solvent
exchange
(acetone)

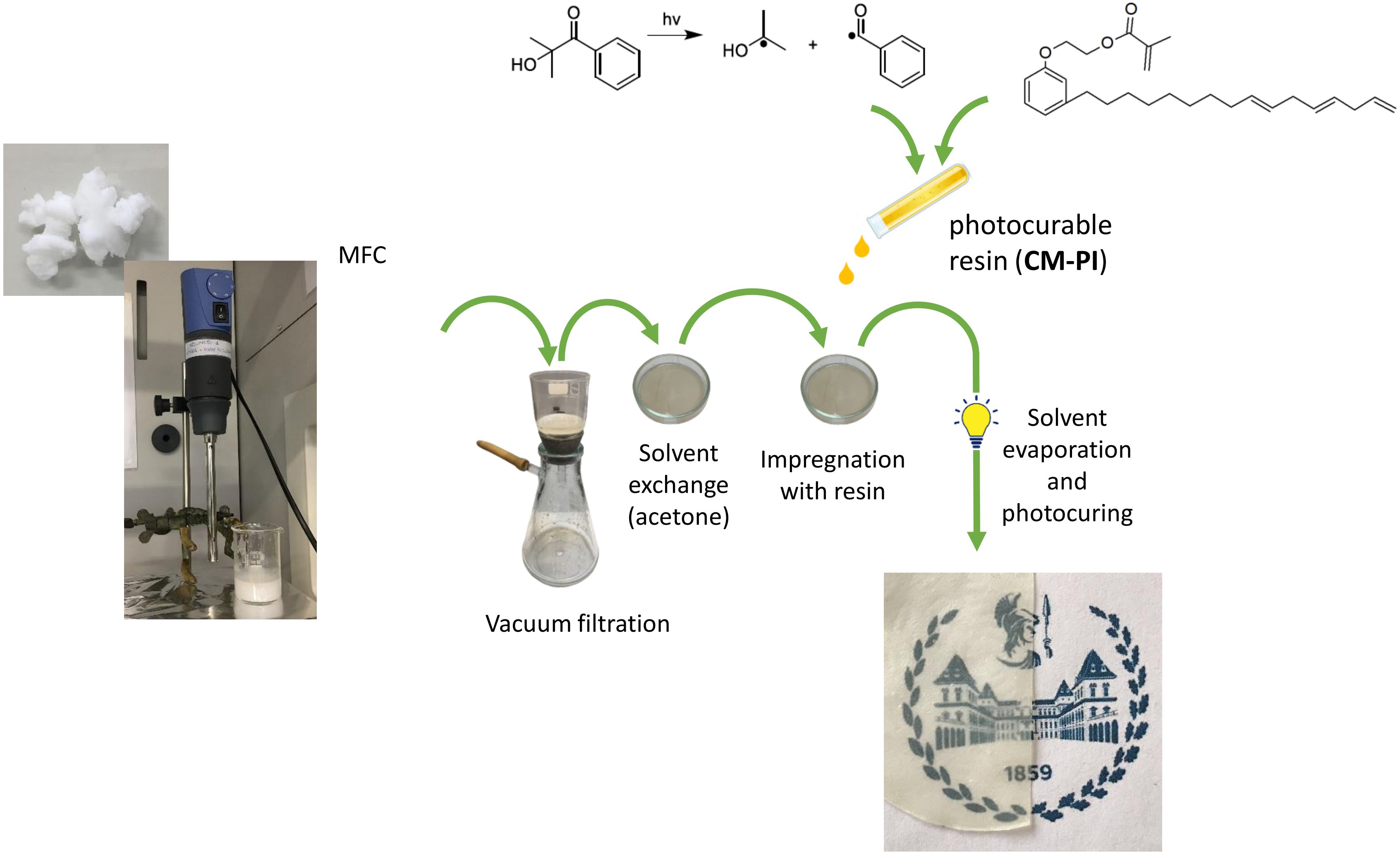
Impregnation
with resin

Solvent
evaporation
and
photocuring

EC-MFC

EC-NC

Cellulose + cardanol based photocurable resin



MFC

photocurable resin (**CM-PI**)

Vacuum filtration

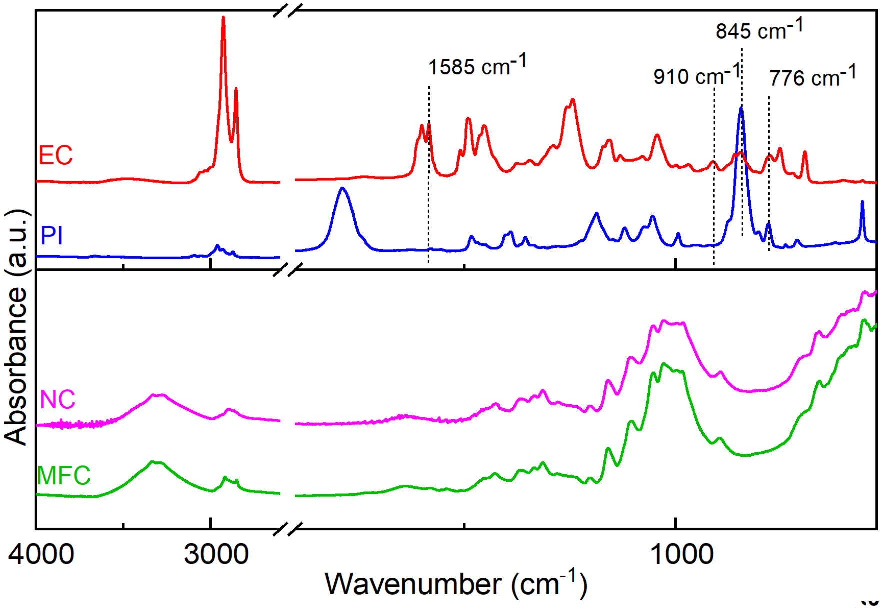
Solvent exchange (acetone)

