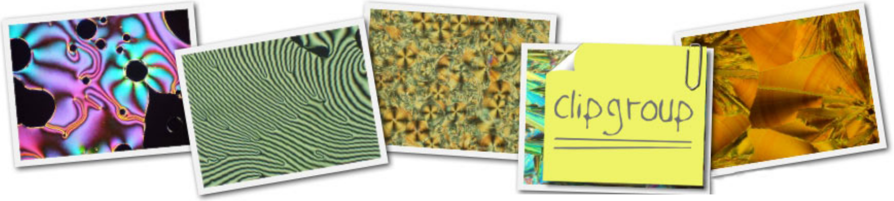


Liquid Crystal and Polymer group

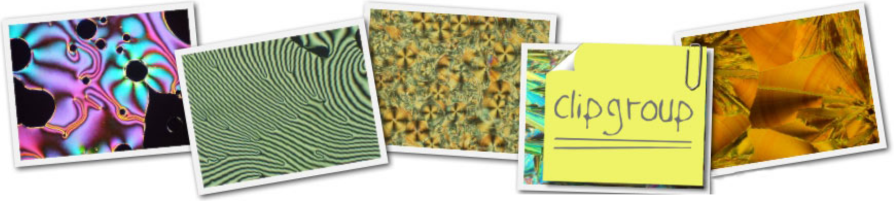
Research line:

FUNCTIONAL POLYMERS
with
CONTROLLED STRUCTURE

/icma/ Instituto de Ciencia de Materiales de Aragón /

CSIC
Consejo Superior de Investigaciones Científicas

Universidad Zaragoza
1542



Liquid Crystal and Polymer group

Milagros Piñol (Prof. Titular, Ciencias)
Rosa Tejedor (Profesora, CUD)
Luis Oriol (Prof. Titular, Ciencias)

M. José Clemente (Dr., Inv. N2, BSH)

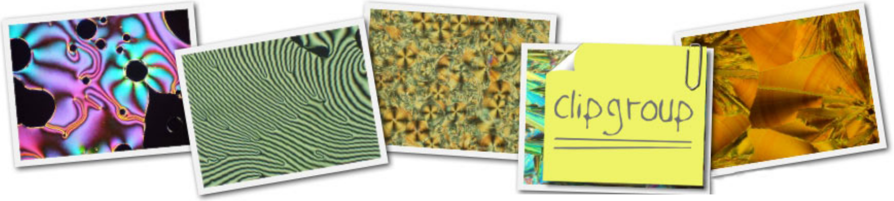
Hugo García (Predoc)
Alejandro Roche (Predoc)

Miriam Abad (TFM)
Alejandro Martínez (TFG)
Daniel Zatón (TFG)

icma Instituto de Ciencia de Materiales de Aragón

CSIC Consejo Superior de Investigaciones Científicas

Universidad Zaragoza 1542



Liquid Crystal and Polymer group

MAT2014-55205-P STIPOL ***Synthesis and applications of smart polymers and supramolecular block copolymers with stimuli-responsive properties (2015-2017)***

ITN 607602 SASSYPOL ***Hierarchical self-assembly of polymeric soft systems*** **(2014-17)**

OTRI 2015-0348 ***Marcado estético digital por láser (2015-16) BSH***

UV MARKING

NETOFNETS ***Training networ on advanced polymeric networks: developing future experts in functional materials and biomaterial (sent for evaluation, coordinator: LO, ICMA)***

icma Instituto de Ciencia de Materiales de Aragón

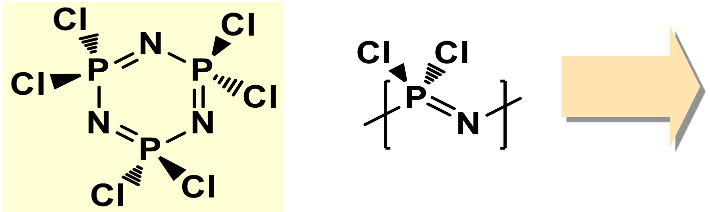
CSIC Consejo Superior de Investigaciones Científicas

Universidad Zaragoza

TOPICS

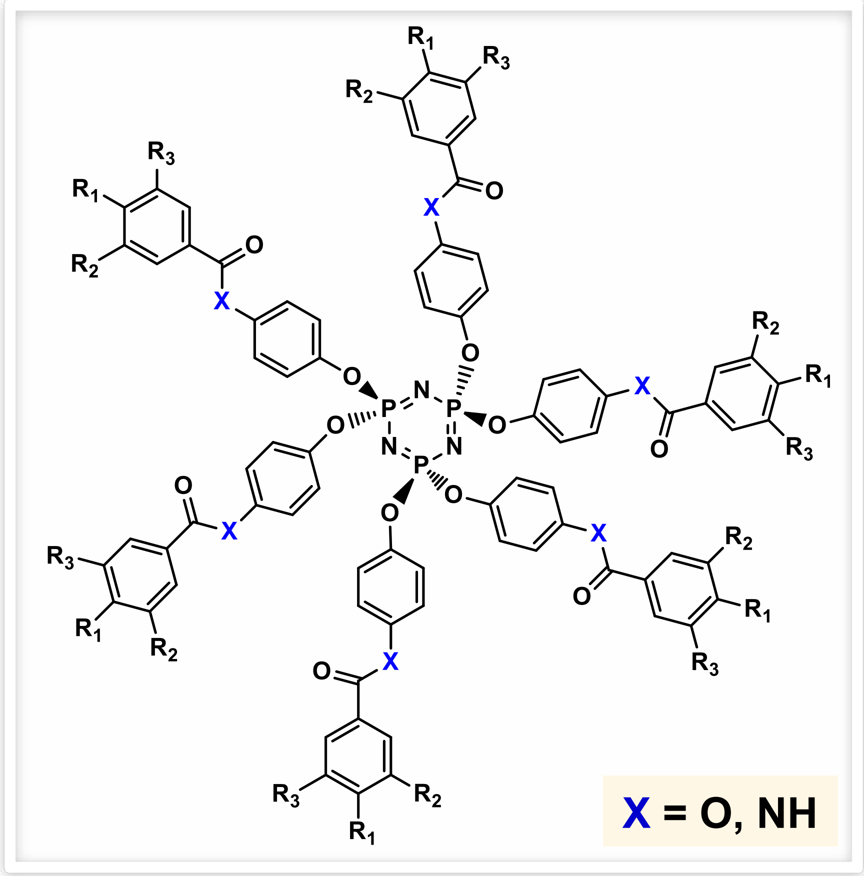
- LIQUID CRYSTALLINE POLYMERS (COLUMNAR AND SUPRAMOLECULAR)
- ANISOTROPIC NETWORKS FOR OPTICAL APPLICATIONS
- BIODEGRADABLE NETWORKS based on alternative photopolymers
- **STIMULI-RESPONSIVE POLYMERS**
  - AZOPOLYMERS: Side chain polymers and dendrimers FOR:
    - NON LINEAR OPTICS
    - HOLOGRAPHY
    - PHOTOINDUCTION OF CHIRALITYcv
  - BLOCK COPOLYMERS for:
    - VOLUME HOLOGRAPHY
    - ENCAPSULATION AND DELIVERY OF CARGO MOLECULES

LIQUID CRYSTALLINE MATERIALS BASED ON CYLOTRIPHOSPHAZENES

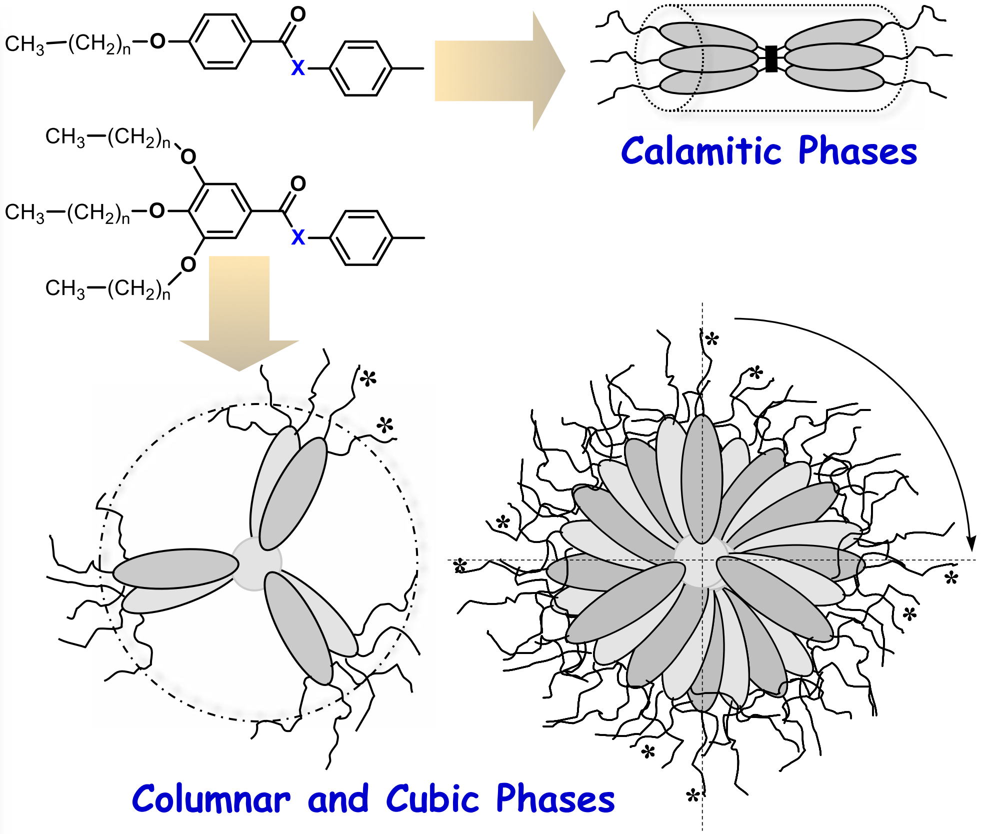


Functionalization with Mesogenic Units (substitution Cl by mesogenic units)

Dpt. Inorganic Chemistry (Dr. J. Jiménez)



X = O, NH



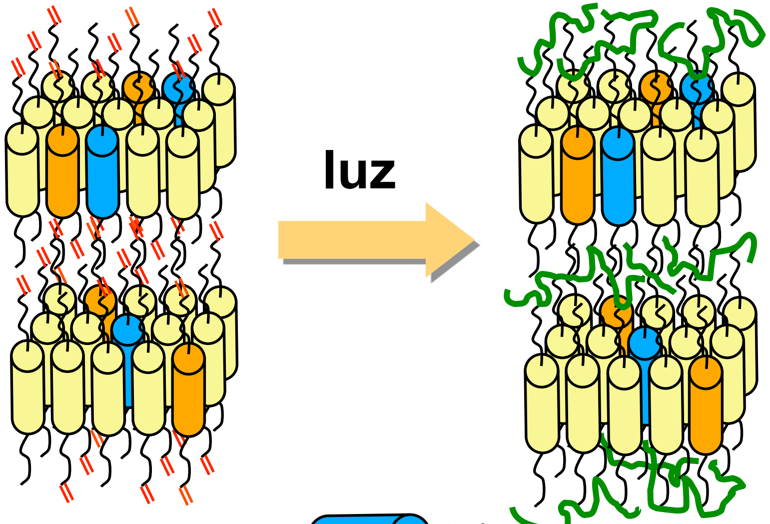
Calamitic Phases

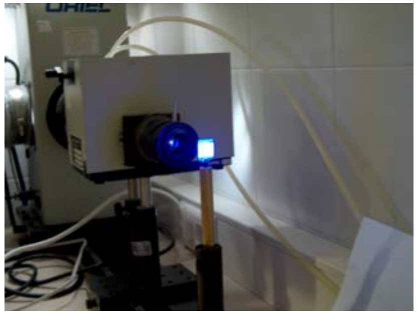
Columnar and Cubic Phases

Chem.-Eur. J. 2012, *18*, 16801

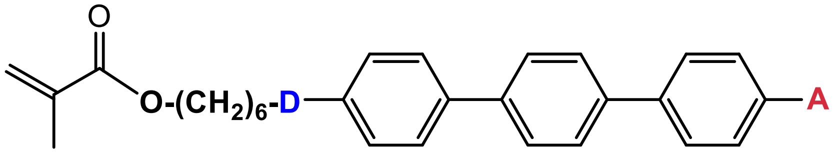
Macromol. Chem. Phys. 2014, *215*, 1551

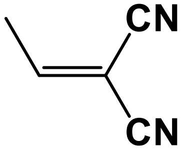
IN-SITU PHOTOPOLYMERIZATION of LCs: POLARIZED LIGHT EMITTING FILMS

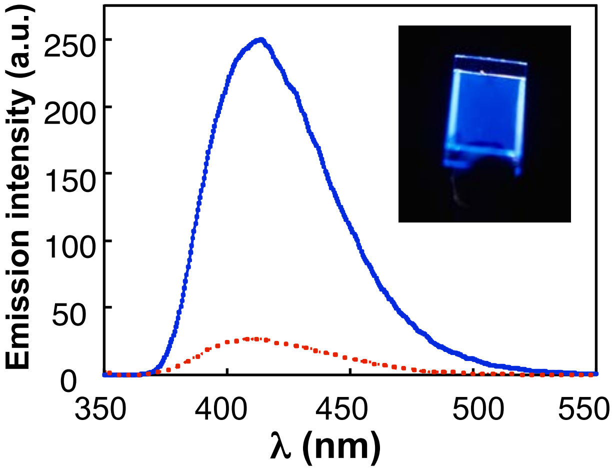




e.g.



D (donor)	A (acceptor)	MO / DSC	λmax(nm)	λem(nm)	Φ (THF)
-O-	-CN	K 124 S_A (t>140 pol)	312	410	0.58
-O-		K 138 N (t>140 pol)	380	535	0.18
$-N(CH_3)-$	-CN	t>115 pol	355	476	0.37

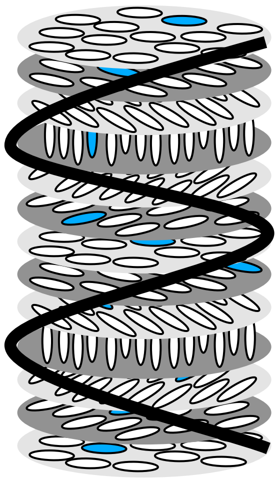


Application of fluorenes to the preparation of laser based on cholesterics

Univ. della Calabria (Italia): Prof. R. Barberi, Prof. G. Chilaya

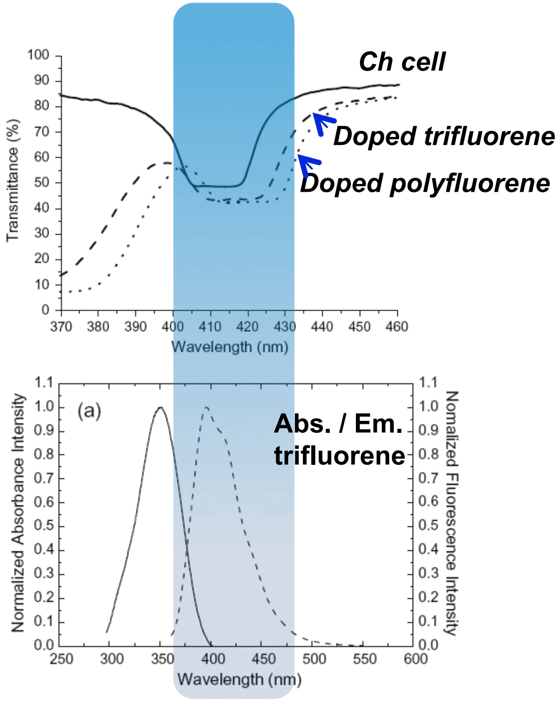
Ch Phase
(helical order)

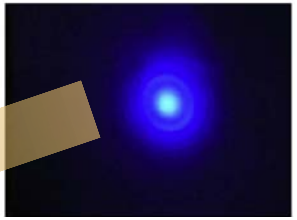
$\lambda = n_m\, p$
$n_m = \frac{1}{2}(n_e + n_o)$
p: helical pitch

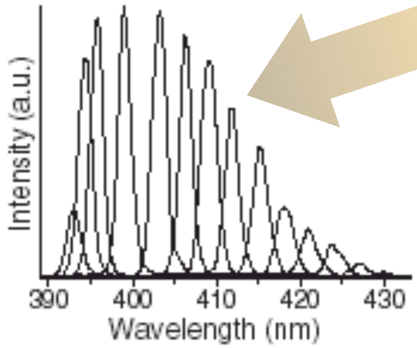


luminophore

If emission matches with λ:
laser emission



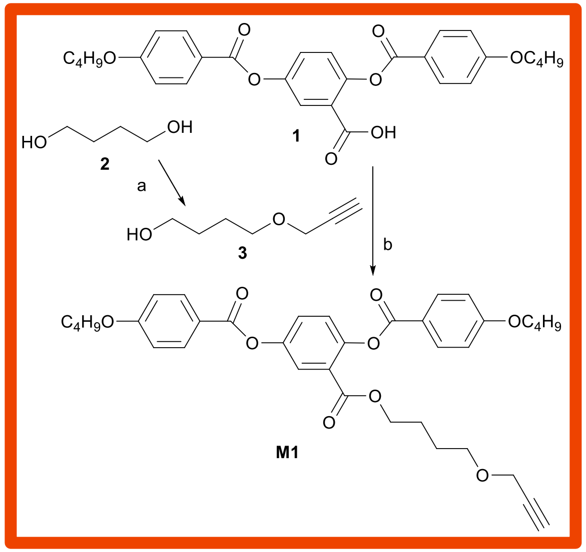


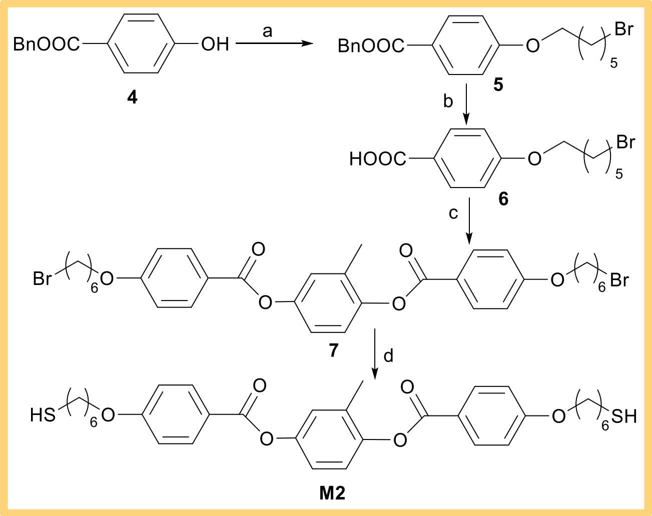


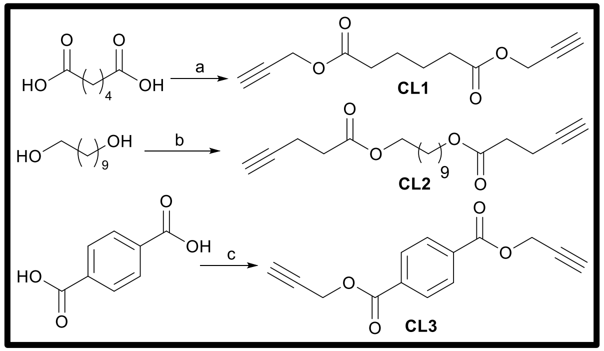
Tuning of laser emission with changing the concentration of luminophore

***Adv. Mater.* 2004, *16*, 791**
***Appl. Phys. Lett. 2005, 86,* 051107**
***Opt. Mater.* 2009, *31*, 1693**

COLLABORATION WITH D.S. WIERSMA, C. PARMEGGIANI, (European Lab. For Non-Linear Spectroscopy, Univ. Florence): MOLECULAR ACTUATORS PREPARED BY PHOTOPOLYMERIZATION







