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ATRP with a light switch: Photoinduced ATRP using a household fluorescent lamp

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Text for TOC: We report on the photoinduced ATRP in solution and from surfaces using a standard fluorescent lamp as the light source.

Abstract

Photoinduced atom transfer radical polymerization (ATRP) was achieved using a simple household fluorescent lamp as the light source. In solution, methyl methacrylate could be polymerized to well-defined polymers, the photoinduced ATRP system did only convert monomers during irradiation and was inactive in the dark. *In situ* monitoring by UV-vis spectroscopy revealed the photoredox cycle between Cu^{II} and Cu^{I} species. The linear development of the polymer number average molar mass with monomer conversion, the low dispersity as well as chain extension experiments showed the controlled nature of the polymerization. The photoinduced ATRP was also used to prepare homo- and block copolymer brushes and patterned brushes on surfaces by photoinduced surface-initiated ATRP (PSI-ATRP).

Introduction

Among the different controlled radical polymerization techniques atom transfer radical polymerization (ATRP) is one of the most versatile and robust techniques to synthesize well-defined polymers.[1] Lately, some disadvantages of ATRP such as the high copper catalyst concentration, easy oxidation of the unstable lower-state metal complexes and others [2] have been overcome by various strategies including activator (re-)generation by electron transfer (AGET or ARGET) ATRP.[3] The generality of these strategies showed that the lower state Cu^{I} required for the ATRP can also be generated *in situ* by the reduction of the respective Cu^{II} complex by various reducing agents,[4, 5] electrochemically [6, 7] or by means of photochemical processes.[8, 9]

Especially the latter is a very versatile approach for controlled ATRP reactions especially if no additional photoactivator is used. Yagci et al.[8] presented the first example of photoinduced controlled radical polymerization (PCRP) based on photochemical generation of the activator in ATRP. They showed that the polymerization of bulk methyl methacrylate (MMA) at room temperature could be initiated by *in situ* generation of the Cu^I complex from Cu^{II} species under UV irradiation at 350 nm. An improved correlation between theoretical and experimental polymer molar mass with quite narrow dispersity (Đ=1.06-1.13) was observed when using methanol as the solvent.[9] Recently, a well-controlled polymerization of MMA at 35℃ was investigated by photomediated ATRP using a light source at $\lambda > 350$ nm to realize a lower $CuBr_2$/PMDETA catalyst amounts to ppm level.[10] Instead of UV light, a safer, less expensive and abundant light source in the visible range is beneficial for polymer synthesis and attractive for a broad range of applications including dentistry, photolithography or holographic memory storage.[11-14]

Recently, first examples have been reported on photoinduced ATRP with light in the visible range. Zhang et al.[11] used light sensitive $Ru(bpy)_3Cl$ to initiate and control the polymerization. However, the obtained polymer molar masses were much higher as expected and showed a high dispersity. In another study, visible light was used to induce the polymerization of MMA by combination $CuCl_2$/PMDETA complex with dyes and photoinitiators.[15] The resulting polymers obtained with a bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide system showed molar masses close to the predicted ones and low dispersities. Photoinduced ATRP was successfully carried out with single-wavelength light of 392 or 450 nm without photoinitiators,[16] and most recently the use of other light sources and photoinitiator systems were reported.[17, 18]

The significant photochemical effect of visible light on ATRP of MMA with CuCl/bipyridine as catalyst has been revealed about one decade ago.[19] The authors concluded that visible light not only can accelerate the polymerization but also improve the livingness of the polymerization at low catalyst level. Inspired by this study, we investigated the possibility if photoinduced ATRP can also be performed with a simple fluorescence lamp (type L58W/880 "SKYWHITE" from Osram®, Germany) used commonly in many households but is also used as a standard light source to illuminate chemical hoods. Our system is based on the *in situ* generation of Cu^I from Cu^{II} species and uses an excess of *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) but no additional reducing agent. The polymerization kinetics, degree of control, dynamic modulation (stop-and-go) by light are reported. Additionally, we transformed the system to enable photoinduced surface-initiated polymerization (PSI-ATRP) and show first results on the synthesis of homogeneous, patterned and block copolymer brushes.