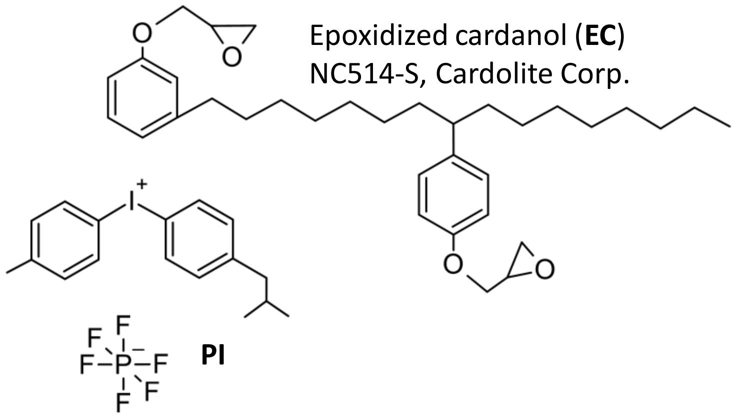
Impregnation with resin

Solvent evaporation and photocuring

Cationic photocuring of EC

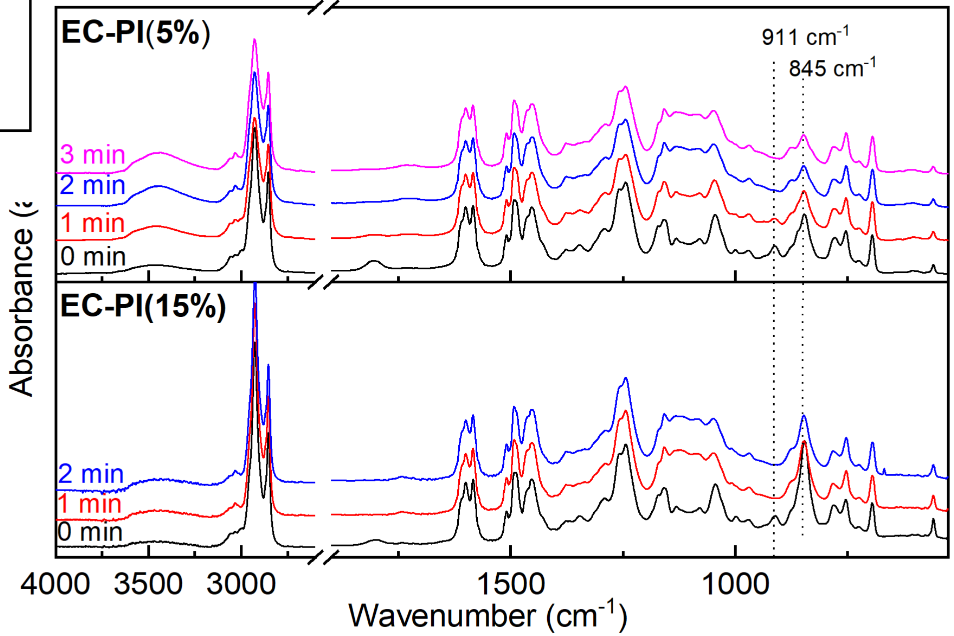
S. Dalle Vacche et al. *Molecules* **2019**, *24*(21), 3858
S. Dalle Vacche et al. *J. Compos. Sci* **2021**, *5*(1), 11





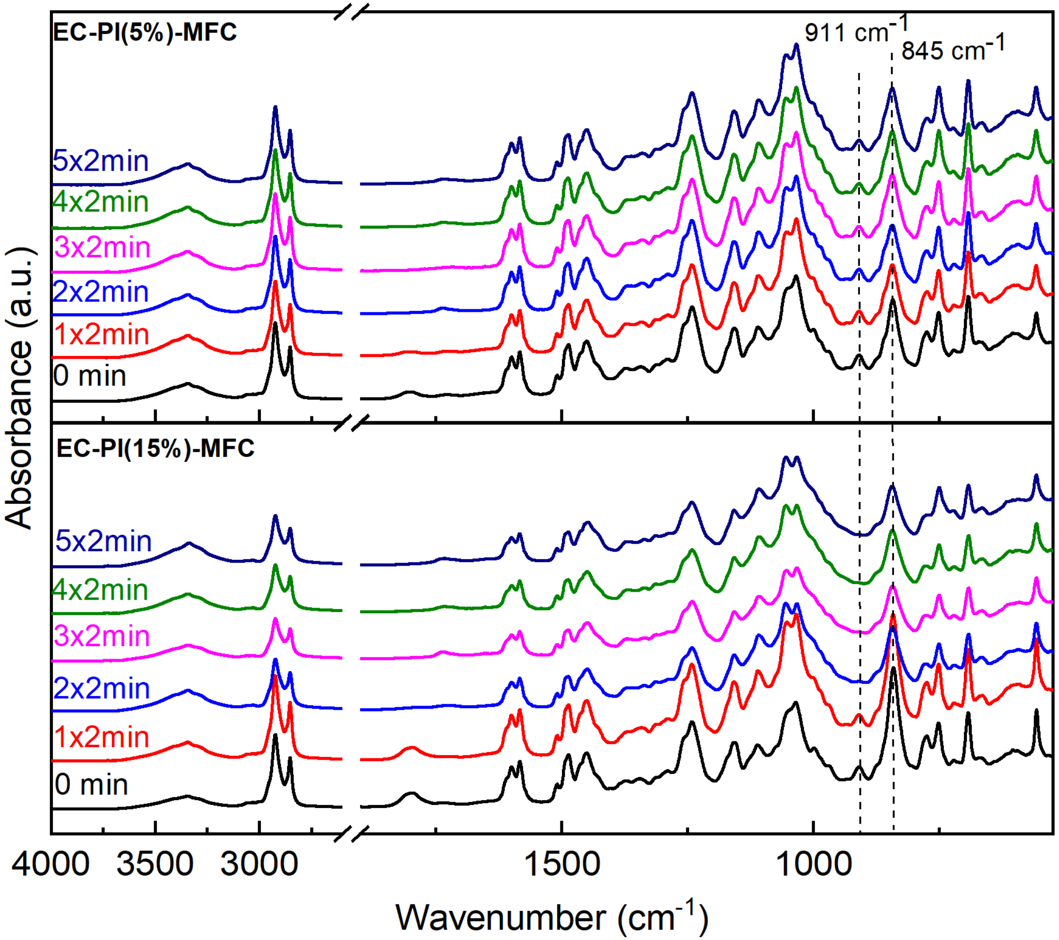
Epoxidized cardanol (**EC**)
NC514-S, Cardolite Corp.

PI



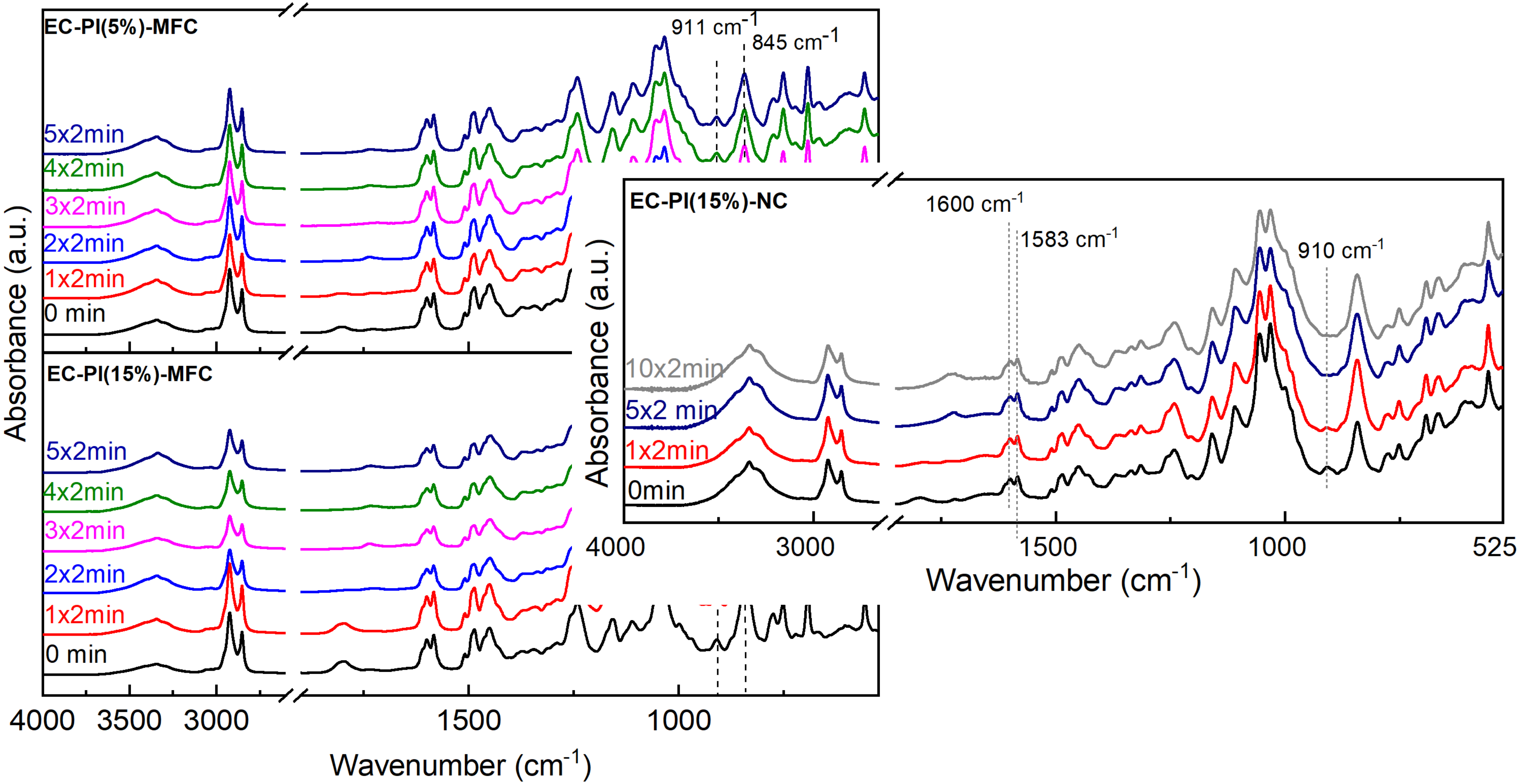
Curing complete within 2 min for 5% PI and within 1 min for 15% PI