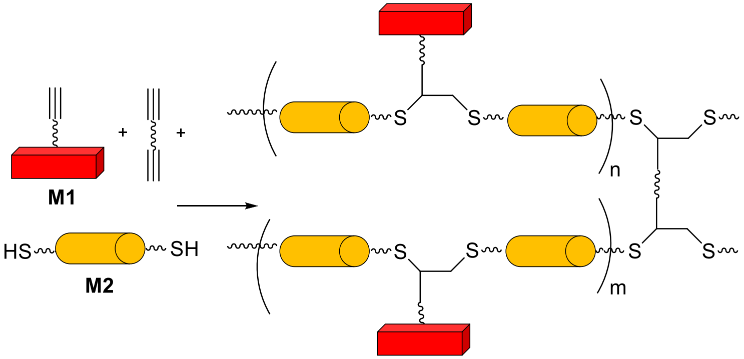
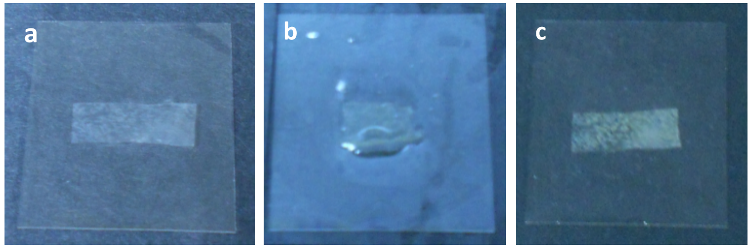


PHOTO-ELASTOMERS HAVING MESOGENS BOTH IN MAIN AND SIDE CHAIN

(improved mechanical properties of actuators)

EXAMPLE OF THERMAL ACTIVATION OF A ELASTOMERIC FILMS



J. Mater. Chem. C, **2015**, *3*, 9003

Objective: Synthesis of new BIODEGRADABLE photopolymers alternative to (meth)acrylates for preparing patterned scaffolds by direct laser writing

CHEMICAL APPROACH:

Light-triggered crosslinking processes involving TWO different reactive groups

Thiol-yne systems

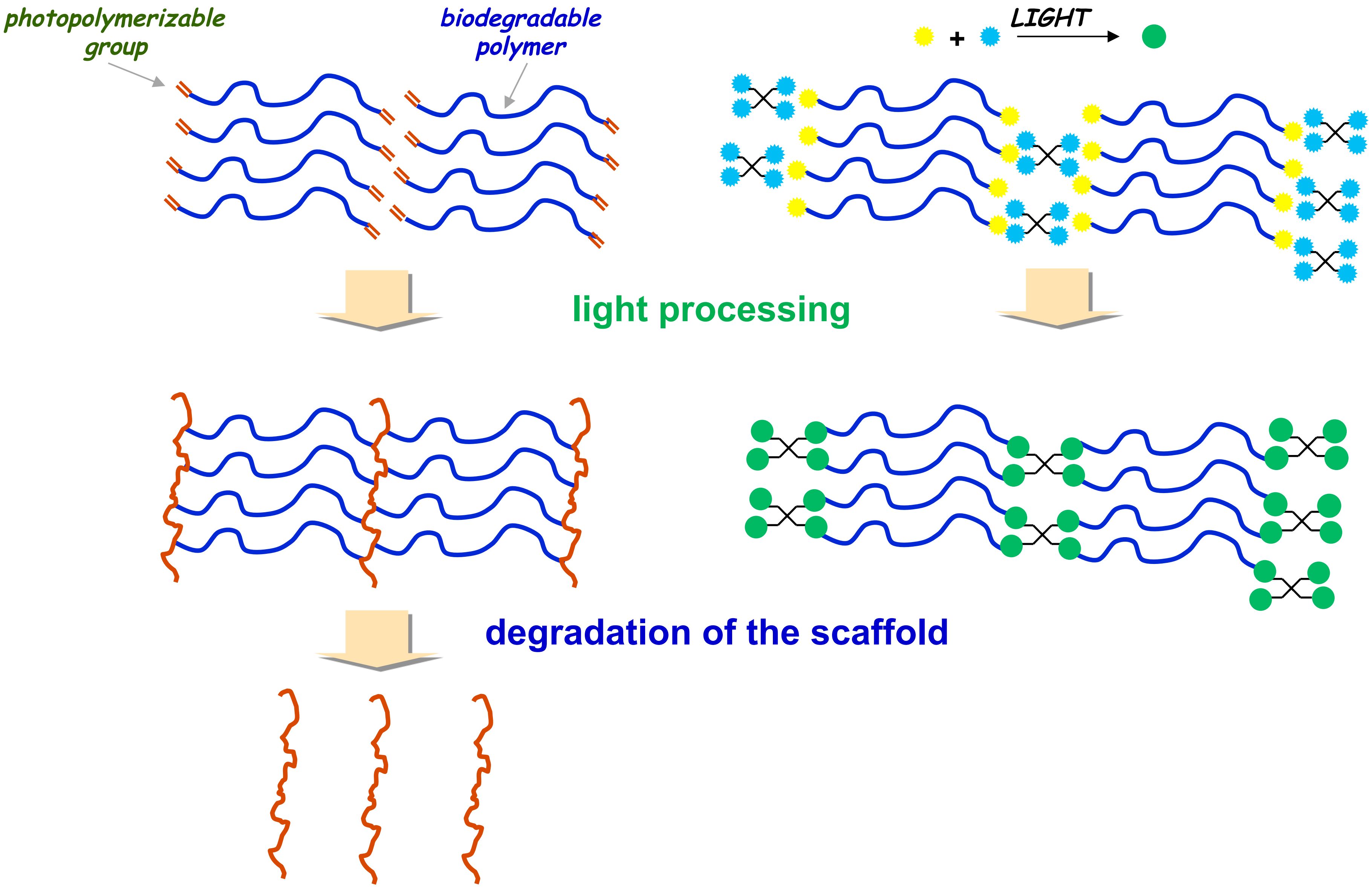
BIODEGRADABLE PHOTOPOLYMERS

Analogs to diazoresins

Colaboration with C. Sánchez-Somolinos, J.M de la Fuente, V. Grazú

Biodegradable networks

ACRILATES **PHOTOPOLYMERIZATION INVOLVING A + B**



light processing

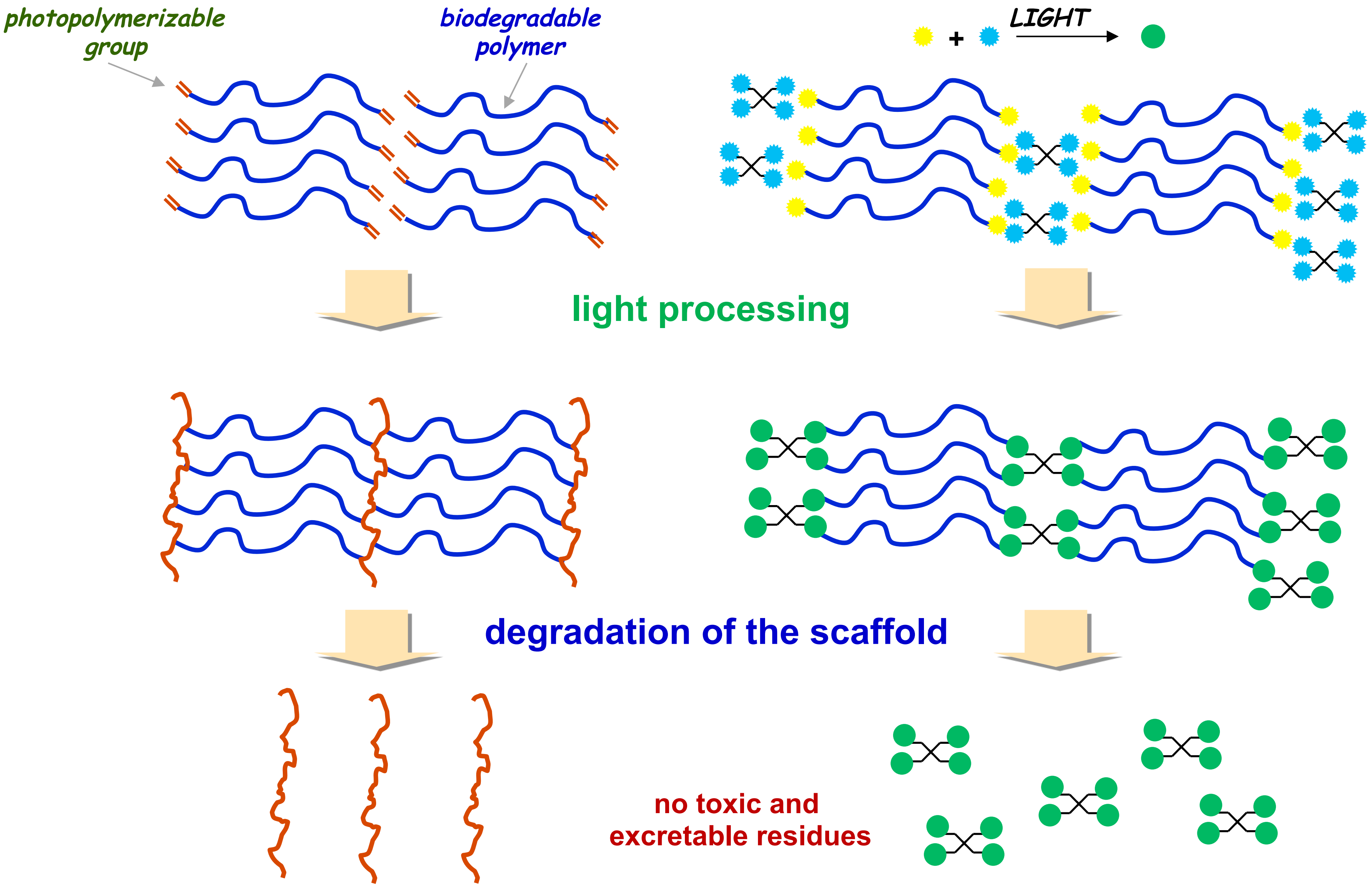
degradation of the scaffold

polymeric acrylic residues

Biodegradable networks

ACRILATES

PHOTOPOLYMERIZATION INVOLVING A + B



light processing

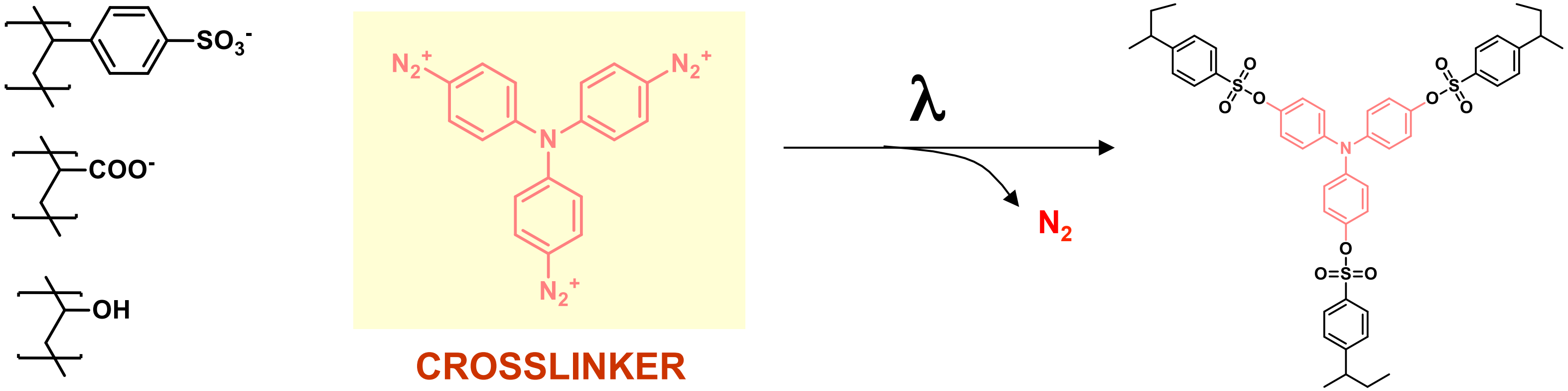
degradation of the scaffold

no toxic and excretable residues

polymeric acrylic residues

PHOTOCROSSLINKING BASED ON THE PHOTODECOMPOSITION OF DIAZONIUM SALTS

proof of principle:



Advantages:

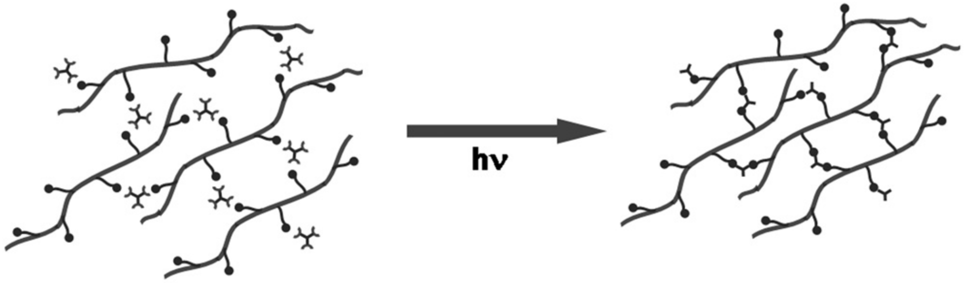
I. water as solvent
II. photoinitiator is not needed
III. different biopolymers with nucleophilic groups can react with diazonium salts

Disadvantages:

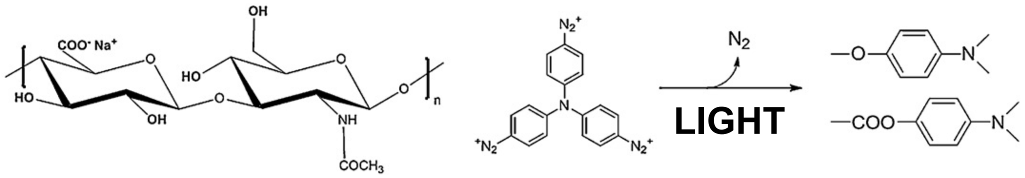
I. low stability of diazonium salts
II. low efficiency of the reaction

IT CAN APPLIED TO ANY SYNTHETIC POLYMER HAVING NUCLEOPHILIC GROUPS IN THE REPEATING UNITS

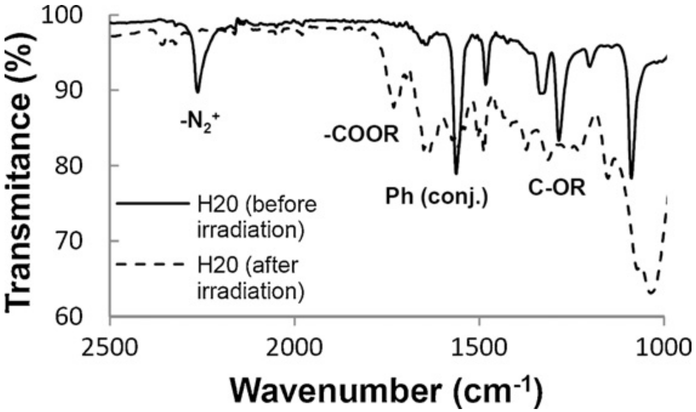
APPLICATION TO BIOPOLYMERS



HYALURONIC ACID:

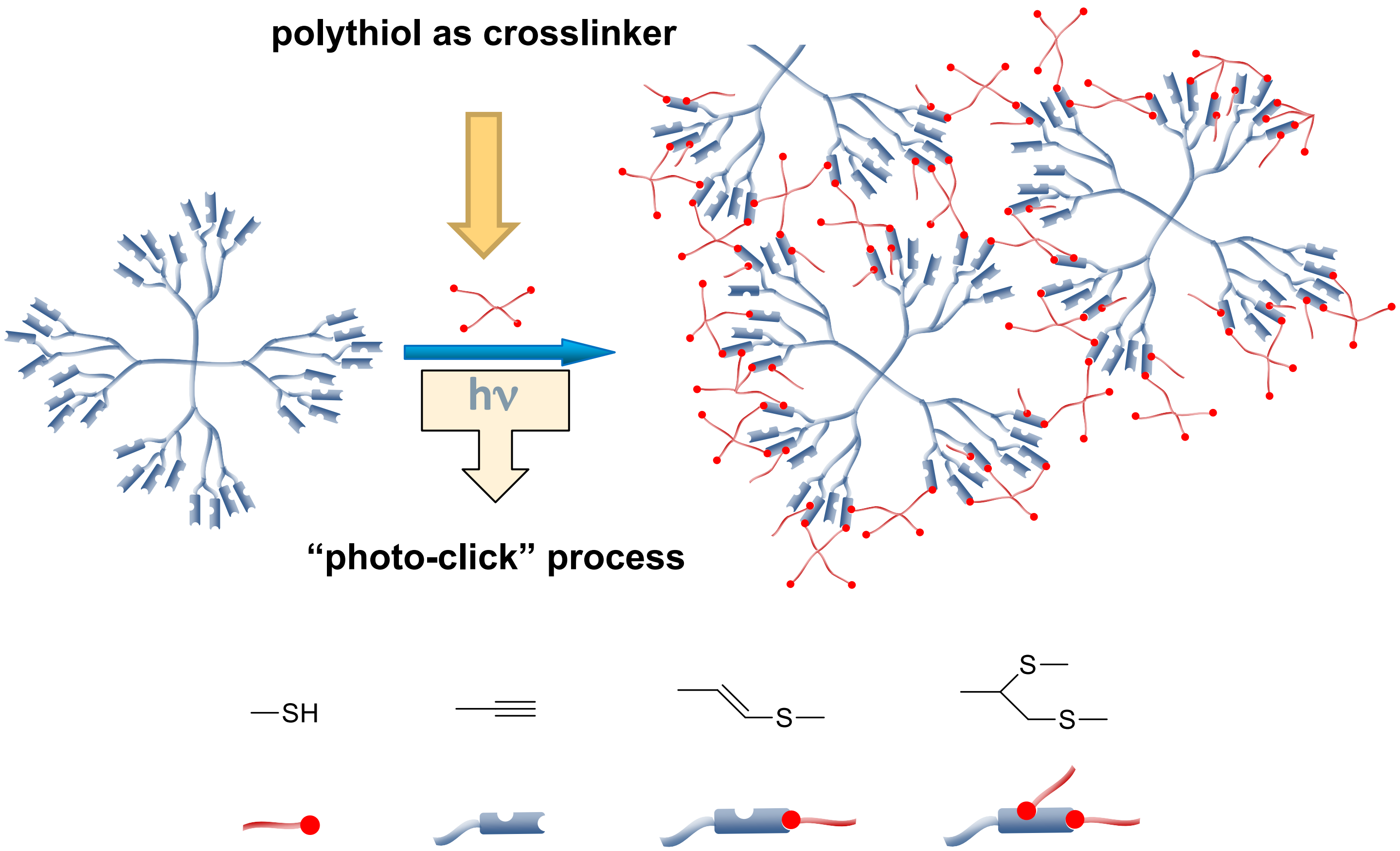


NO chemical modification of the biopolymer is needed



PROCESSING, PATTERNING AND SELECTIVE ELIMINATION OF UNCROSSLINKED REGIONS using aqueous solutions