Experimental Section

Materials

Methyl methacrylate (MMA, 99%) and *tert*-butyl methacrylate (tBMA) were purchased from Sigma-Aldrich and purified before use by passing through a basic alumina column to remove the inhibitor. Ethyl 2-bromoisobutyrate (EBiB, 98%), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA, 99%), copper(II) bromide ($CuBr_2$, 99%), copper(I) bromide (CuBr, 99.99%), 3-aminopropyltriethoxysilane (APTES), 2-bromoisobutryl bromide (BIBB), N,N-dimethylformamide (DMF) and methanol (all from Sigma-Aldrich) were used as received.

General Procedure for the Photoinduced ATRP

In a Schlenk flask (Duran glass) with dry $CuBr_2$ (4.18 mg, 0.0187 mmol), a mixture of DMF

(1.0 mL), methanol (0.5 mL), PMDETA (12.44 µL, 0.0569 mmol), and MMA (2 mL, 18.70 mmol) was added under a dry argon atmosphere. The reaction mixture was purged with dry argon for 30 min before EBiB (23.28 µL, 0.1870 mmol) was added. The reaction flask was placed in the middle of two standard fluorescent lamps (type L 58 W/880 "SKYWHITE" from Osram, Germany with 58 W, 8000 K color temperature and a luminous flux of 4900 lm at 25°C for the entire lamp) emitting light in the spectral range of 400-750 nm at an approximate distance of 10 cm to each lamp and the reaction mixture was stirred throughout the experiments. After indicated irradiation times, aliquots of the reaction mixture were collected and the polymer product isolated by precipitation in methanol. Reprecipitation was performed until a colorless powder was obtained. The polymer products were dried in vacuum (r.t.) to a constant weight and analyzed. Monomer conversion was determined gravimetrically.

Photoinduced Surface-initiated ATRP (PSI-ATRP)

Silicon wafer pieces with a 300 nm SiO_2 layer were functionalized with a self-assembled monolayer (SAM) of ATRP-initiator (BiBB) as described in the literature.[20] The functionalized substrates were immersed into a reaction mixture prepared as described above. After the PSI-ATRP reaction, the substrates were removed from the polymerization solution, exhaustively rinsed with acetone and repeatedly ultrasonicated for several minutes in fresh acetone to remove all traces of physisorbed polymer. Finally, the substrates were blow-dried by a stream of nitrogen and analyzed.

Patterned initiator SAMs were prepared by photolithography using UV illumination (200 W Hg(Xe) lamps, LOT-oriel, Germany) through a photomask (TEM grids).

Characterization

UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Gel permeation chromatography (GPC) was performed on a PL-GPC-120 (Polymer Laboratories) running under WinGPC software (PSS, Mainz, Germany) with two consecutive Gram columns (2 x 100 Å) with N,N-dimethylacetaminde (DMAc) (5 g/L LiBr, 70 °C, 1 mL/min) as eluent and calibrated against PMMA standards from PSS, Mainz, Germany. Molar masses were also determined by end group analysis using ^{1}H NMR spectroscopy data recorded on a Bruker DRX 500 spectrometer at room temperature in $CDCl_3$. Atomic force microscopy (AFM) was performed on a NTEGRA Aura from NT-MDT in semicontact mode (probes with curvature radius of 6 nm, a resonant frequency of 47−150 kHz, and a force constant of 0.35−6.10 N/m).