Cationic photocuring of EC composites



S. Dalle Vacche et al. *Molecules* **2019**, *24*(21), 3858
S. Dalle Vacche et al. *J. Compos. Sci* **2021**, *5*(1), 11

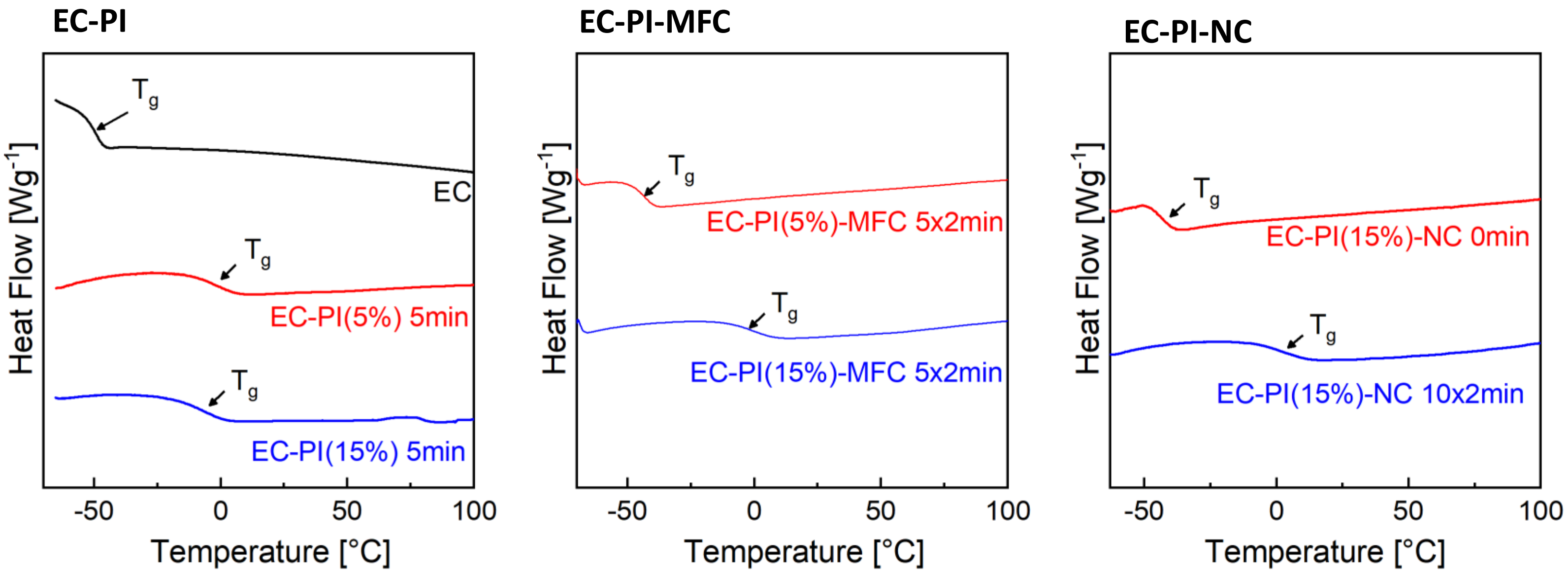
Cationic photocuring of EC composites



Need 15% PI (!) to complete curing within 2 to 5 min of irradiation per side

S. Dalle Vacche et al. *Molecules* **2019**, *24*(21), 3858
S. Dalle Vacche et al. *J. Compos. Sci* **2021**, *5*(1), 11

EC composites : glass transition temperature (T_g)



T_g : -49°C → ca. 0°C

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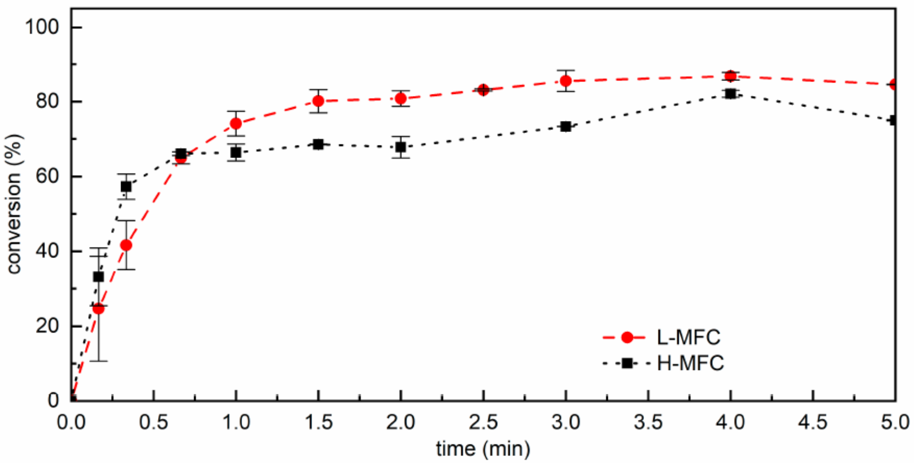
Radical photocuring of CM composites