PHOTOCROSSLINKING OF THIOL-YNE SYSTEMS



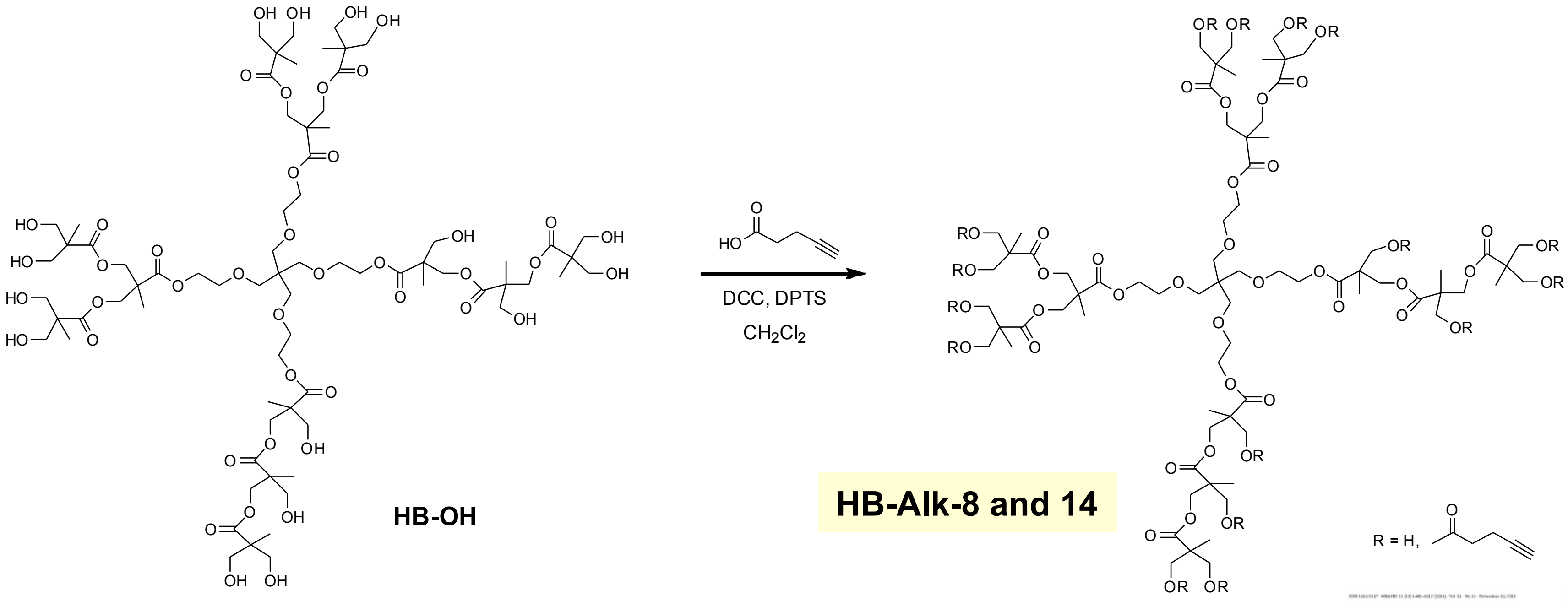
polythiol as crosslinker

hν

“photo-click” process

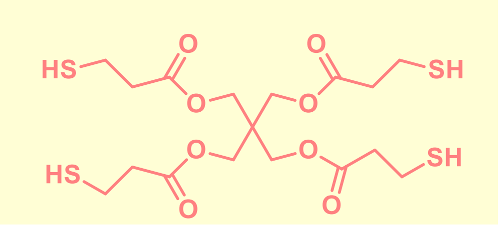
- **Densely crosslinked networks: GOOD STRATEGY FOR PHOTOPOLYMERIC NETWORKS**
- **Combination of click processes: CuAAC + thiol-yne**
- **Less explored that thiol-ene chemistry in the field of materials and biomaterials (first report on materials chemistry in 2004 and intense upsurge since 2009)**

PHOTOCROSSLINKING OF THIOL-YNE SYSTEMS



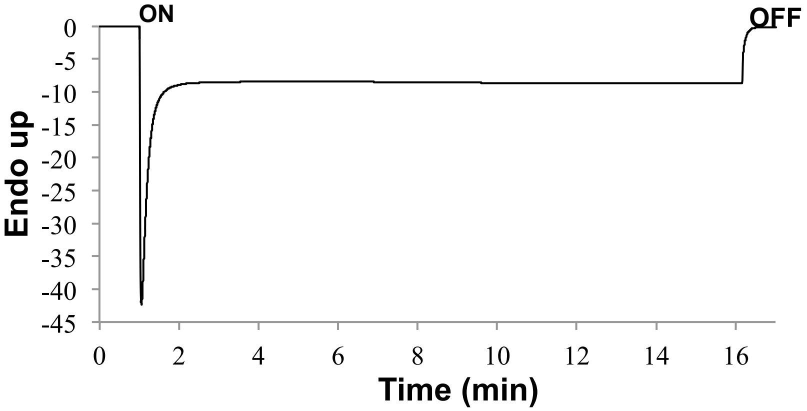
HB-OH

HB-Alk-8 and 14

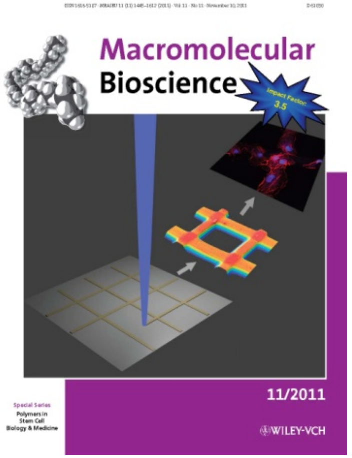


non-citotoxic

(Photoiniciador: Irgacure 369)



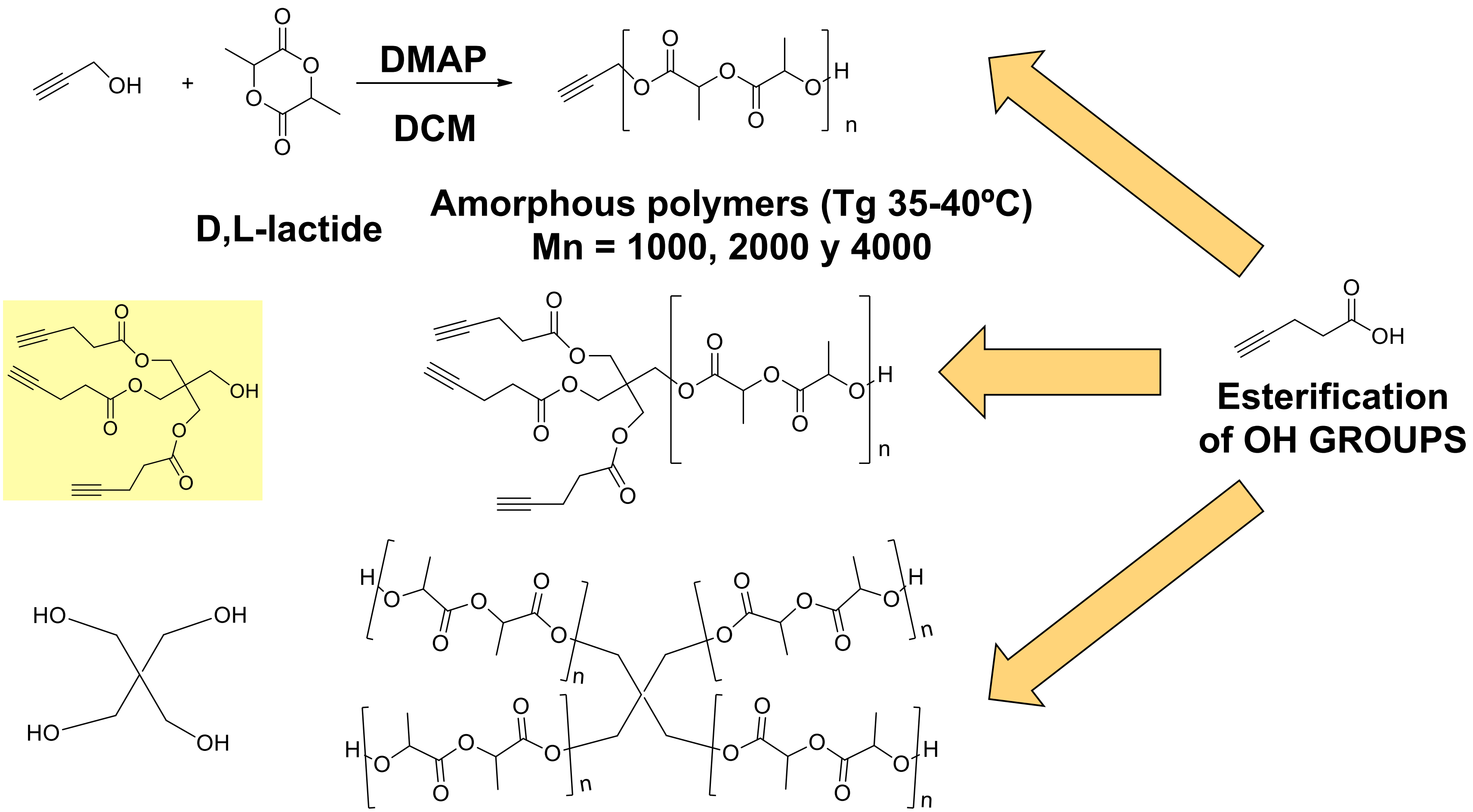
✓Commercial polymers
✓high degree of functionalization



Macromol. Biosci. 2011, *11*, 1445

ALTERNATIVE ALIPHATIC, BIODEGRADABLE POLYESTERS WITH A GOOD CONTROL OF MOLECULAR WEIGHT

polylactide, polycaprolactone



D,L-lactide

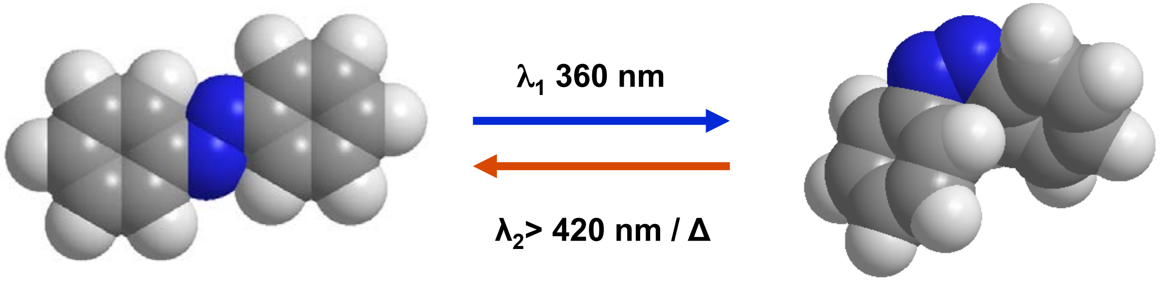
Amorphous polymers (Tg 35-40ºC)
Mn = 1000, 2000 y 4000

Esterification of OH GROUPS

PHOTOADDRESSABLE POLYMERS WITH AZOBENZENE PHOTOCHROMIC UNTIS

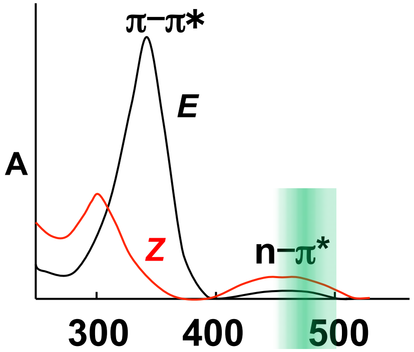
AZOPOLYMERS

Reversible photoisomerization E-Z

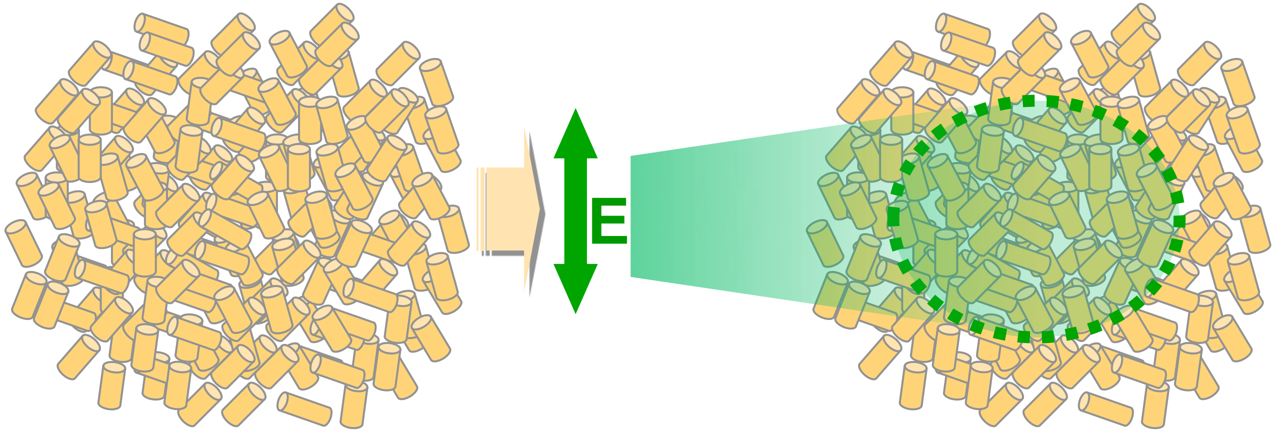


μ= 0.0 D
rod-like geometry (compatible with LCs)

μ= 3.0 D
bent-like geometry



Irradiation with linearly polarized light?



PHOTOADDRESSABLE POLYMERS WITH AZOBENZENE PHOTOCHROMIC UNTIS

AZOPOLYMERS

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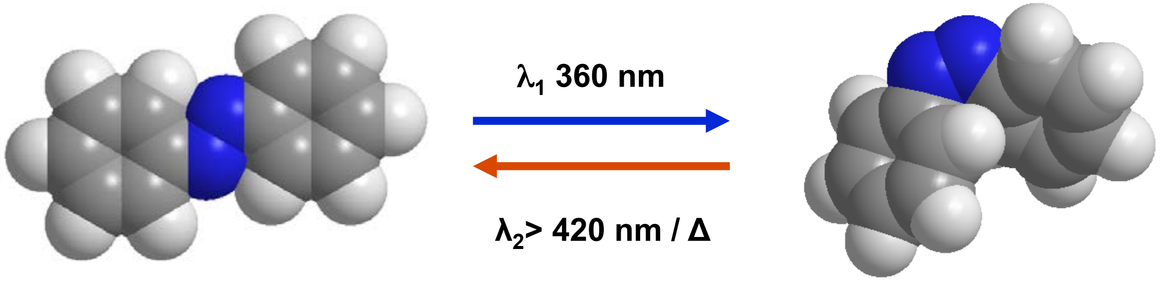

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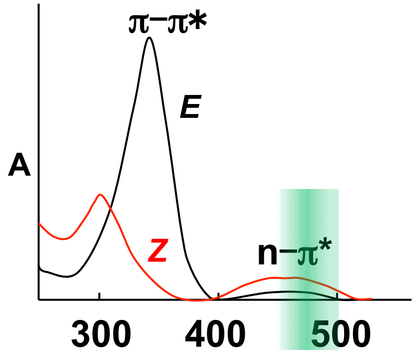
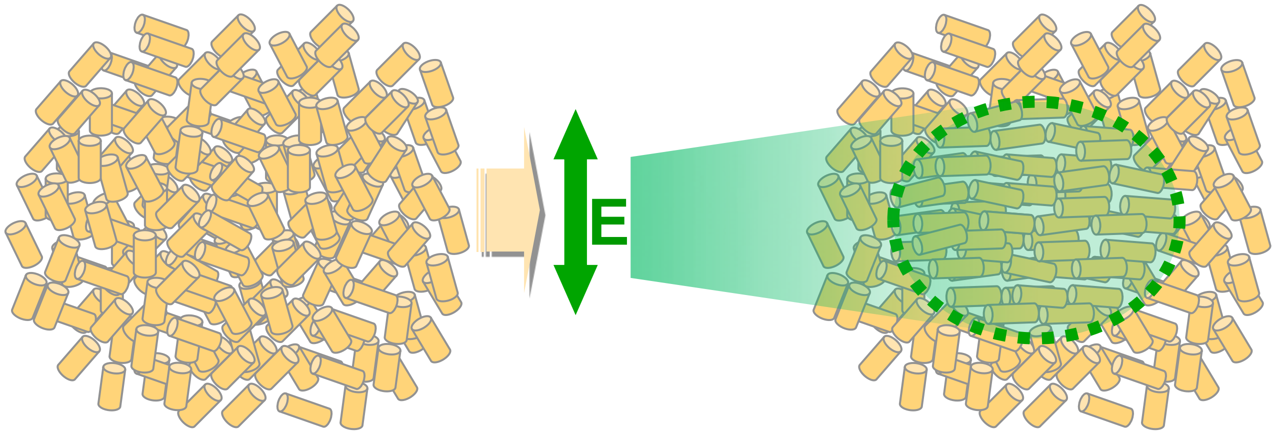


Irradiation with linearly polarized light?

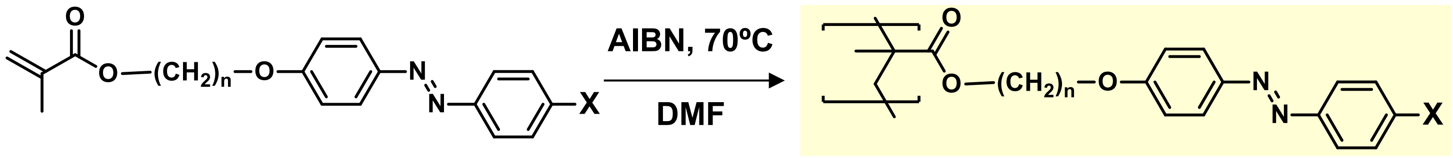


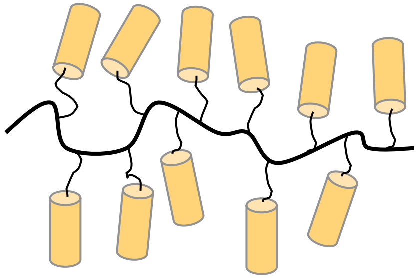
PHOTOINDUCED ANISOTROPY
Birefringence Δn
Dichroism

✓Optical storage
✓Photomechanical actuators
✓…..