Results and Discussion

1. Photoinduced ATRP in solution

The polymerization of MMA with $CuBr_2$/PMDETA was performed under visible light irradiation using a standard commercially available fluorescent lamps (type L58W/880 "SKYWHITE" from Osram®, Germany) at room temperature. To ensure reproducibility of the experiments, the reaction flasks (Duran glass, cut-off $\lambda \lesssim 300$ nm) were placed in the middle of two fluorescent light tubes ($\lambda = 400$-750 nm) at a distance of approx. 10 cm to each lamp. All other light was excluded. In a typical procedure, the reaction mixture containing the monomer (methyl methacrylate, MMA), copper salt ($CuBr_2$), ligand (*N,N,N′,N″,N″*-pentamethyldiethylenetriamine, PMDETA) and the initiator (ethyl 2-bromoisobutyrate, EBiB) were dissolved in a DMF/methanol (1:0.5, v/v) mixture under argon atmosphere at a ratio of [MMA]:[EBiB]:[$CuBr_2$]:[PMDETA]=100:1:0.1:0.3. The reaction vial was irradiated for 5 h and the obtained polymer immediately isolated and then analyzed. This procedure readily resulted in poly(methyl methacrylate) (PMMA) with a quite narrow dispersity of Đ = 1.21 and an number average molar mass of M_n = 5.2 kg/mol as determined by gel permeation chromatography (Table 1 entry #1). The monomer conversion after 5 h was determined to be 25 %. A longer irradiation time of 22 h resulted in a higher monomer conversion (85 %), higher number average molar mass (M_n = 8.7 kg/mol) of the polymer and similar dispersity (Table 1 #2). Increasing the ratio of the ligand PMDETA from 0.3 to 1 resulted in higher monomer conversion and higher M_n at a slightly better dispersity (Table 1 #3). The results of both reactions indicate that the polymerization of MMA proceeds by the controlled atom transfer radical polymerization. However, performing the same experiment in the absence of light (Table 1 #4) no polymer product could be obtained. This indicates the essential role of visible light for the polymerization reaction. Moreover, the influence of the PMDETA ligand concentration was investigated. If no ligand was added or the ligand concentration was less or equal to the added Cu^{II} salt, no polymerization was observed, independent of the irradiation (Table 1 #5). Interestingly, our attempts of running the ATRP with an 10fold excess of PMDETA with respect to the Cu^{II} salt in order to use the ligand as a reducing agent as reported by Matyjaszewski et al.[21] only gave a polymer product under additional irradiation (Table 1 #4 *vs.* #3). This is in accordance with later reports by the same group [22] as well as the recent observation by Yagci et al.[15] who found that PMDETA can not reduce Cu(II) to Cu(I) in the absence of light.

Without the initiator, light irradiation for 5 h resulted in a small portion of high molar mass and broadly dispersed PMMA (Đ = 3) (Table 1 #6). A control experiment (no copper (II) salt, no ligand) gave no polymer product (Table 1 #7). Finally, the ATRP polymerization reaction was conducted by using copper (I) instead of copper (II) bromide. Reaction for 5 h in the absence of light (Table 1 #8) gave again only very little polymer product (3 % monomer conversion) of higher dispersity. However, under irradiation (Table 1 #9), the polymerization proceeded nicely and gave almost identical results to the reaction starting with copper (II) salt (Table 1 #1).

Table 1. Experiments for the photoinduced ATRP of methyl methacrylate.

entry #	MMA:EBiB: Cu: PMDETA	light	time [h]	conversion [%]	$M_{n,theo}$ [g/mol]	$M_{n,GPC}$ [g/mol]	M_{NMR} [g/mol]	$Đ$
$1^{a)}$	100:1:0.1:0.3	on	5	25.22	2722	5249	3520	1.21
$2^{a)}$	100:1:0.1:0.3	on	22	85.27	8727	9865	8812	1.20
$3^{a)}$	100:1:0.1:1	on	5	31.26	3326	6162	4374	1.19
$4^{a)}$	100:1:0.1:1	off	5	-	-	-	-	-
$5^{a)}$	100:1:0.1:0.1	on/off	5	-	-	-	-	-
$6^{a)}$	100:0:0.1:1	on	5	3.05	-	23865	-	2.51
$7^{a)}$	100:1:0:0	on	5	-	-	-	-	-
$8^{b)}$	100:1:0.1:0.3	off	5	3.40	540	1790	1501	1.60
$9^{b)}$	100:1:0.1:0.3	on	5	26.15	2815	5916	4520	1.21

$^{a)}$ copper (II) bromide; $^{b)}$ copper (I) bromide; $^{c)}$ $M_{n,theo}$=([MMA]$_0$/[EBiB]$_0$$\times$conversion $\times M_{monomer}$).