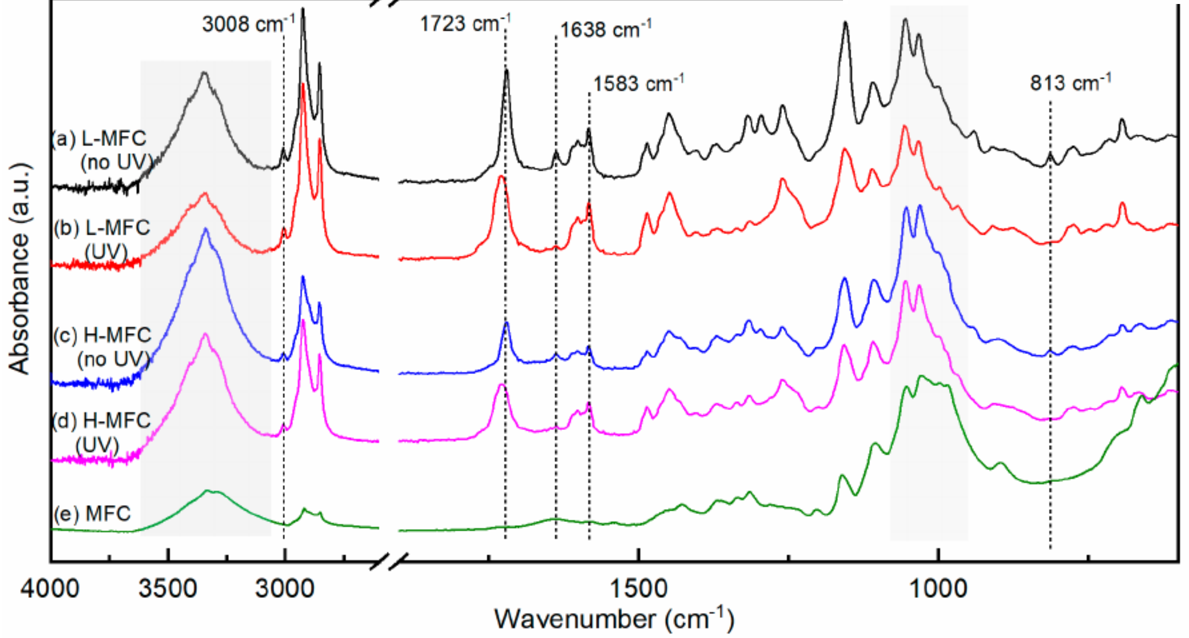
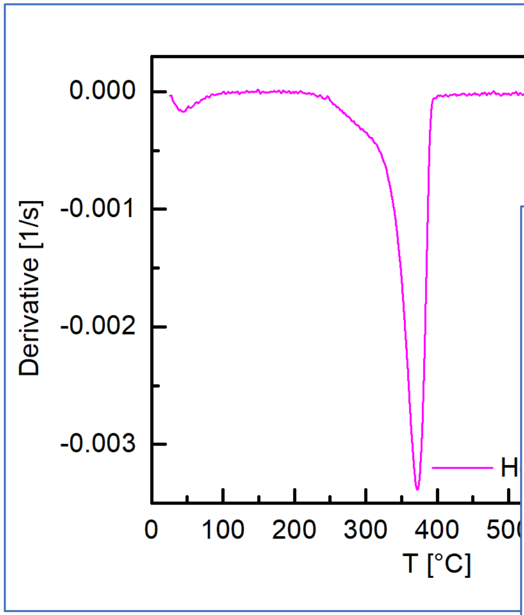
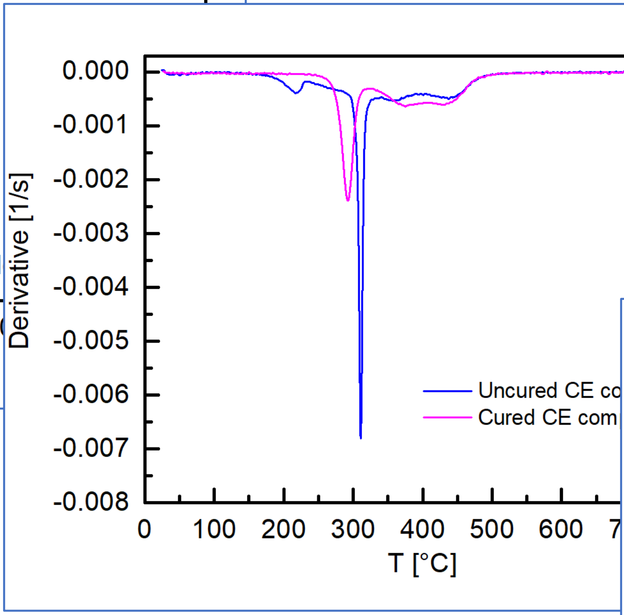


Figure 6. FTIR spectra acquired in ATR mode of: (**a**,**b**) L-MFC and H-MFC before irradiation (**c**,**d**) L-MFC and H-MFC after irradiation under nitrogen for 5 min at 100 mW cm^{-2}; (**e**) dry MFC.

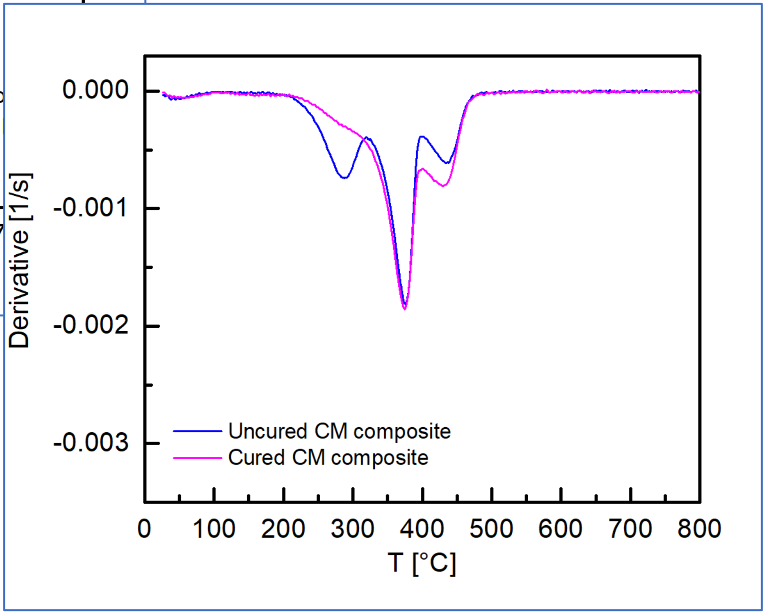
A. Vitale et al., Materials **2022**, 15, 339.

Thermal stability of cardanol based composites





Cationic photocuring: cellulose decomposition shifts to lower temperature



Radical photocuring: cellulose decomposition temperature does not change

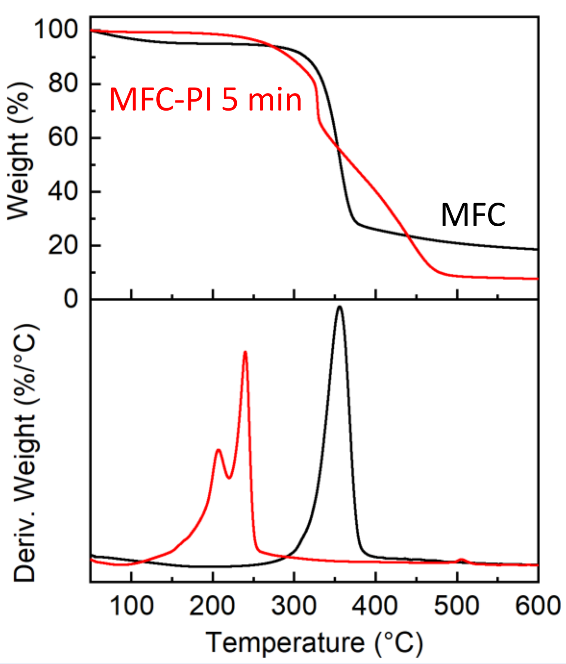
S. Dalle Vacche et al. *Molecules* **2019**, *24*(21), 3858
S. Dalle Vacche et al. *J. Compos. Sci* **2021**, *5*(1), 11
A. Vitale et al., Materials **2022**, 15, 339.

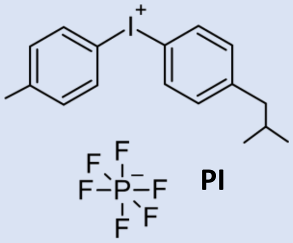
Cationically photocured composites

- Higher amount of photoinitiator
- Lower thermal stability of cellulose

?