SIDE-CHAIN LIQUID CRYSTALLINE POLYMERS

Polymethacrylates synthesized by conventional free radical polymerization





Atactics
Mn, aprox. 10000-60000
Polydispersity aprox. 1.5 - 2

some examples of HOMOPOLYMERS:

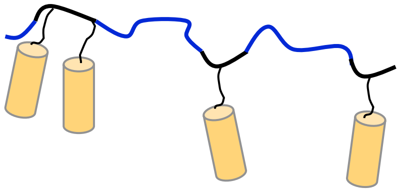
Homopolymer	X	n	Phase transitions
PC0	CN	0[a]	g 170 N 285 I
PC2	CN	2	g 105 N 158 I
PC6	CN	6	g 56 S_A 163 I
PC10	CN	10	g 28 S_A 131 I
POMe	OCH_3	6	g 64 S 89 N 126 I

[a] without spacer

Polymer 2004, *45,* 2341

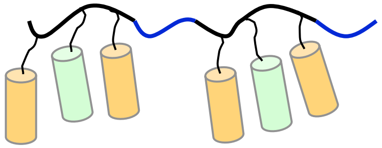
AZO COPOLYMERS: THICK FILMS FOR VOLUME HOLOGRAPHY COLLABORATION WITH R. ALCALÁ, C. SÁNCHEZ

Statistical Copolymers



Low cooperativity among azobenze units

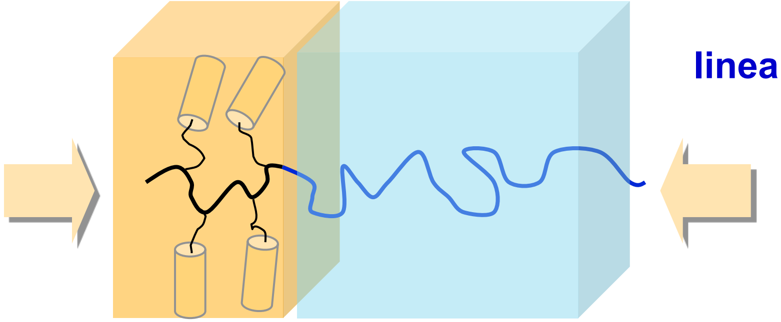
Statistical Terpolymers



Slow response

HOW TO DECREASE THE AZO CONTENT BUT MANTAINING THE AZOBENZENE COOPERATIVITY'

BLOCK COPOLYMERS



Azobenzene confined in nanodomains: COOPERATIVITY

linear "transparent" block e.g. PMMA

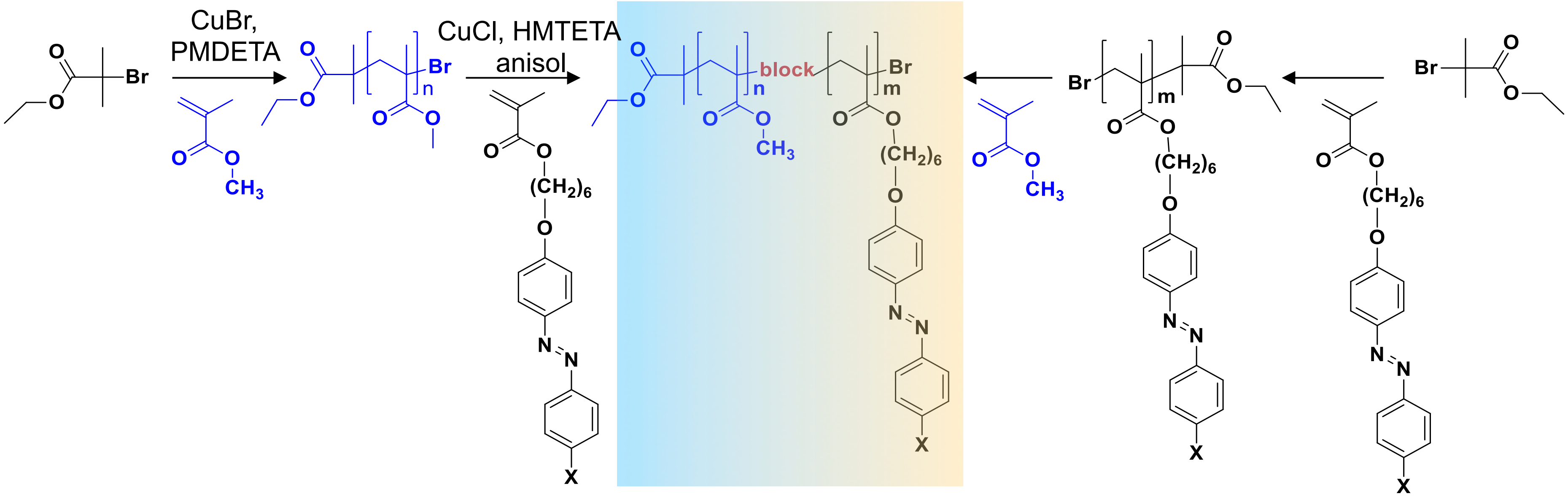
- ✓**dilution of azo**
- ✓**processability**

SYNTHESIS OF LINEAR-LINEAR AZO-BCPs

Synthetic approaches by sequential ATOM TRANSFER RADICAL POLYMERIZATION

Approach: PMMA-macroinitiator

Approach: AZO-macroinitiator



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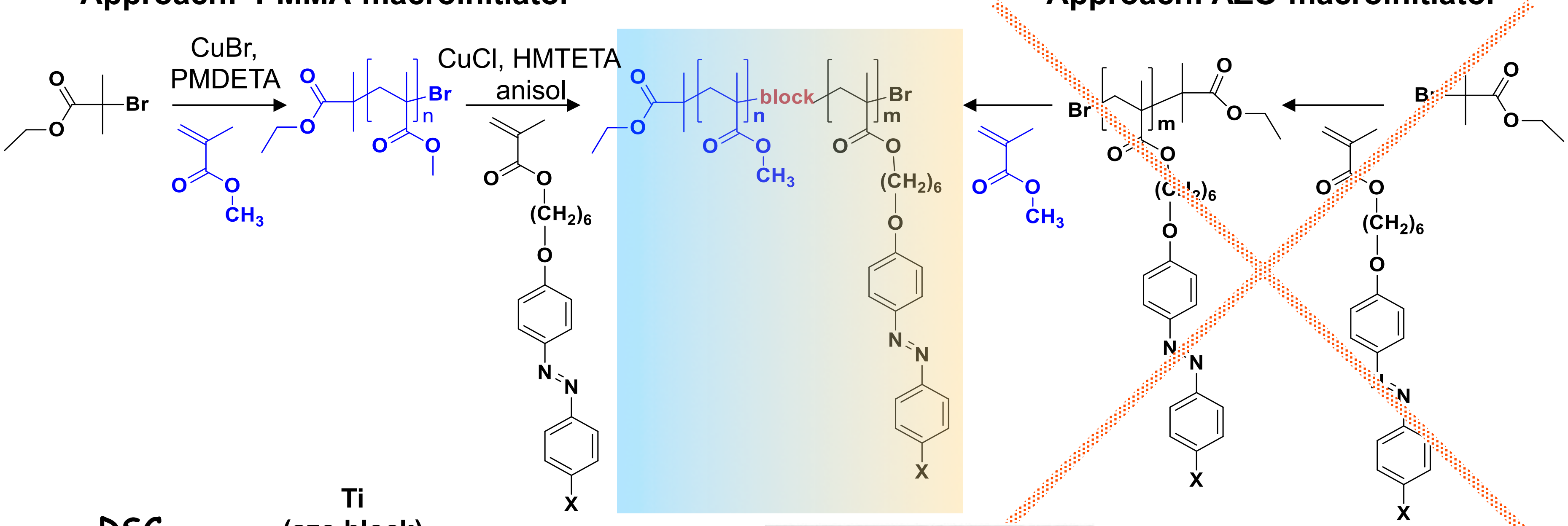
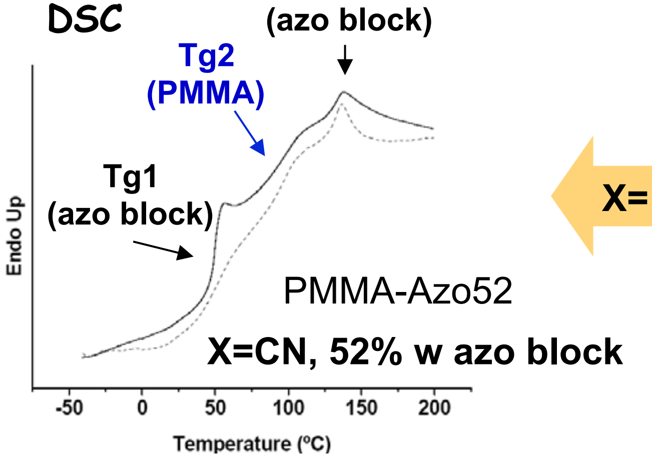
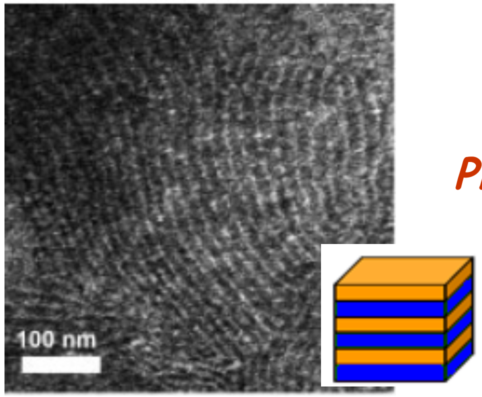




X= CN



Phase microsegregation

***J. Polym. Sci. Polym. Chem.* 2007, 45, 1899**

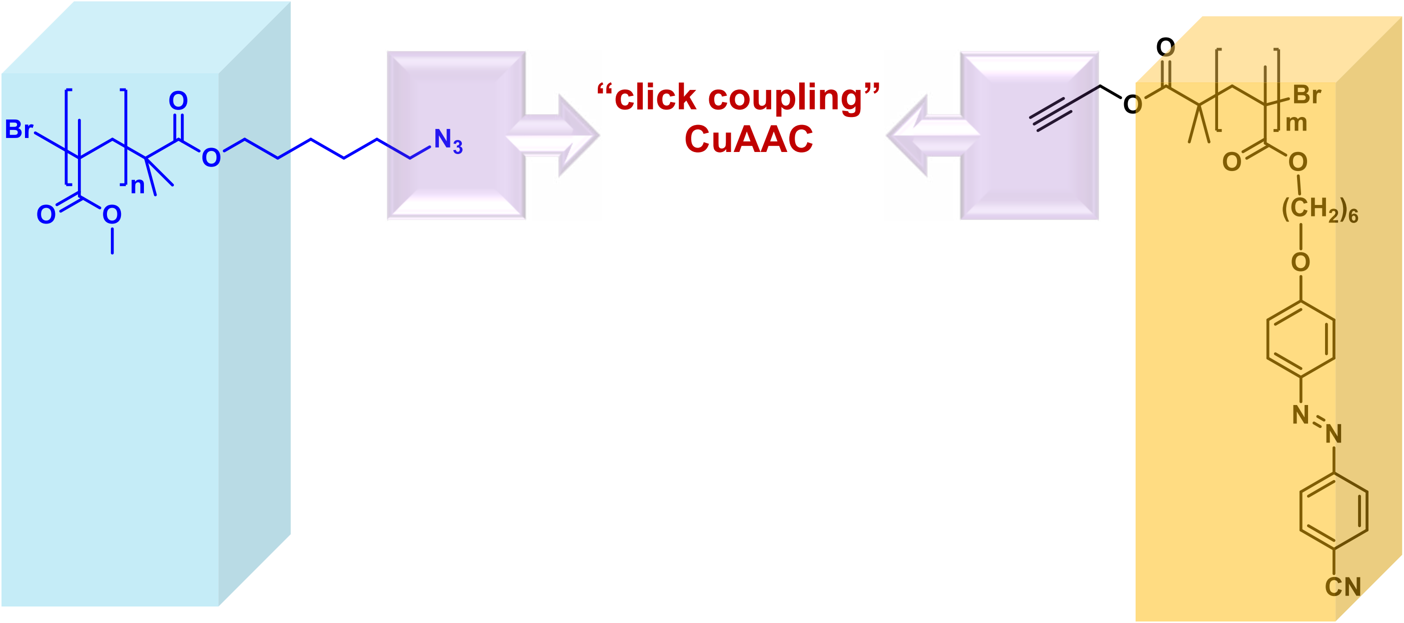
AZO BLOCK COPOLYMERS: alternative synthesis of block copolymers by click chemistry

Low degrees of polymerization of AZO BLOCK obtained from PMMA macroinitiator

ALTERNATIVE: COUPLING OF PREFORMED BLOCKS

PMMA having an azide terminal group

Azopolymer having an alkyne terminal group (higher DPs than alternative synthesis)



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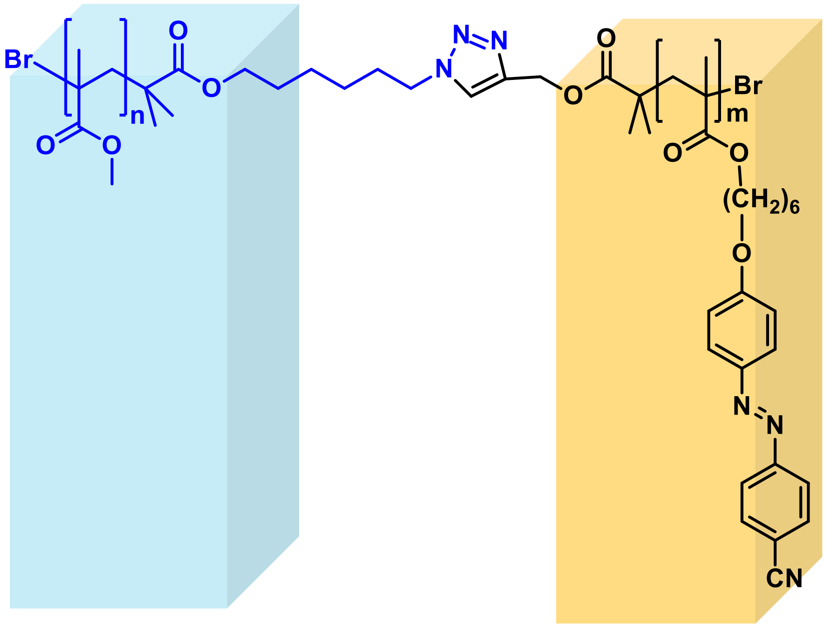
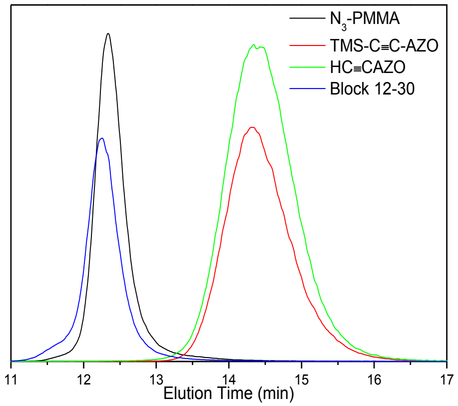


(n=800; m=30)

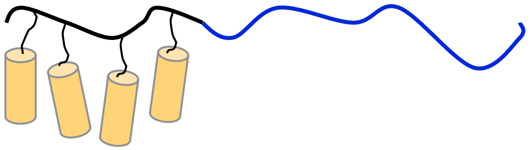


no evidences of residual blocks were observed by NMR or GPC

***Eur. Polym.* 2012, *48*, 613**

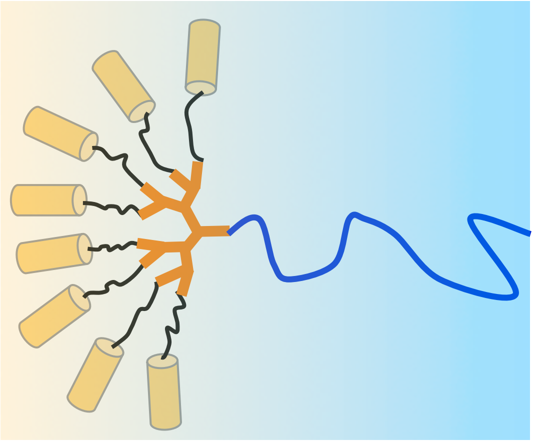
LINEAR-LINEAR vs. LINEAR-DENDRITIC BLOCK COPOLYMERS

Linear-linear Azo-BCPs



It is difficult to control the polymerization of azobenzene-containing monomers

Linear-dendritic Azo-BCPs



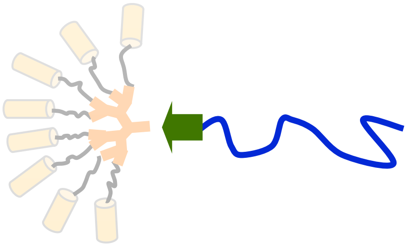
Avoidance of the polymerization of azobenzene-containing monomers via CRP techniques

Exact control of the number of azobenzene moieties in the BC through the dendritic block

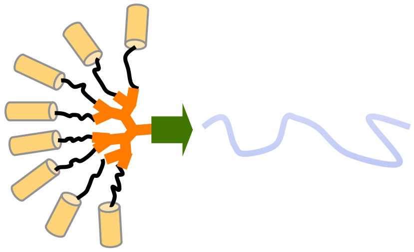
SYNTHESIS OF LINEAR-DENDRITIC BLOCK COPOLYMERS:

ALTERNATIVES:

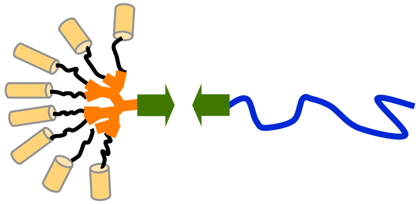
1. Divergent synthesis of the dendron from an activated linear chain



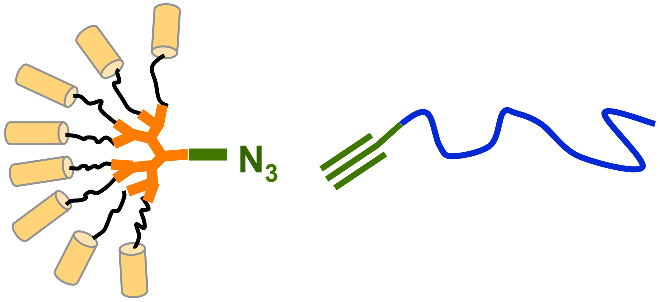
2. Synthesis of the linear chain using a dendritic macroinitiator



3. Coupling of preformed blocks using highly efficient reactions

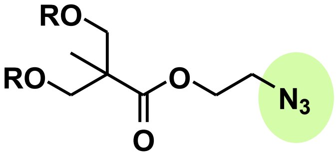


Copper (I)-Catalyzed 1,3-Dipolar Cycloaddition of Azides and Alkynes



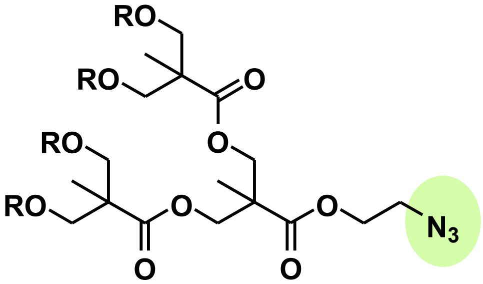
SYNTHESIS OF AZODENDRONS (DENDRITIC BLOCKS)

G: generation of dendron; number of azo-units n= 2^G



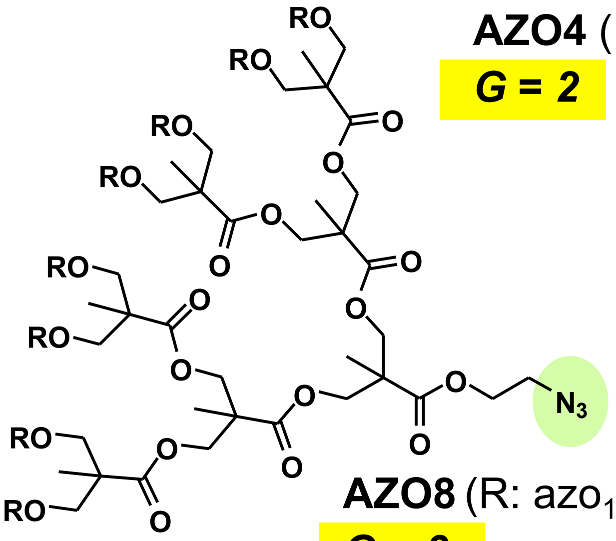
AZO2 (R: azo_{10})

G = 1



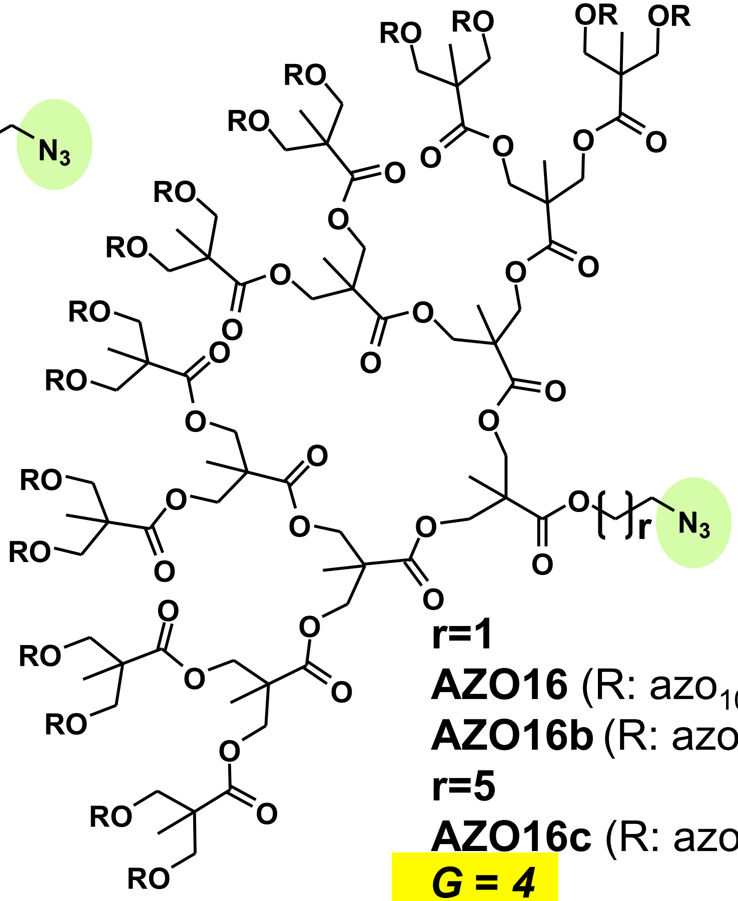
AZO4 (R: azo_{10})