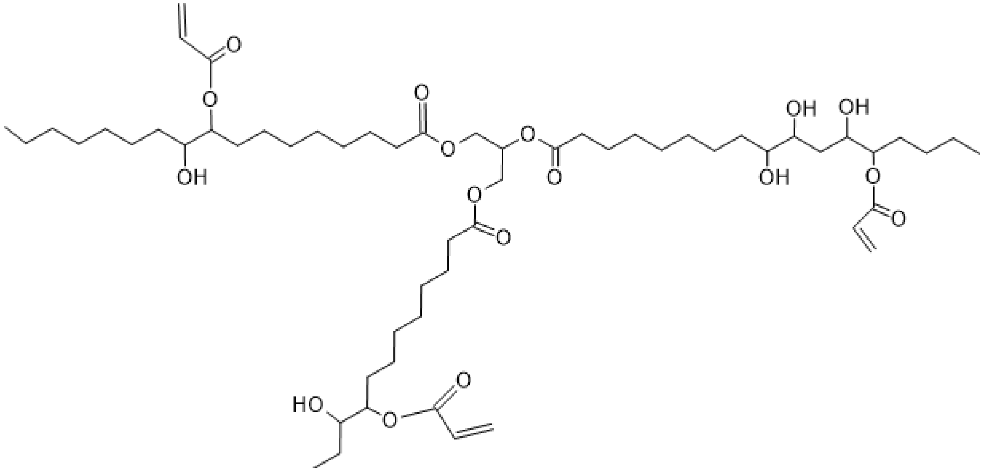
UV irradiation of MFC impregnated with PI (MFC-PI)



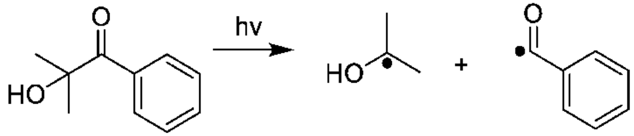


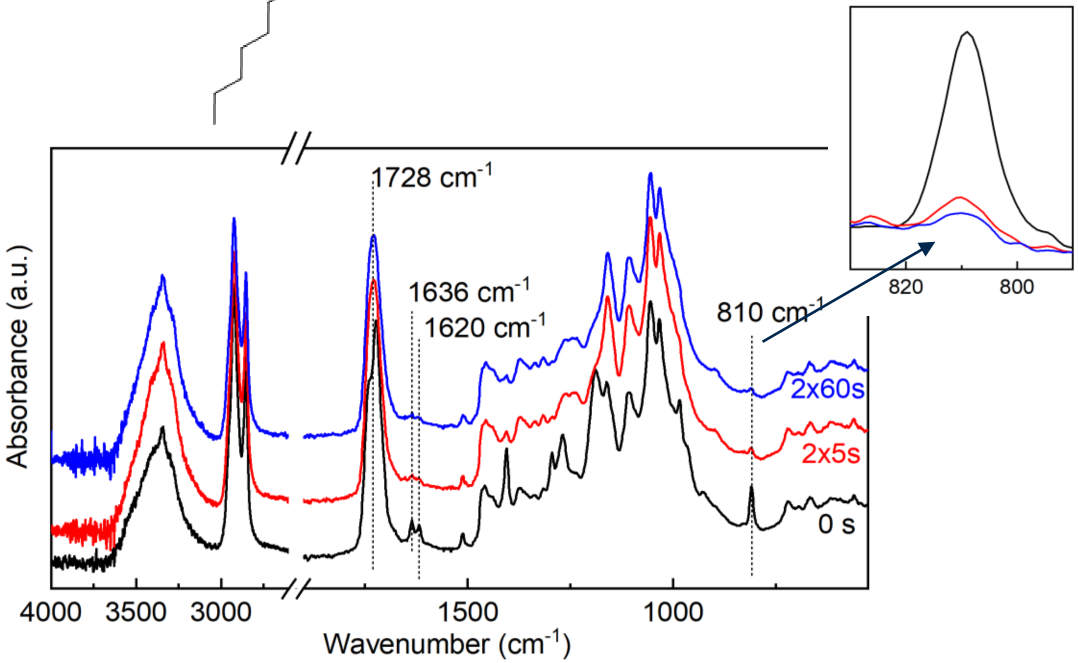
PI

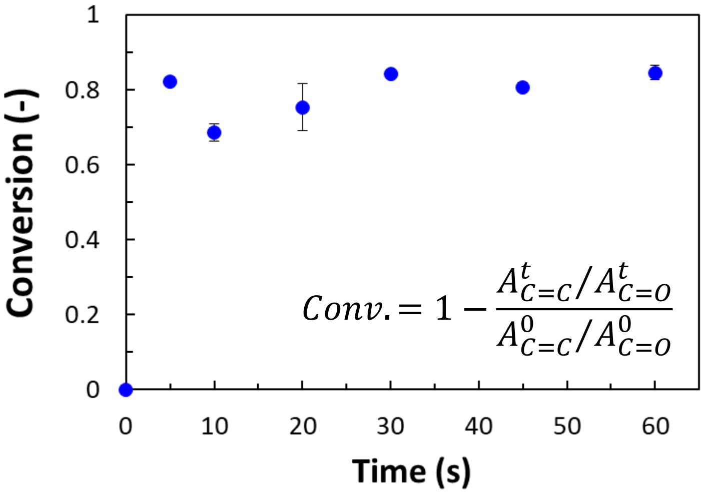
Photocuring of SOEA-PI composites



PI: Darocur 1173 (2%)





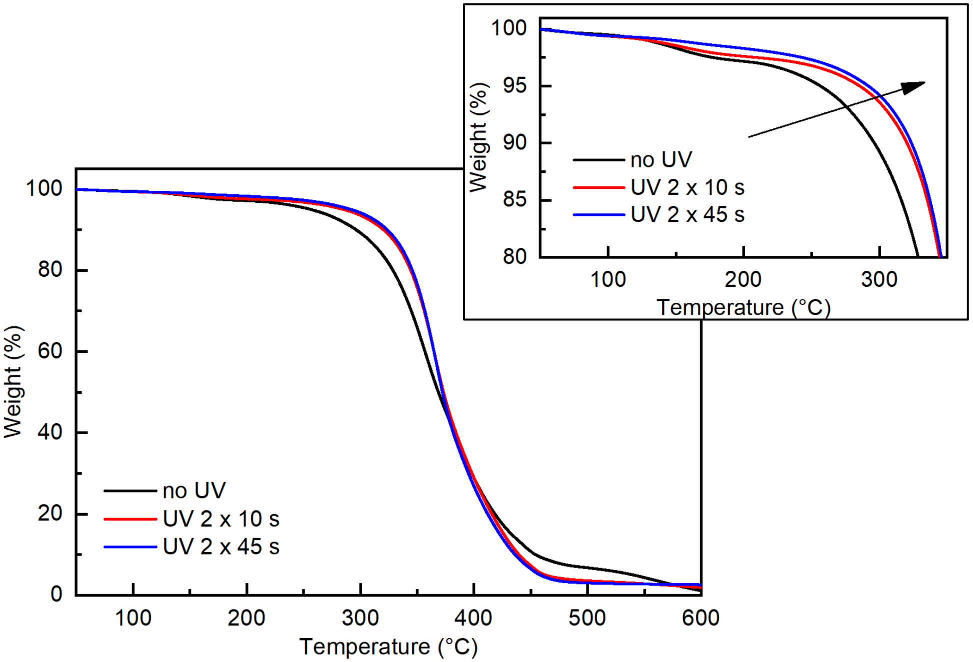


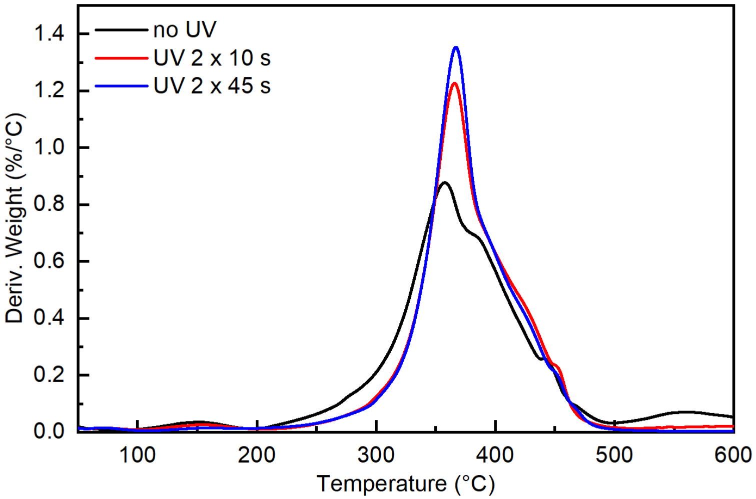
$$Conv. = 1 - \frac{A^t_{C=C}/A^t_{C=O}}{A^0_{C=C}/A^0_{C=O}}$$

Conversion reaches its maximum within seconds, the cellulosic filler does not hinder the polymerization reaction

Dalle Vacche, unpublished

Thermal stability of SOEA composites

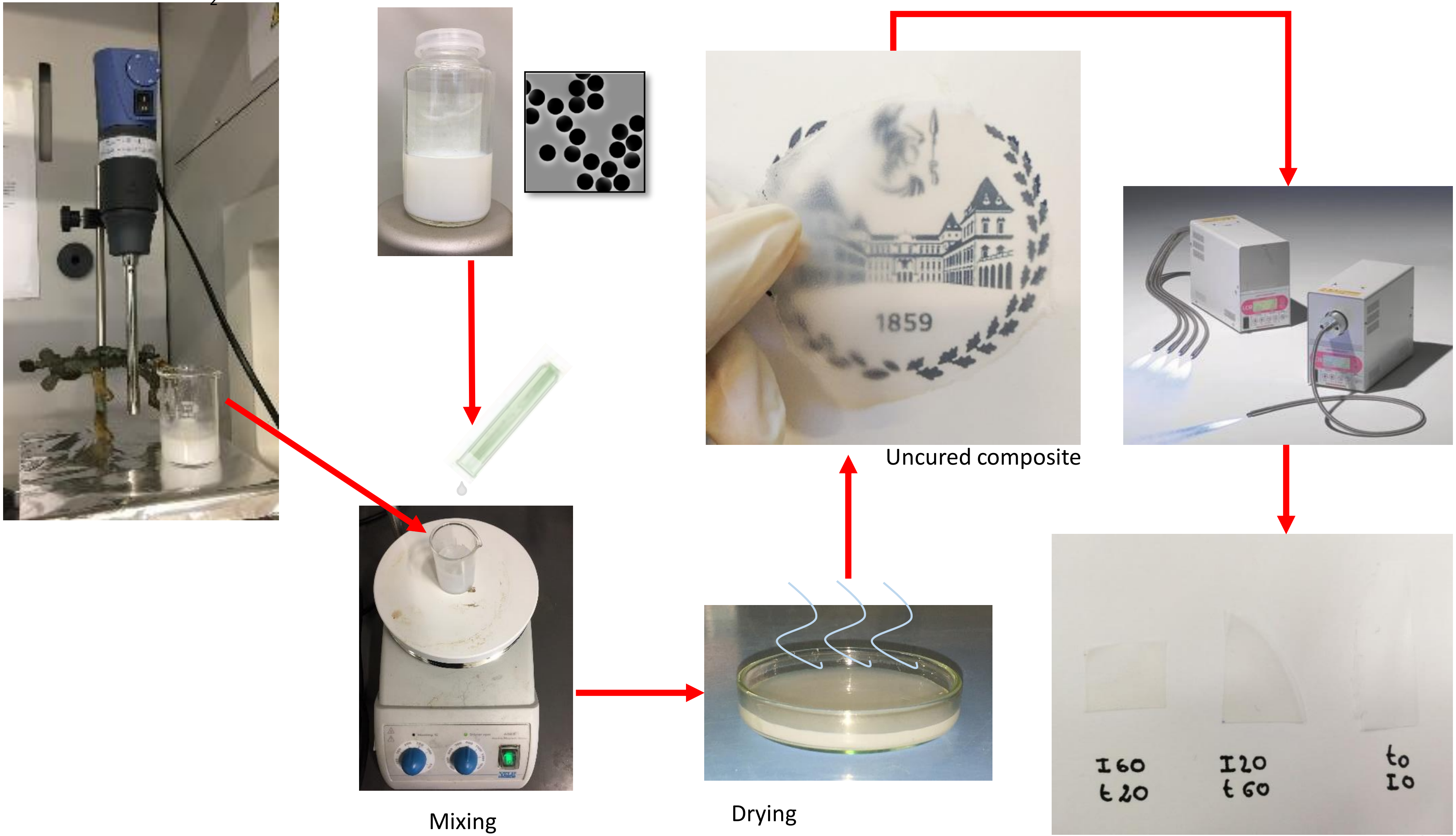




The onset of thermodegradation shifts to higher temperatures with curing
The maximum weight loss rate temperature for cellulose degradation slightly increases

Dalle Vacche, unpublished

Composites: latex-based process



Dilute MFC in H_2O

Poly(EDMA-*co*-CMA) Latex

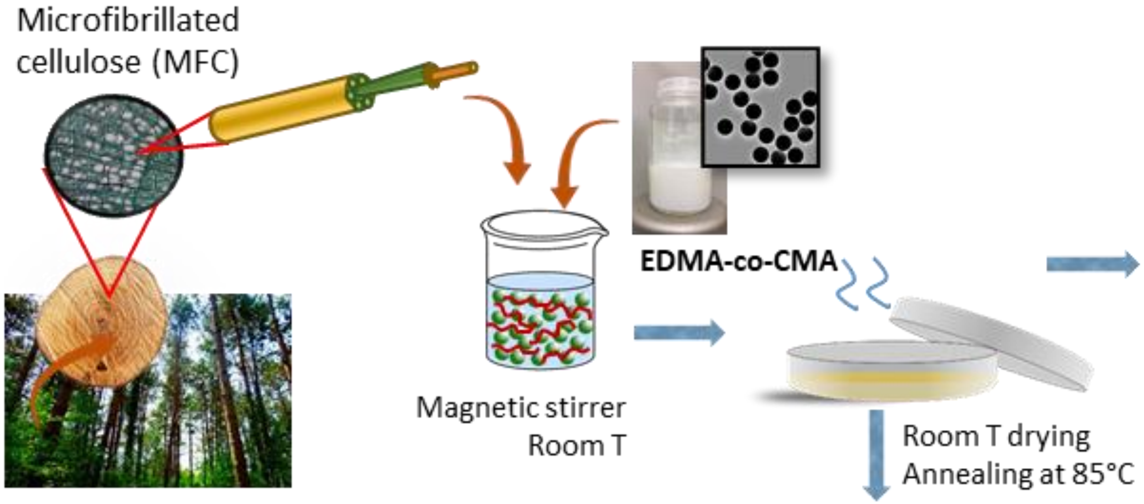
Mixing

Drying

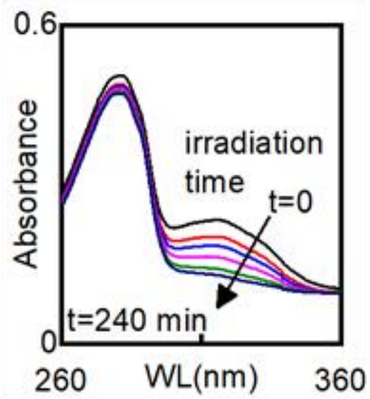
Uncured composite

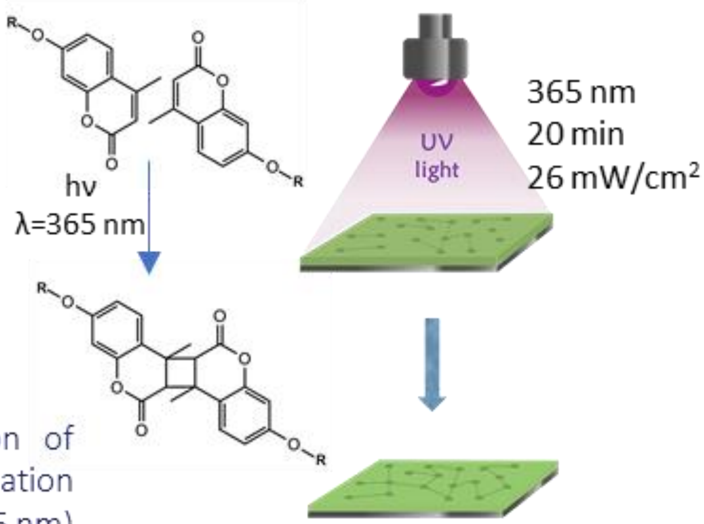
Dalle Vacche et al. submitted to Chemical Engineering Transactions