G = 2



AZO8 (R: azo_{10})

G = 3



r=1

AZO16 (R: azo_{10})

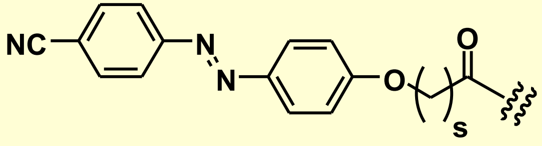
AZO16b (R: azo_5)

r=5

AZO16c (R: azo_{10})

G = 4

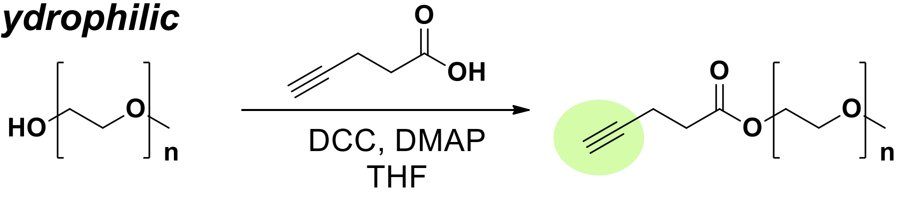
R:



azo_s (s = 5, 10)

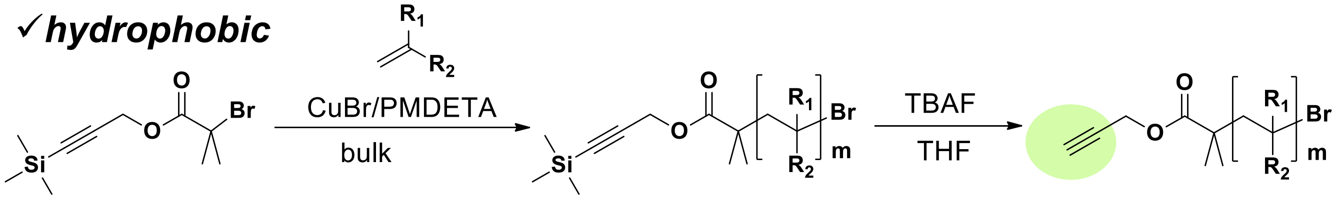
SYNTHESIS OF LINEAR BLOCKS

✓ ***hydrophilic***

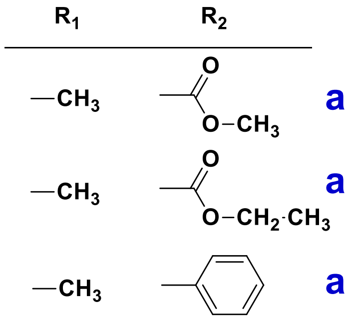


alk-PEG25 (n=25)
alk-PEG45 (n=45)
alk-PEG114 (n=114)

✓ ***hydrophobic***

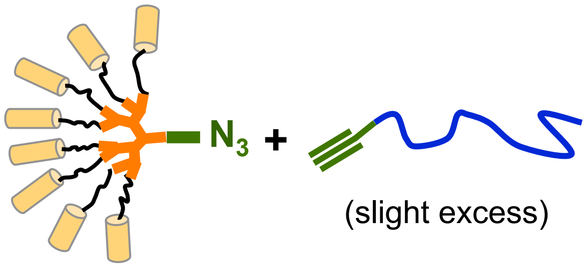


Polymers with two Mn:
aprox. 10000 and 20000



alk-PMMA
alk-PEMA
alk-PS

CLICK REACTION



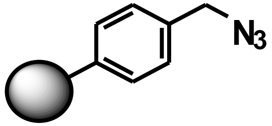
(slight excess)

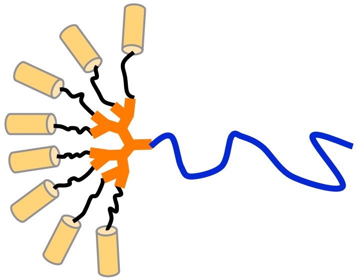
Hydrophilic linear block (PEG)

1) PMDETA/CuBr
DMF, RT
2) "*washing*": Ethanol

Hydrophobic linear block (PMMA, PS, PEMA)

1) PMDETA/CuBr
DMF, RT
2)



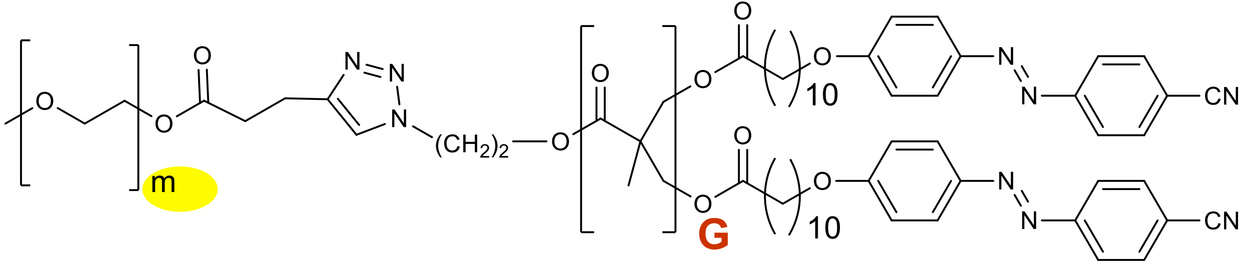


Macromolecules **2009, *42,* 5752**
J. Polym. Sci. Polym. Chem. **2010, *48,* 232**
Polymer **2012, *53,* 4604**

AMPHIPHILIC DENDRITIC-LINEAR AZO-BCPs: POLYMERIC ASSEMBLIES

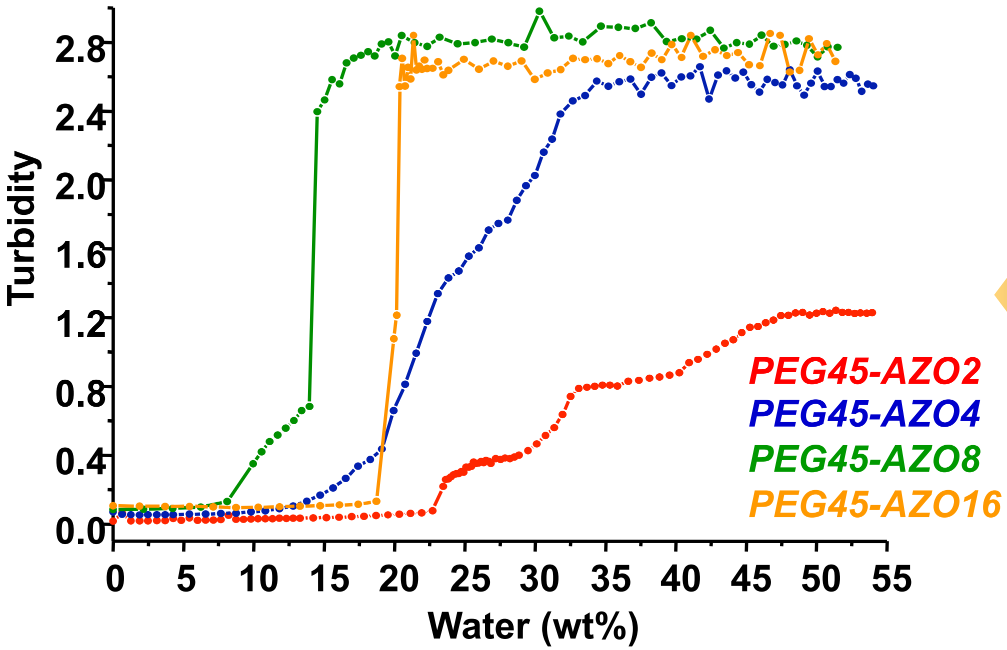
Linear block: *PEGm*

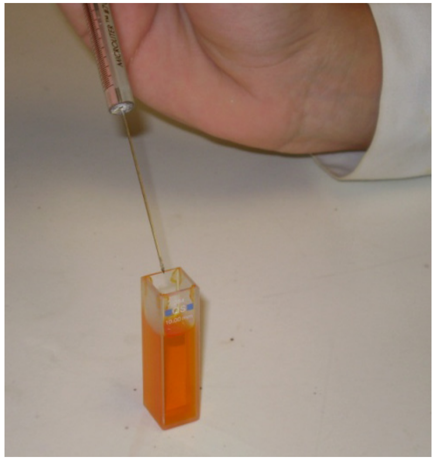
Dendritic block: *Azon (n: number azo units)*



PEGm-AZOn **G: generation of dendron; number of azo-units n= 2^G**

1) Co-solvent method: BCs were first dissolved in dioxane and water was carefully added

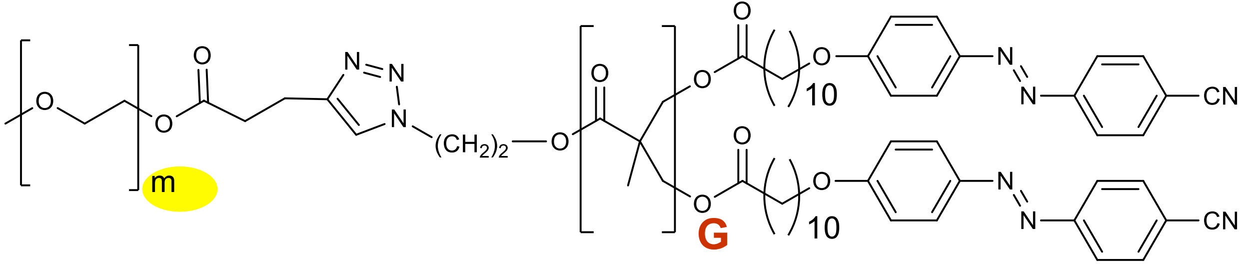




e.g. PEG (Mn aprox. 2000 or m= 45) and different dendron generations

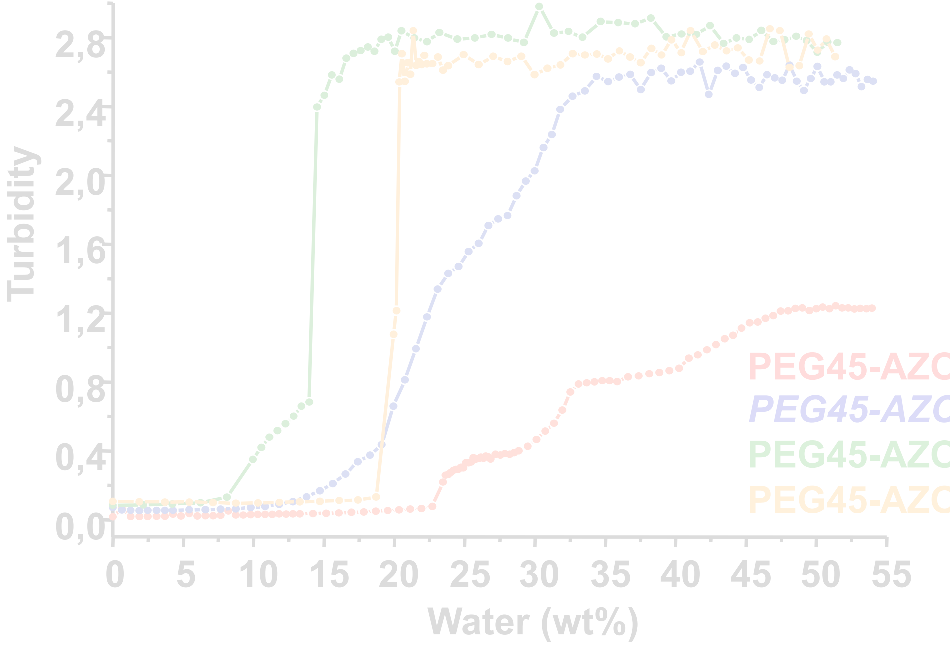
AMPHIPHILIC DENDRITIC-LINEAR AZO-BCPs: POLYMERIC ASSEMBLIES

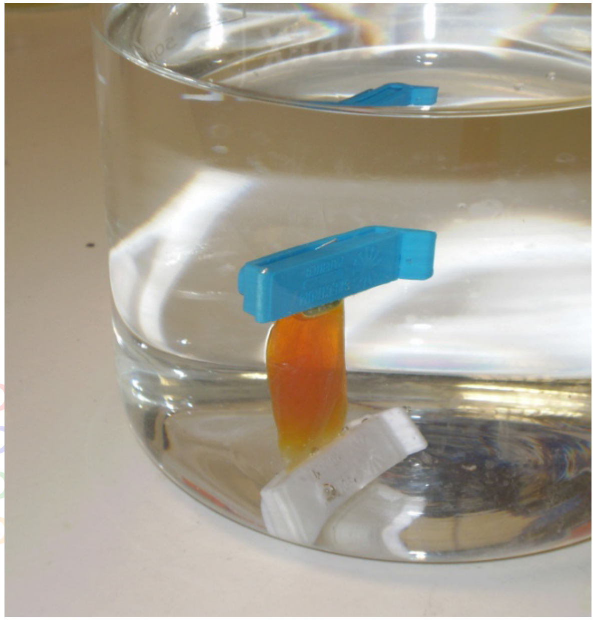
Linear block: *PEGm* **Dendritic block: *Azon (n: number azo units)***



PEGm-AZOn **G: generation of dendron; number of azo-units n= 2^G**

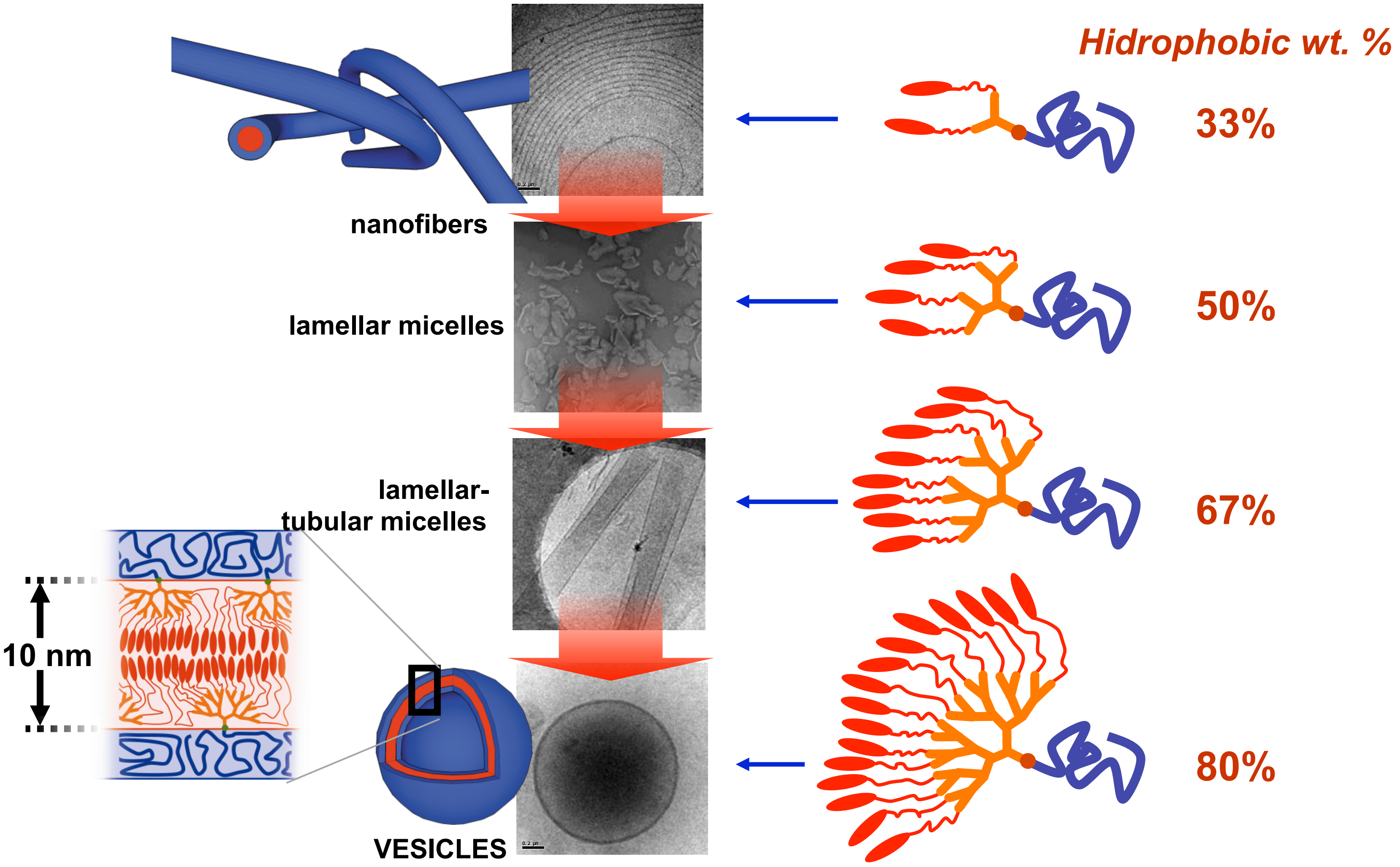
2) Solutions were dyalized against water





AMPHIPHILIC LINEAR-DENDRITIRC AZO BLOCK COPOLYMERS: PEG-b-dendron

Morphological evolution of the micellar aggregation in water



Hidrophobic wt. %

nanofibers

33%

lamellar micelles

50%

lamellar-tubular micelles

67%

10 nm

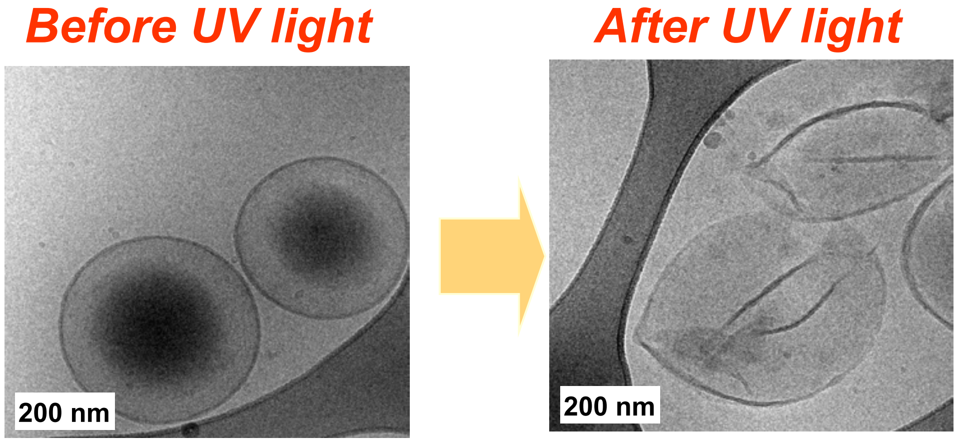
VESICLES

80%

J. Am. Chem. Soc. 2010, *132*, 3762

RESULTS PREPARATION OF WATER-DISPERSED AGGREGATES of PEGm-AZOn

UV irradiation of the aqueous polymersome dispersion: light-responsive vesicles?