Biobased composites by photocycloaddition

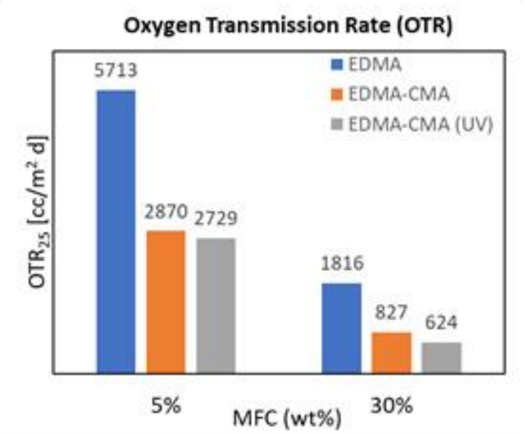


The composites were transparent, with a homogeneous distribution of MFC





Photochemical cycloaddition of coumarin upon irradiation (absorbance decrease at 315 nm)

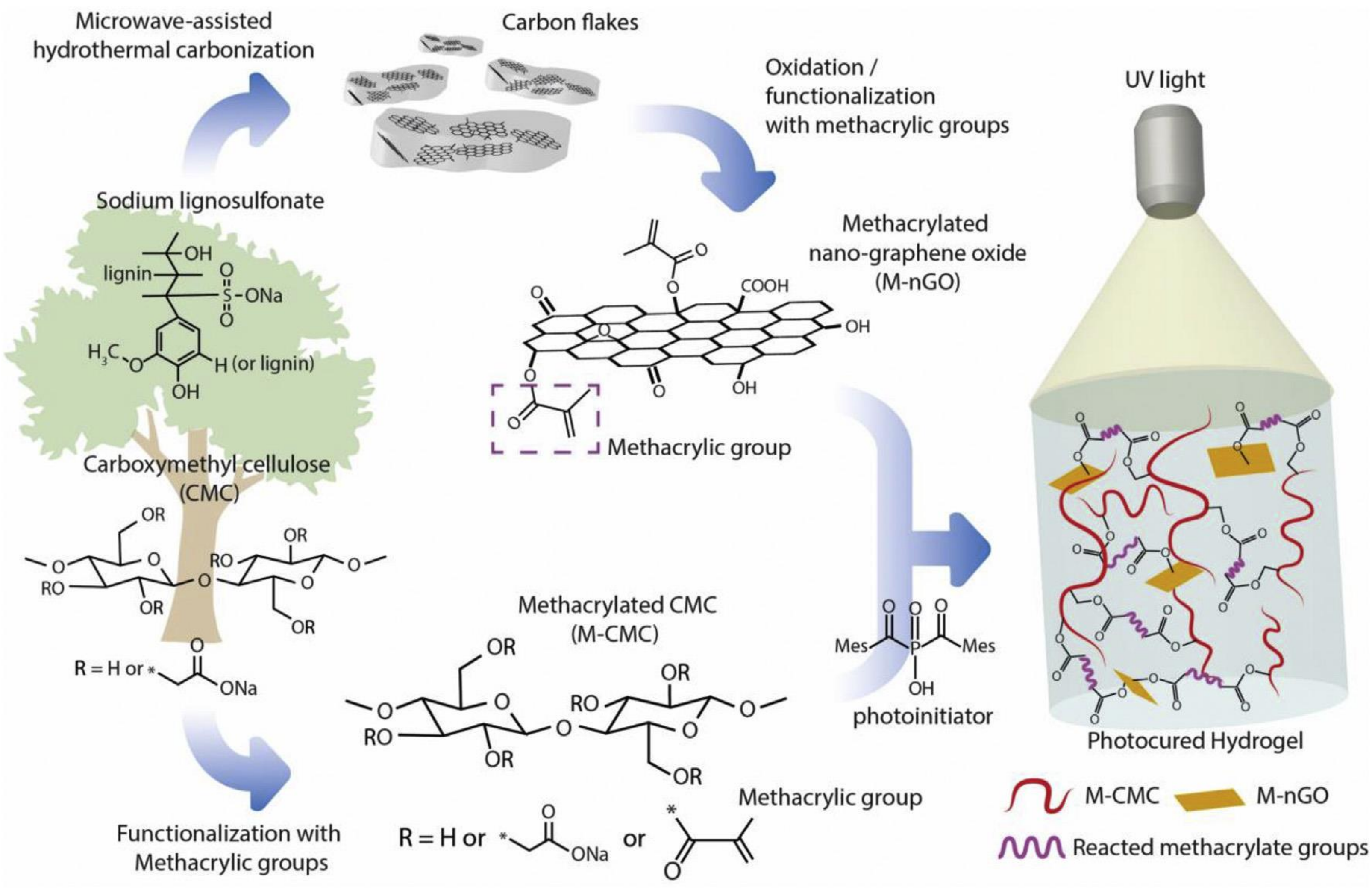


The Oxygen Transmission rate was measured at 23 °C and 50% RH

About 25% reversibility upon irradiation at 254 nm

Dalle Vacche et al. submitted to Chemical Engineering Transactions

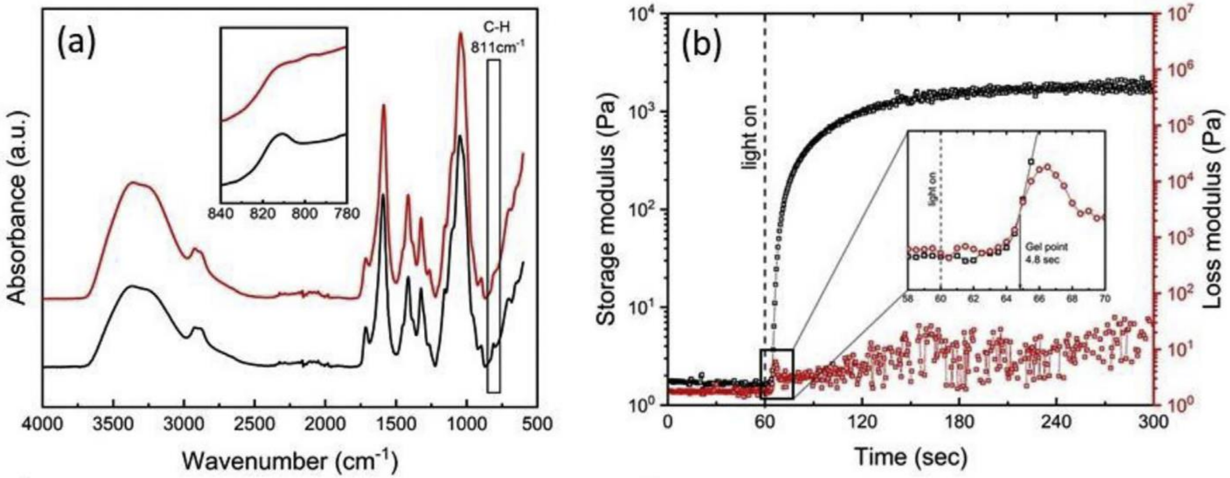
Photocured all lignocellulose nanocomposites