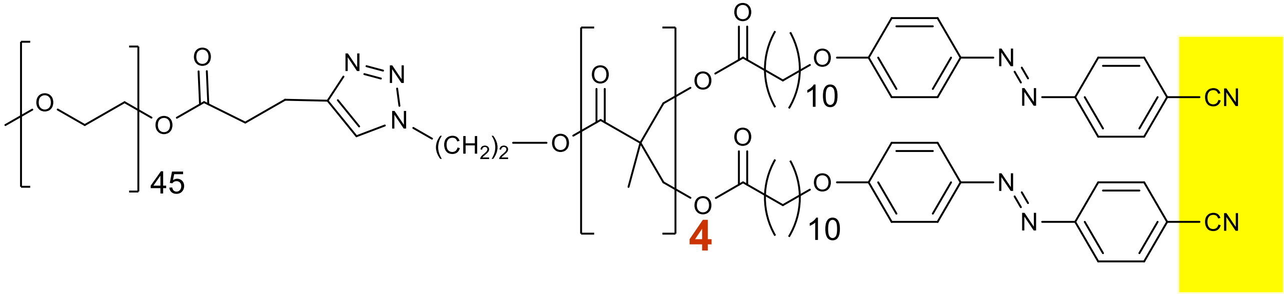


Before UV light

After UV light

Cryo-TEM images of self-assemblies of PEG45-AZO16 before and after UV illumination

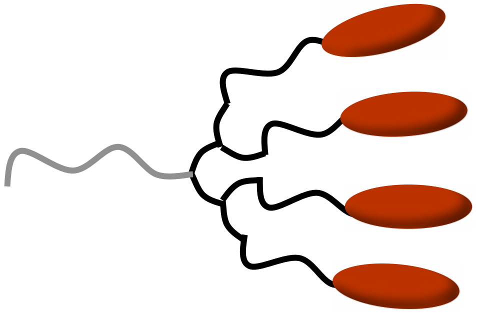
360 nm, aprox. 150 mW/cm^2, 35 min

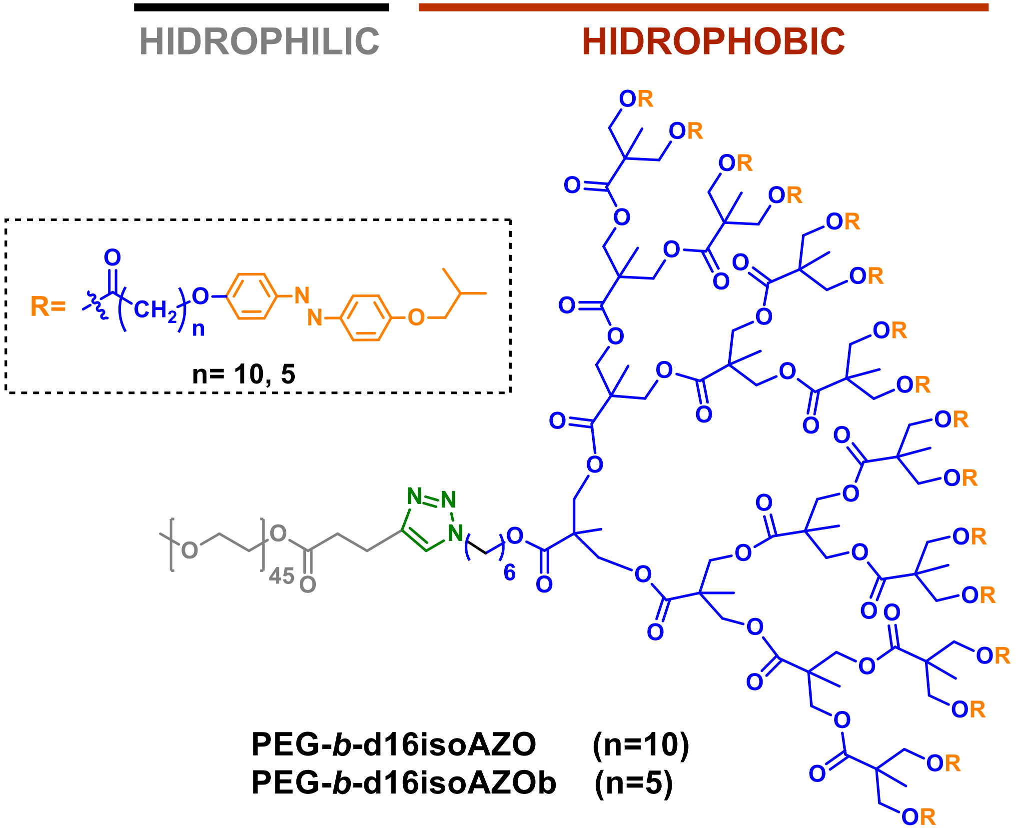


4

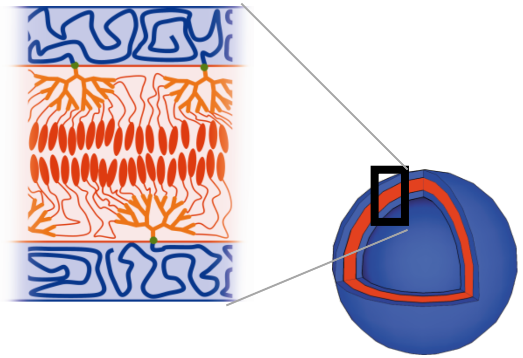
- ✓**High tendency to strong antiparallel arrangement**
- ✓**Low contrast of polarity between trans and cis isomers**
- ✓**Fast back conversion *cis-trans***

AMPHIPHILIC LIGHT-RESPONSIVE, LINEAR-DENDRITIC BCs



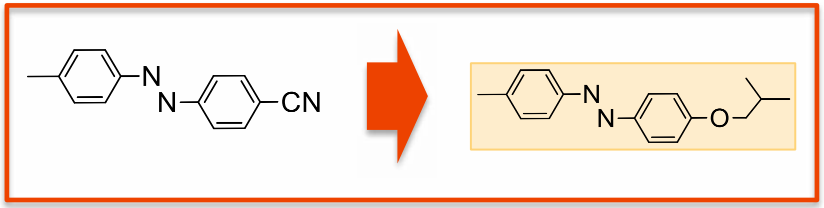


PEG-*b*-d16isoAZO (n=10)
PEG-*b*-d16isoAZOb (n=5)



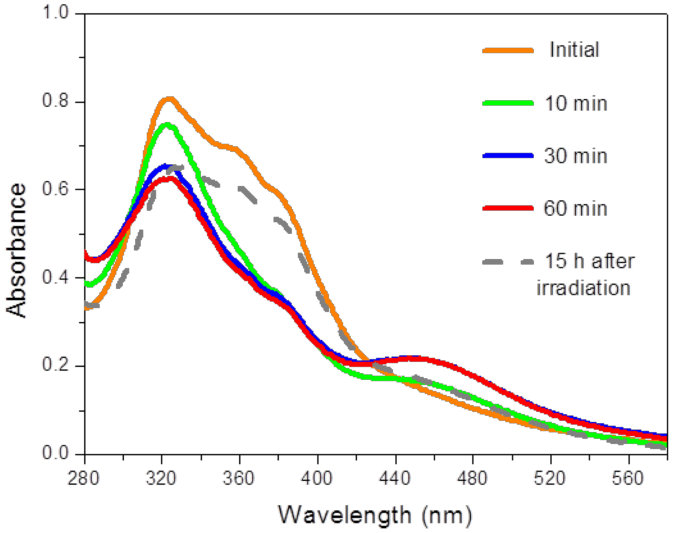
VESICLES

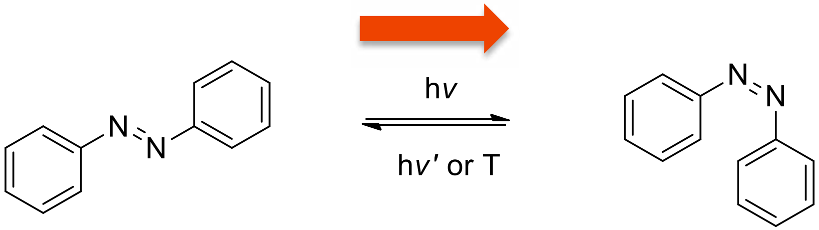
Encapsulation
and
PHOTOINDUCED RELEASE?



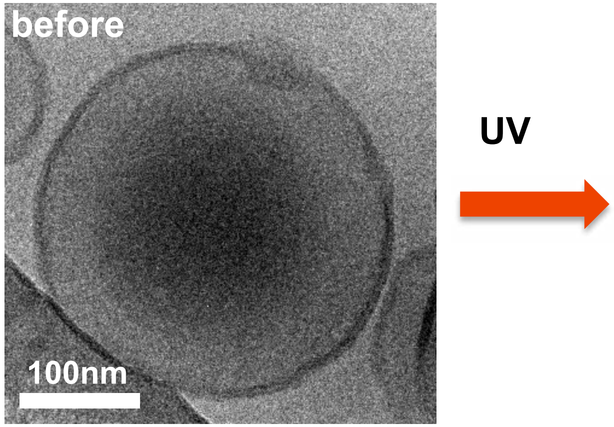
MODIFICATION OF TERMINAL GROUP TO FAVOR PHOTOISOMERIZATION

UV IRRADIATION (365 nm, 2.6 mW/cm^2) ⇦ **LOW POWER LAMP**





***trans*-to-*cis* isomerisation**

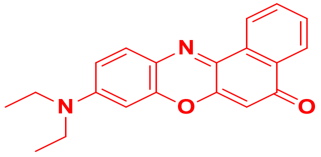


Cryo-TEM **Cryo-TEM**

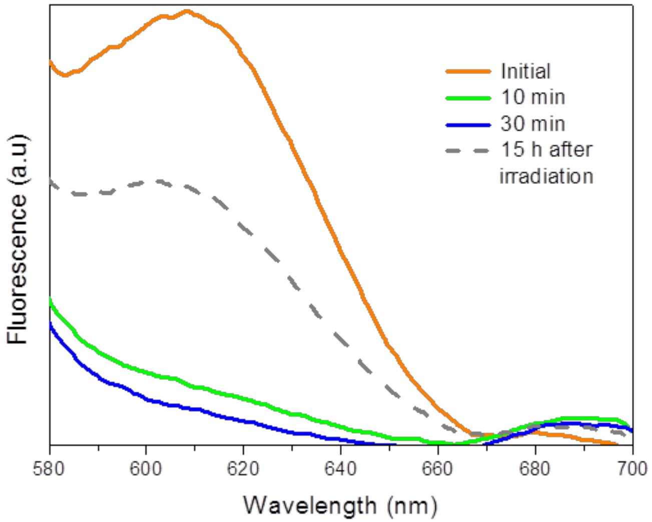
Exposure of the vesicles to UV irradiation caused significant spectral changes as well as morphological changes

ENCAPSULATION AND PHTOINDUCED RELEASE OF FLUOROPHORES AS MOLECULAR PROBES

NILE RED (hydrophobic)

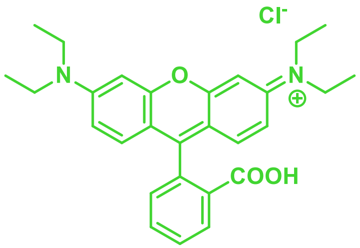


UV IRRADIATION
(365 nm, 2.6 mW/cm^2)



Upon UV irradiation, decrease on fluorescence intensity of Nile Red was observed

RHODAMINE B (hydrophilic)



UV IRRADIATION
(365 nm, 2.6 mW/cm^2)

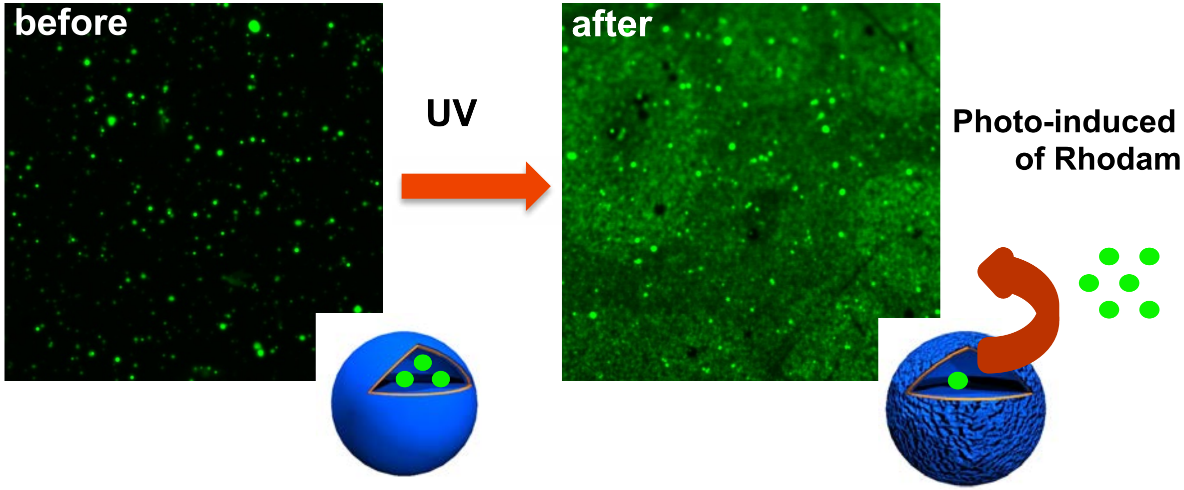
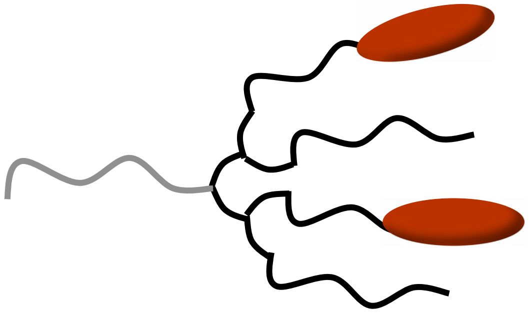
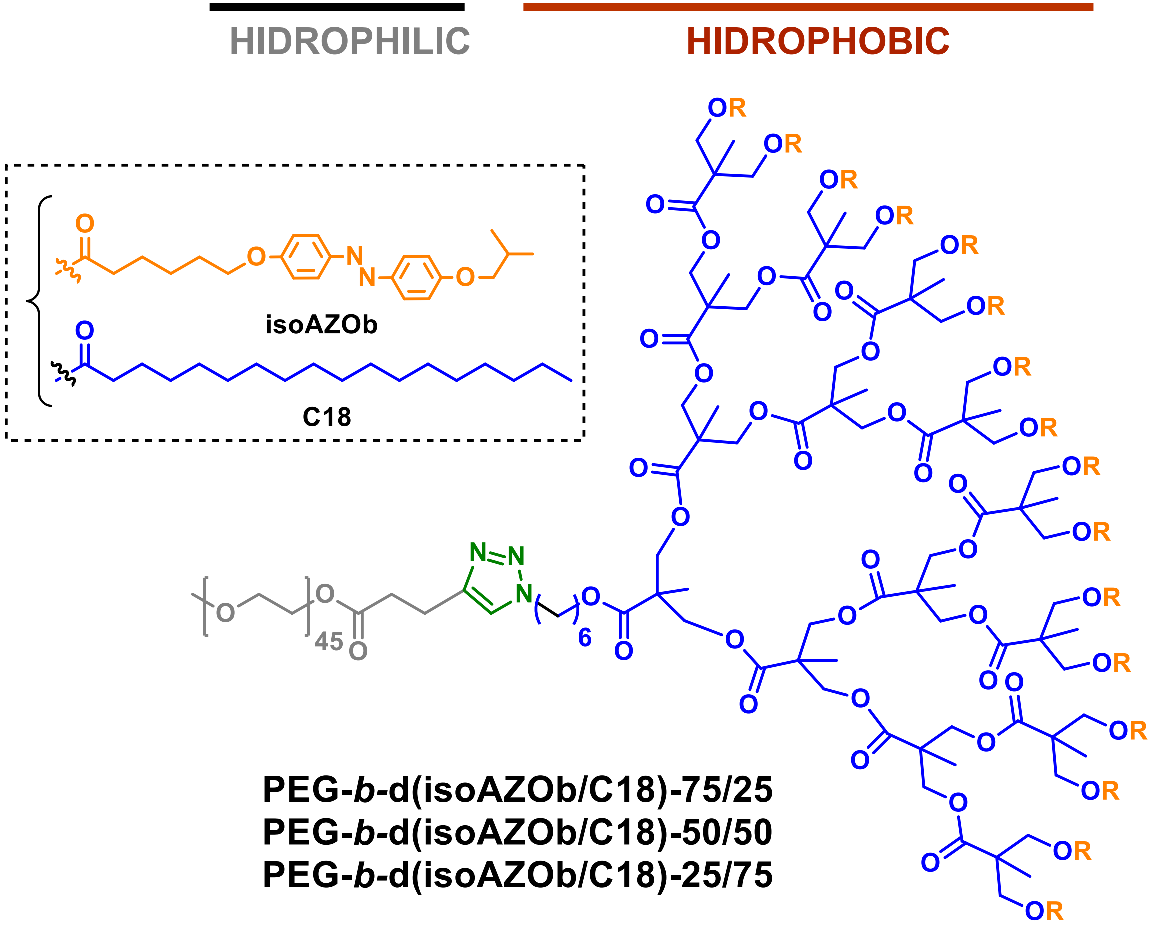


Photo-induced realease of Rhodamine B

Polym. Chem. 2013, 4, 2246-2254

AMPHIPHILIC LIGHT-RESPONSIVE, LINEAR-DENDRITIC BCs: codendrons





isoAZOb/C18

75/25

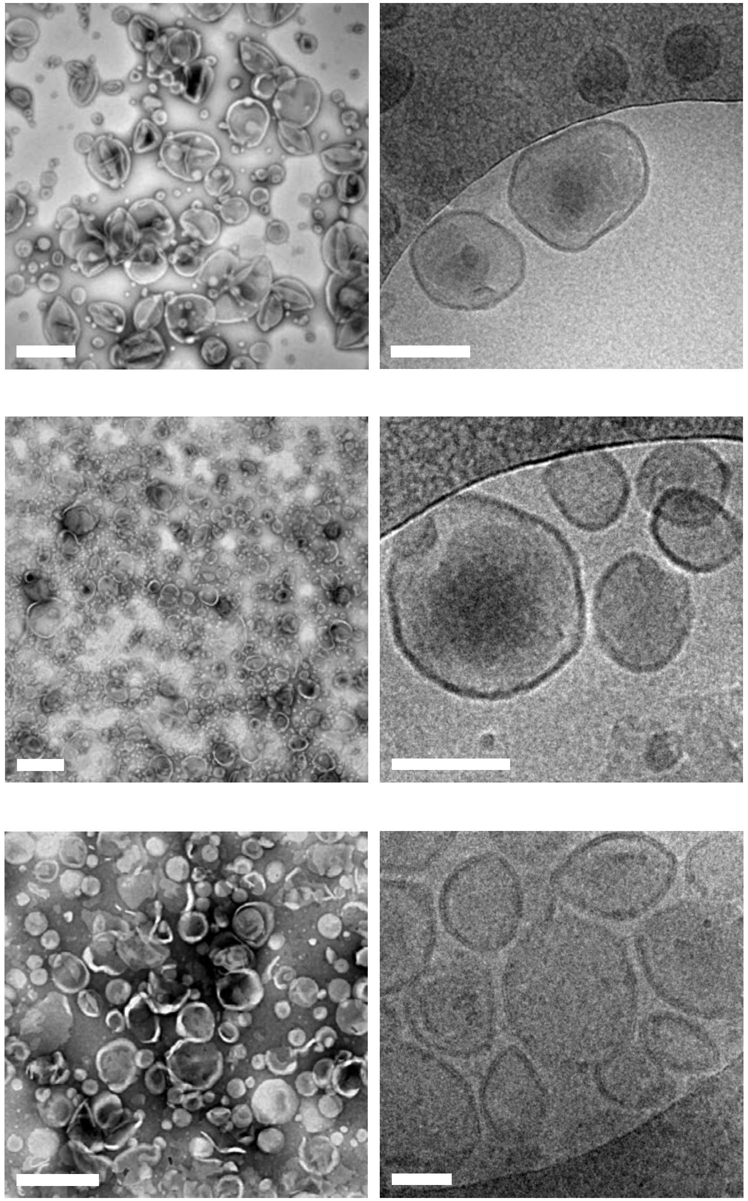
50/50

25/75

PEG-*b*-d(isoAZOb/C18)-75/25
PEG-*b*-d(isoAZOb/C18)-50/50
PEG-*b*-d(isoAZOb/C18)-25/75