Melilli et al. Sustainable Materials and Technologies 27 (2021) e00243

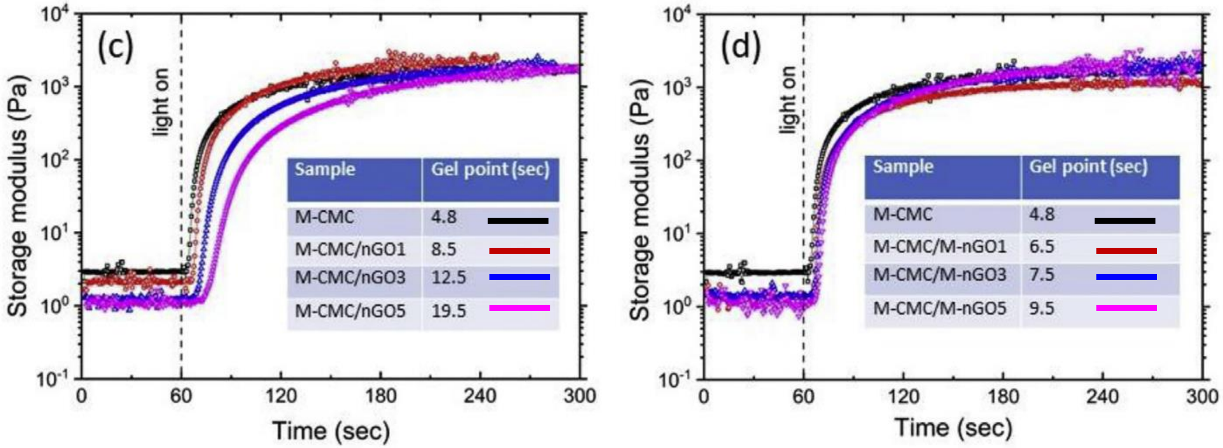
Photocured all lignocellulose nanocomposites

Resin



Resin
Gel point: 4.8 s
Max conversion: 120 s

Composites with
pristine nGO



Sample	Gel point (sec)	
M-CMC	4.8	▬
M-CMC/nGO1	8.5	▬
M-CMC/nGO3	12.5	▬
M-CMC/nGO5	19.5	▬

Sample	Gel point (sec)	
M-CMC	4.8	▬
M-CMC/M-nGO1	6.5	▬
M-CMC/M-nGO3	7.5	▬
M-CMC/M-nGO5	9.5	▬

Composites with
methacrylated nGO

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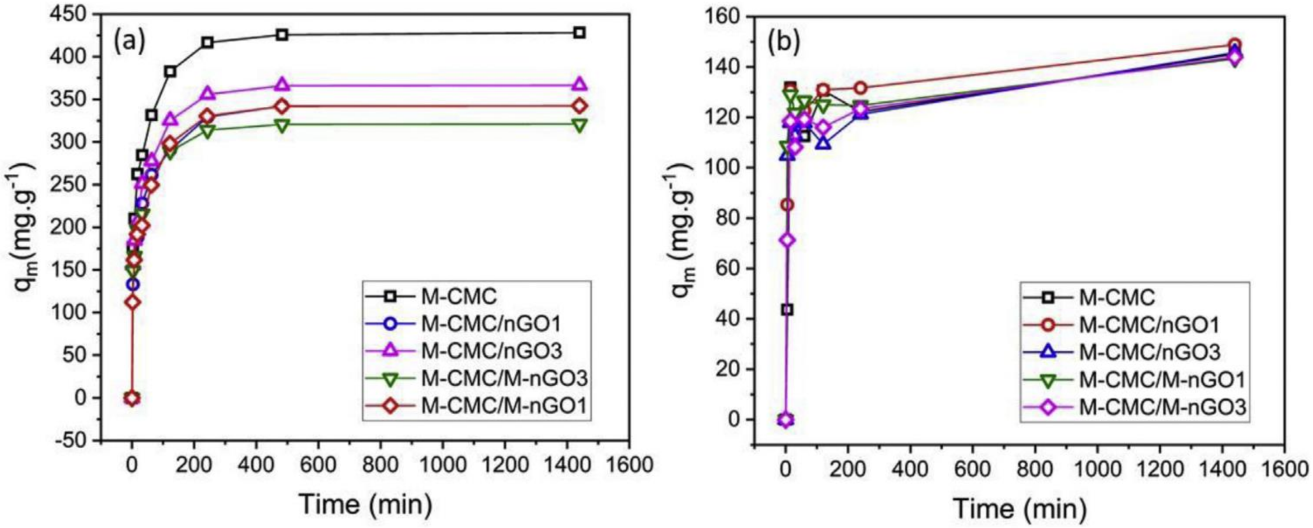
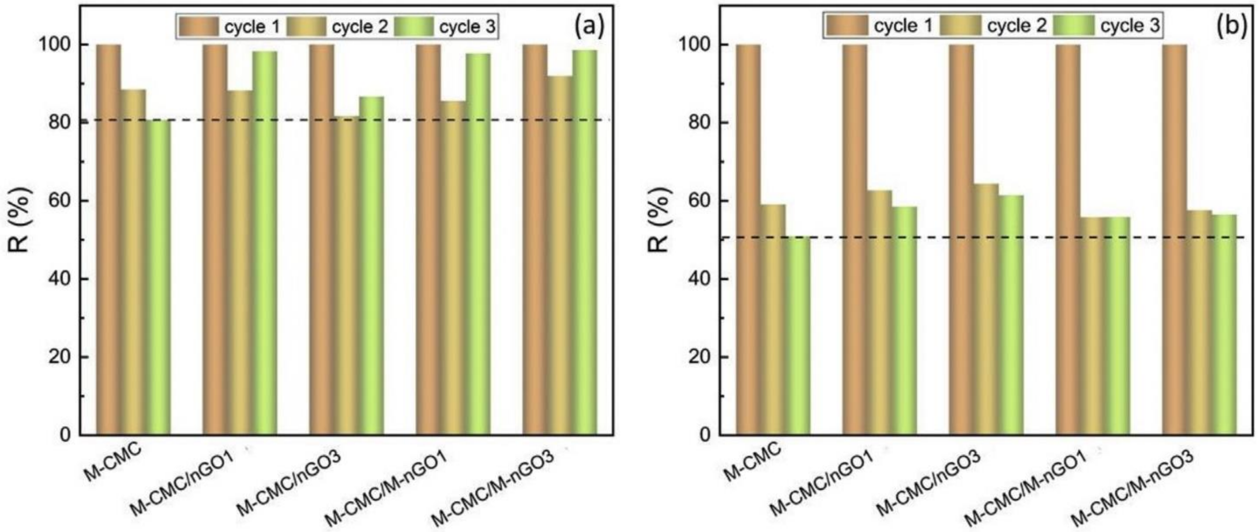
Photocured all lignocellulose nanocomposites

adsorption of cationic contaminants



q_m vs time for (a) MB adsorption (initial concentration 65 mg/L, and (b) Cu(II) adsorption (initial concentration 300 mg/L)



recycling efficiency (R%) of the hydrogels for (a) MB, and (b) Cu(II) adsorption.

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THANKS

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