Stimuli-responsive polymers

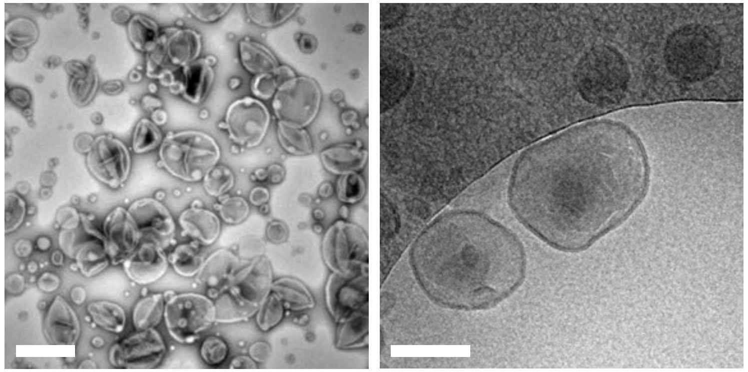
isoAZOb/C18 TEM Cryo-TEM

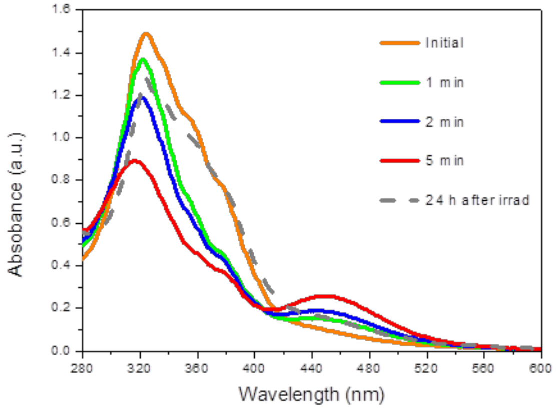


isoAZOb/C18 **TEM** **Cryo-TEM**

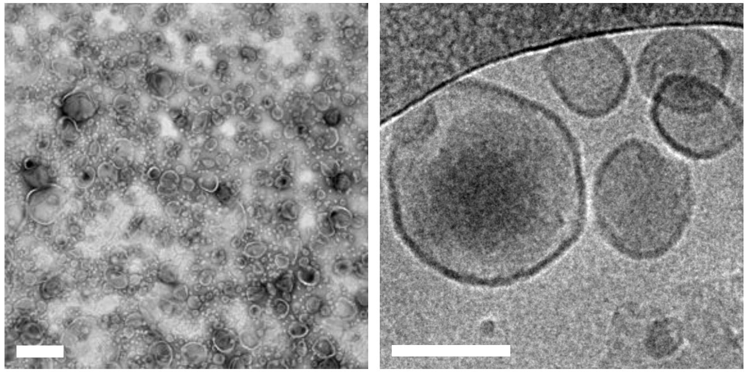
UV irradiation (350-400nm)

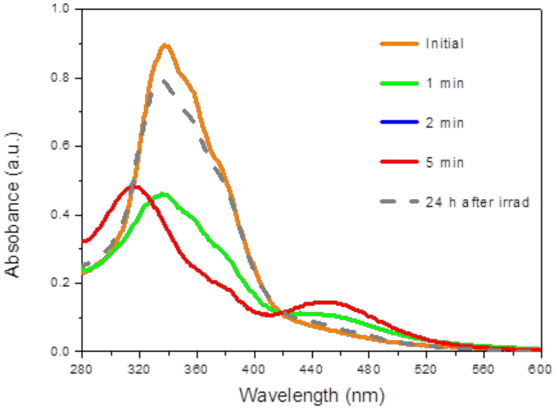
75/25



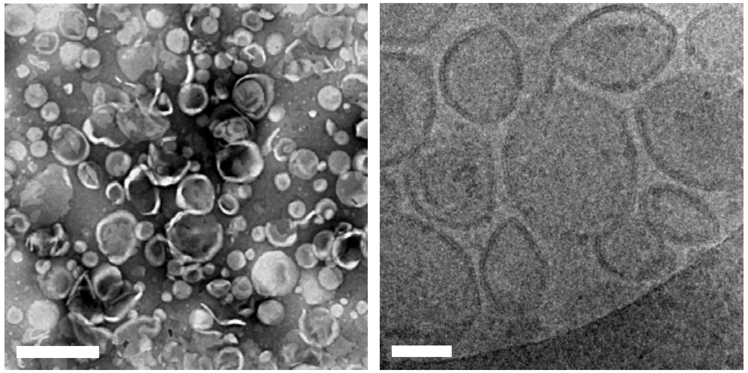


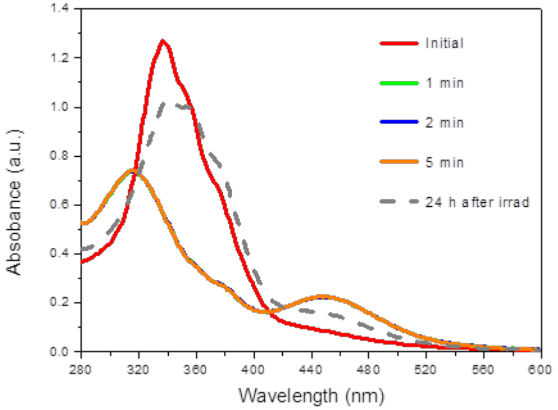
50/50



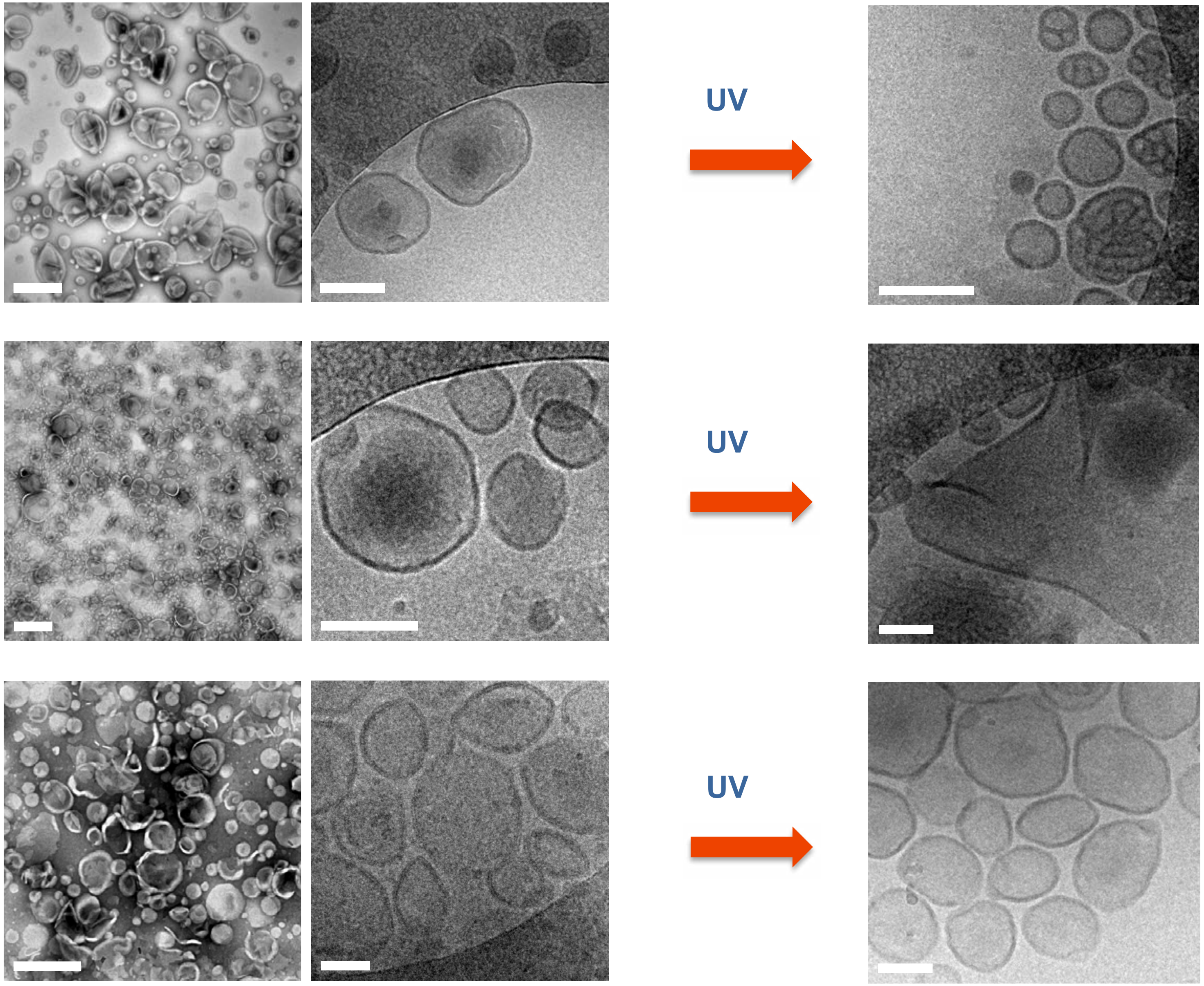


25/75





isoAZOb/C18



TEM

Cryo-TEM

Cryo-TEM

75/25

UV

50/50

UV

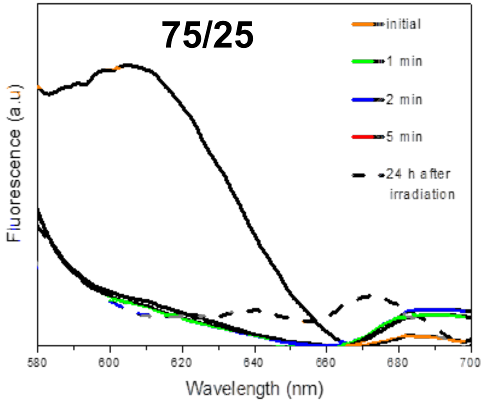
25/75

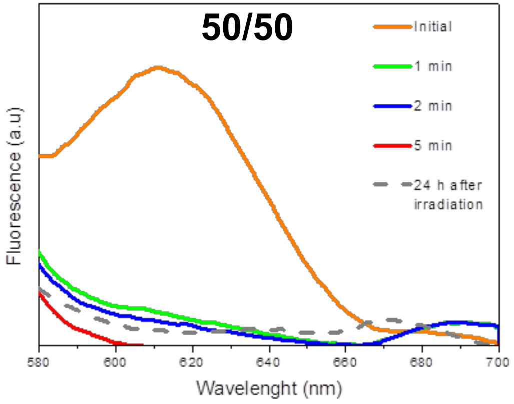
UV

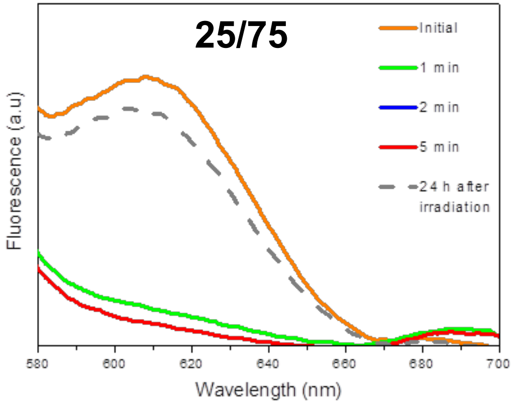
RELEASE PROPERTIES DEPENDING ON POLYMER STRUCTURE

NILE RED (hydrophobic)

UV IRRADIATION
(350-400nm)



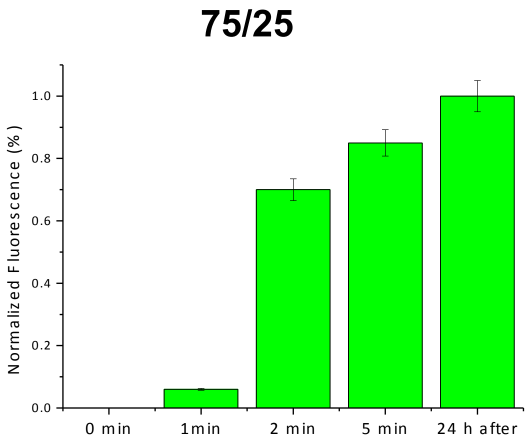


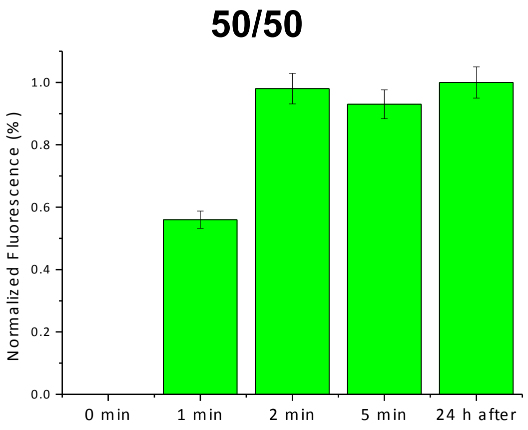


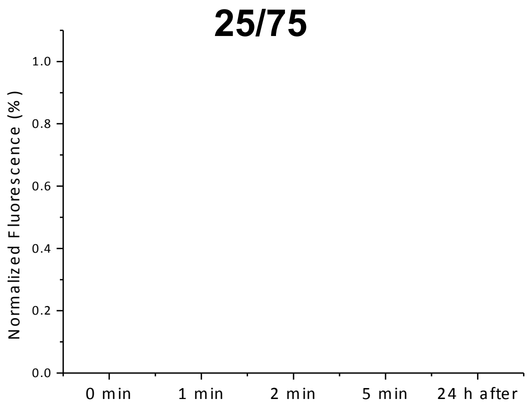
RELEASE

NON-RELEASE

RHODAMINE B (hydrophilic)

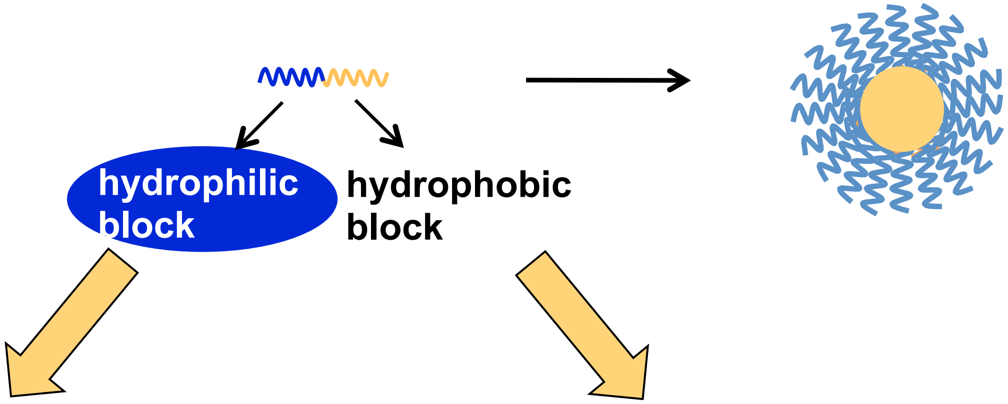






Macromolecules 2013, 46, 5951–5960

AMPHIPHILIC BC SELF-ASSEMBLY: MICELLES having a dual response
COLLABORATION WITH C. BARNER-KOWOLLIK, KIT

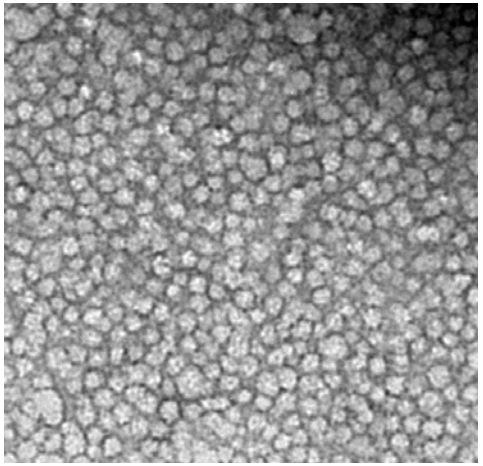


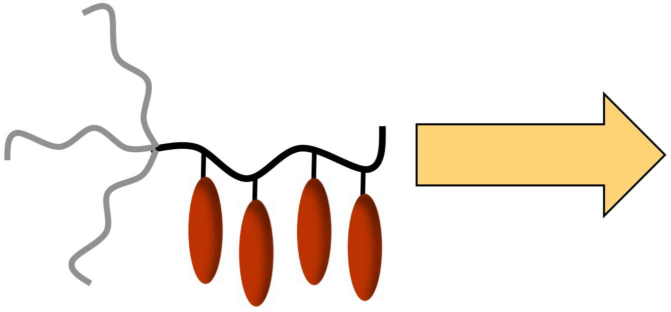
hydrophilic block

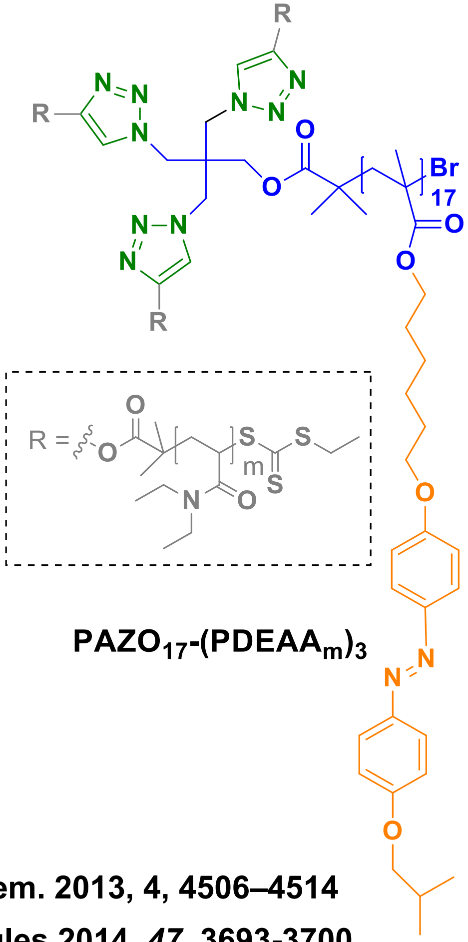
hydrophobic block

Philic/Phobic depending on TEMPERATURE

LIGHT-responsive







$\mathrm{PAZO_{17}\text{-}(PDEAA_m)_3}$

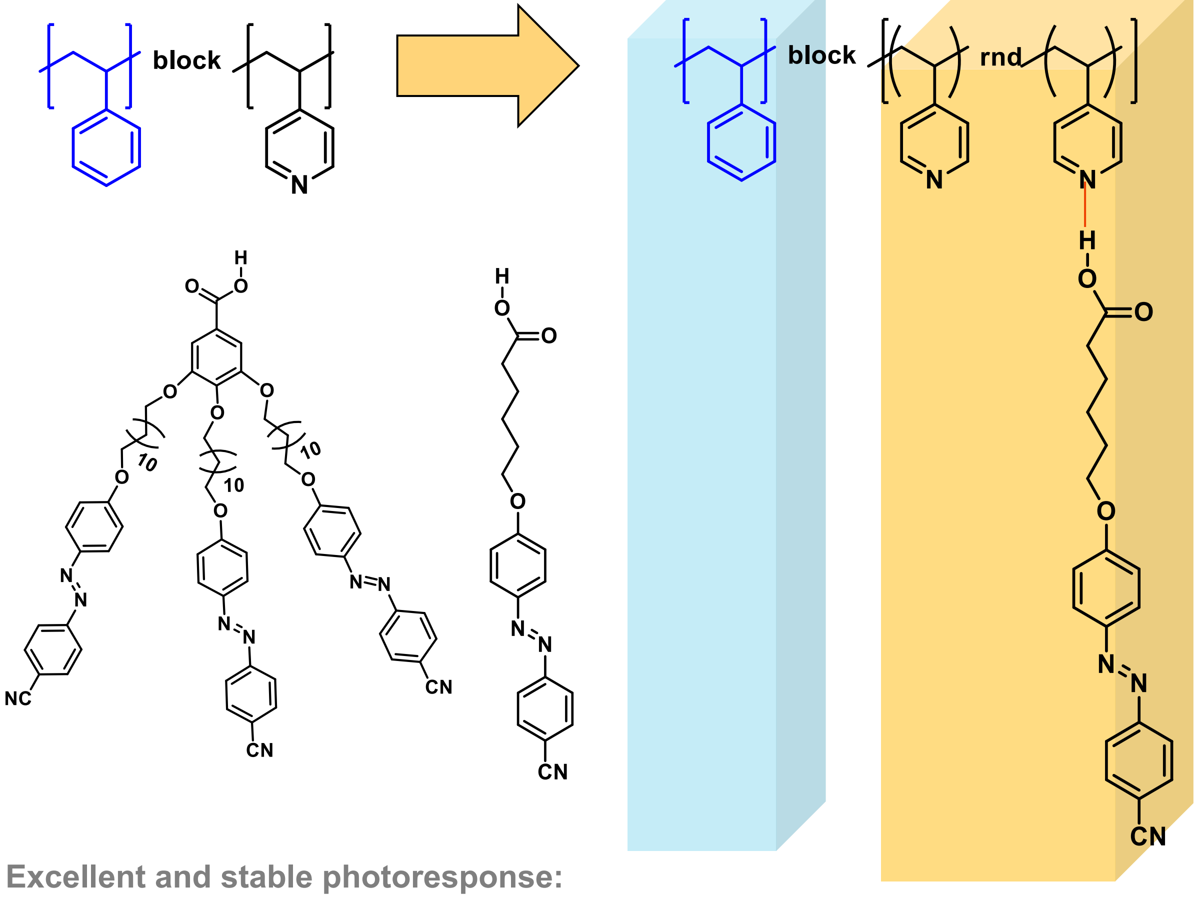
Polym. Chem. 2013, 4, 4506–4514

Macromolecules 2014, *47,* 3693-3700

AZO BLOCK COPOLYMERS: *supramolecular approach*

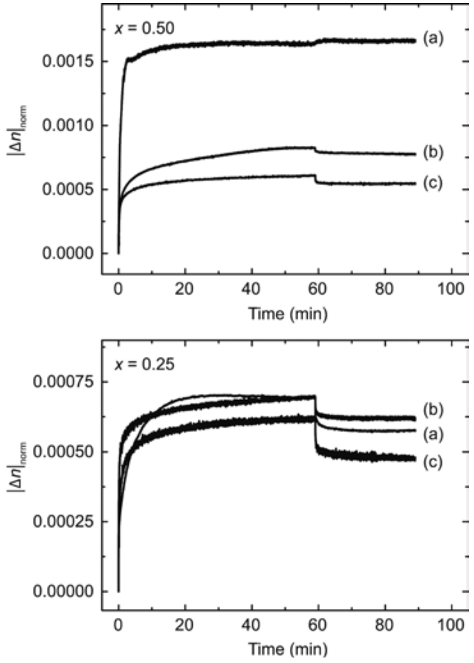
Supramolecular modfication of commercial block copolymers

ALTERNATIVE: COUPLING OF PREFORMED BLOCKS



Excellent and stable photoresponse:
Cooperativity effect of dendrons

Liquid crystalline BCs with morphology depending on degree of complexation

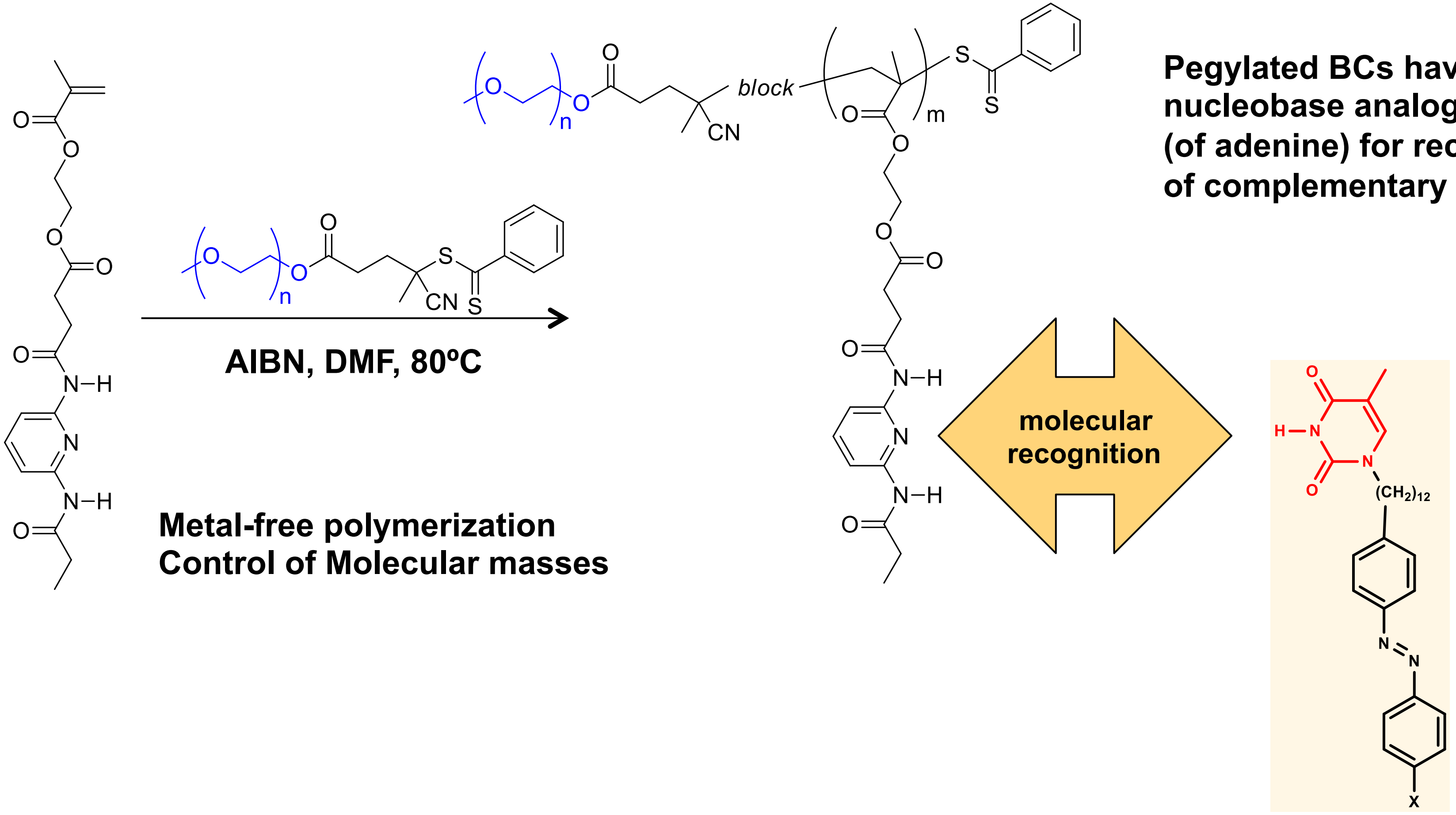


J.Polym. Sci. Polym. Chem. **2013, *51*, 1716**

Macromolecules **2014, *47*, 897-906**

STIMULI-RESPONSIVE BLOCK COPOLYMERS: *supramolecular approach*

RAFT POLYMERIZATION of NUCLEOBASE ANALOGUE methacrylate



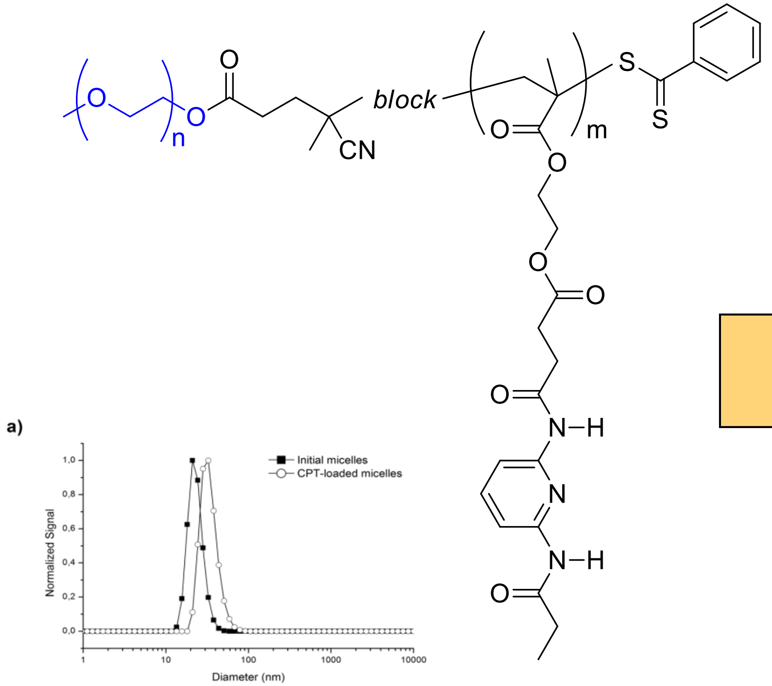
AIBN, DMF, 80ºC

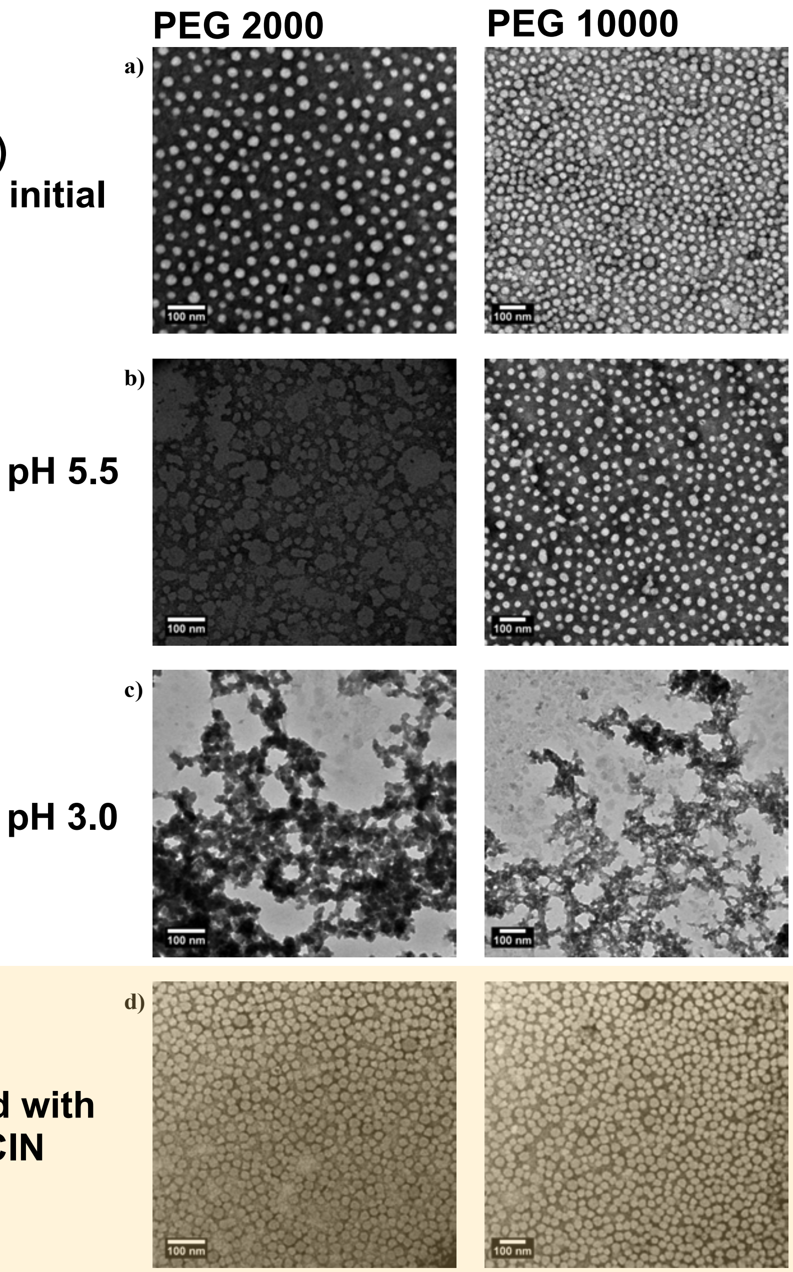
Metal-free polymerization
Control of Molecular masses

Pegylated BCs having a nucleobase analogue (of adenine) for recognition of complementary units

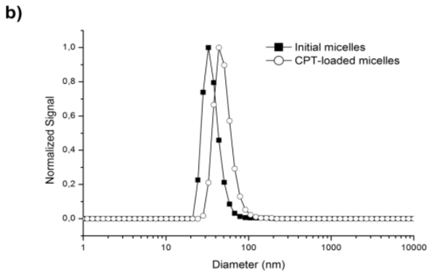
Stimuli-responsive polymers

EXCELLENT SEFL-ASSEMBLY PROPERTIES
BIOCOMPATIBLE (Colloboration Olga Abián –BIFI-)
pH RESPONSIVE



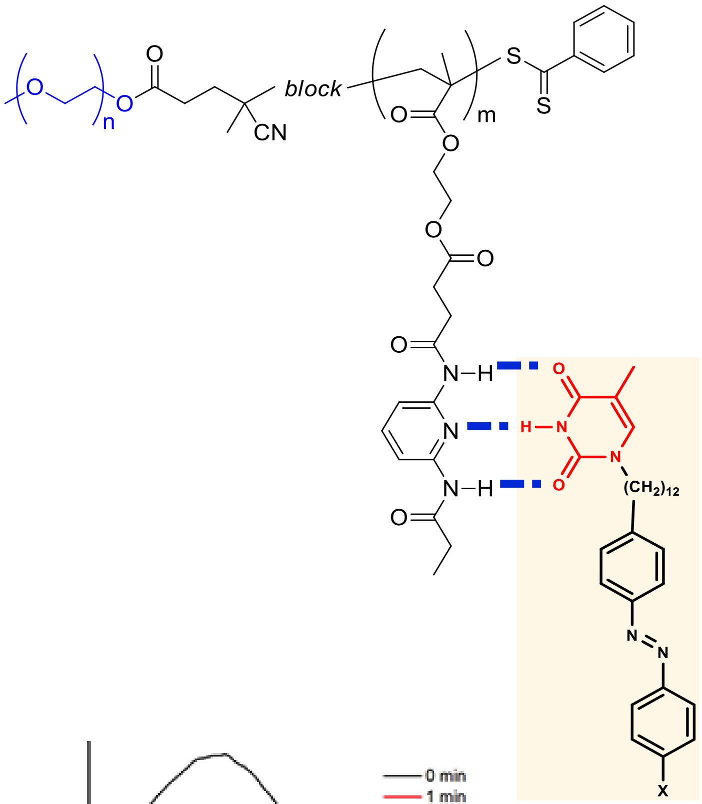


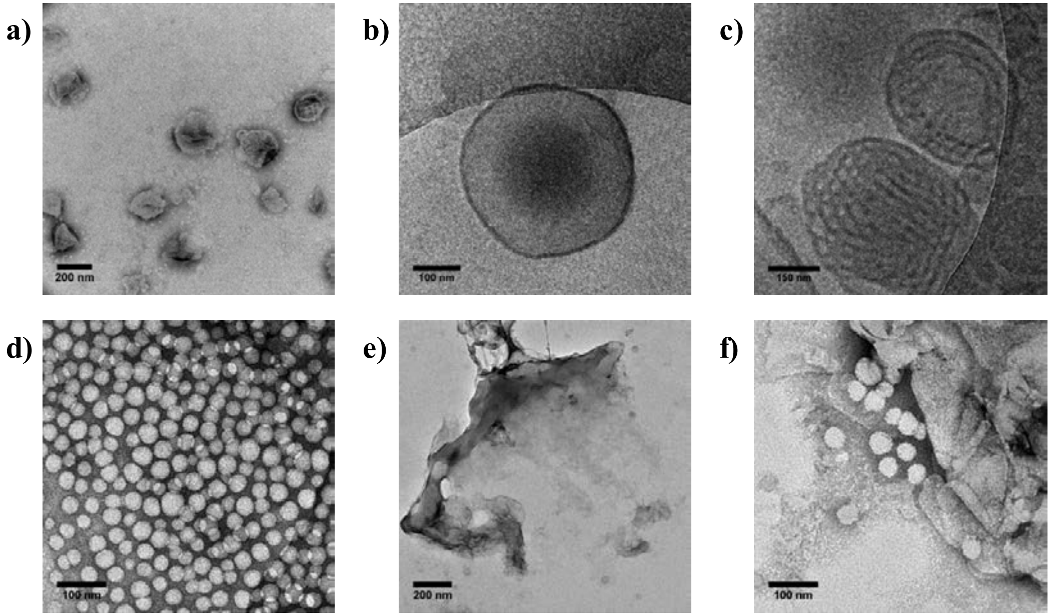
Micelles loaded with CAMPTOTHECIN



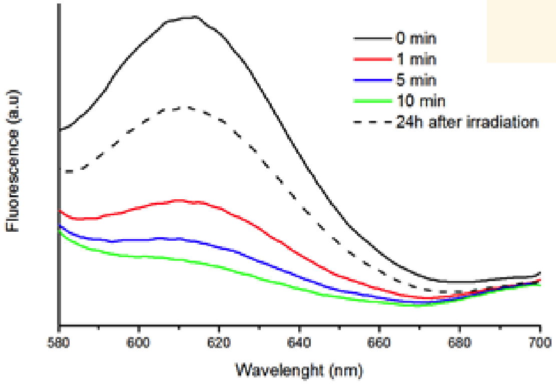
ANTIVIRAL PROPERTIES

Stimuli-responsive polymers

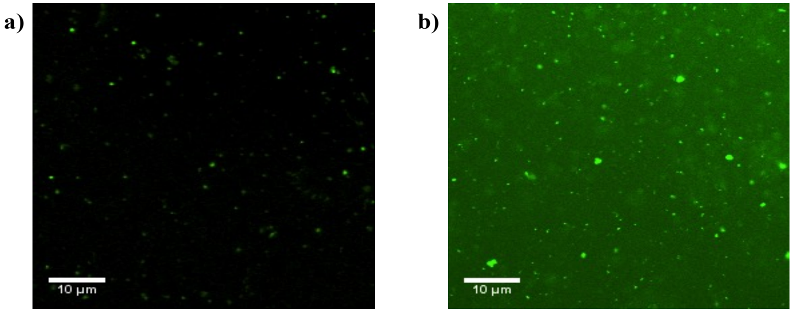




TEM image of: a) {PEG_2-*b*-PDAP • $tAZO_i$} non-irradiated vesicles. Cryo-TEM images of {PEG_2-*b*-PDAP • $tAZO_i$} vesicles: b) before and c) after UV irradiation. TEM images of {PEG_{10}-*b*-PDAP • $tAZO_i$} micelles: d) before, e) after and f) 24h after irradiation .



Emission spectra of the Nile Red encapsulated self-assemblies of: {PEG_{10}-*b*-PDAP • $tAZO_i$} recorded after irradiation for different time intervals.



Fluorescence microscopy images of water suspension of loaded {PEG_2-*b*-PDAP • $tAZO_i$} vesicles a) before and b) after irradiation for 10 min

IN PROGRESS

- **MICELLES PREPARATION BY MICROFLUIDICS (collaboration M. Arruebo)**
- **NIR RESPONSE USING UP-CONVERSION NPs (collaboration M. Arruebo)**
- **BIOCOMPATIBLE UNITS WITH DIRECT RESPONSE TO NIR (Hugo García)**
- **BCs based ON BIODEGRADABLE FUNCTIONAL POLYMERS (Alejandro Roche)**
- **ACTIVE ENDING GROUPS TO INTRODUCE OTHER FUNCTIONALITIES into polymeric NPs**

MAT2014-55205-P STIPOL

Synthesis and applications of smart polymers and supramolecular block copolymers with stimuli-responsive properties

EXPERTISE

- ✓ **MONOMER ORGANIC SYNTHESIS**
- ✓ **PREPARATION OF FUNCTIONAL POLYMERS**
  - ◆ **Radical chain polymerization**
  - ◆ **Step polymerization**
  - ◆ **CONTROLLED RADICAL POLMERIZATION: ATRP / RAFT**
  - ◆ **ROP**
- ✓ **CHARACTERIZATION OF POLYMERS**
- ✓ **PROCESSING AND STUDY OF POLYMER PROPERTIES**