From these experiments we conclude that light as emitted from a standard fluorescence lamp has a significant photochemical effect on the ATRP reaction. Acceleration of the ATRP reaction rate by visible light as well as improvement of the control of the polymerization was reported before by Guan and Stuart [19] but using a 275 W sunlamp. And recently, the group of Yagci et al. [8, 9] reported analog results on the photoinduced ATRP with the PMDETA/Cu^{II} system using UV light (350 nm). Apparently, also under visible light irradiation the PMDETA is able to constantly reduce Cu^{II} to Cu^{I} and a well-controlled ATRP is enabled under these simple experimental conditions. The respective reaction mechanism is outlined in Fig. 1 along with the emission spectrum of the fluorescent lamp as provided by the lamp manufacturer.

- FIGURE 1 -

Fig. 1 Reaction mechanism for the photoinduced ATRP. Even light in the visible range as emitted by a standard fluorescent lamp (type L58W/880 "SKYWHITE" from Osram®, Germany, emission spectrum as provided by the manufacturer) is able to close the Cu^{II}/Cu^{I} redox cycle. Such lamps are a common light source and also used to illuminate laboratory hoods.

We investigated the kinetics of the photoinduced ATRP using MMA as the standard monomer and development of the polymer number average molar mass (M_n) as a function of the monomer conversion (Fig. 2). As apparent form the strictly linear relationship of $\ln([M_0]/[M])$ with the reaction time (Fig. 2 a), the polymerization is of first-order with respect to the monomer concentration and the concentration of active radicals remains constant throughout the polymerization. A short induction period was observed which is in accordance to the reaction mechanism given in Fig. 1. First, the photoreduction needs to generate Cu^{I} species and establish the equilibrium between the catalyst CuBr/PMDETA and the catalyst precursor $CuBr_2$/PMDETA. The highly controlled character of the photoinduced ATRP is demonstrated by the strictly linear increase of M_n as a function of the monomer conversion at narrow dispersities ($Đ \leqq 1.2$) (Fig. 2b) and monomodal distributions (Fig. 2c). It is noteworthy that for all obtained polymers the determined M_n were found to be slightly higher than theoretically expected from the $[M_0]/[I]$ ratio. This was observed earlier by others and ascribe to a low initiating efficiency of EBiB because of its back strain effect.[10, 23]

"Livingness" of the photoinduced ATRP is demonstrated by an additional chain extension experiment with a PMMA-Br macroinitiator. First, the PMMA-Br macroinitiator was synthesized by photoinduced ATRP for 5h as described above, isolated and analyzed (M_n = 6 kg/mol and $Đ$ = 1.20). The chain extension was then performed under the same experimental conditions for 7 h ([MMA]:[PMMA-Br]:[$CuBr_2$]:[PMDETA] ratio of 250:1:0.1:0.3). The reaction yielded PMMA with M_n = 13.2 kg/mol and $Đ$ = 1.17. The GPC traces of the macroinitiator and the product are displayed in Fig. 2d. The clear shift of M_n and no detectable traces of remaining macroinitiator indicate a quantitative chain extension by reinitiation.

- FIGURE 2 -

Fig. 2 Photoinduced ATRP of MMA. (a) First-order kinetic plot, (b) evolution of the polymer molar mass and dispersity, Đ, with the monomer conversion and (c) respective GPC traces. Reactions were performed at a molar ratio of [MMA]:[EBiB]:[$CuBr_2$]:[PMDETA] =100:1:0.1:0.3. d) GPC traces for a PMMA-Br used as a macroinitiator (pink) and resulting PMMA (blue) after 7 h irradiation of [MMA]:[PMMA-Br]:[$CuBr_2$]:[PMDETA] = 250:1:0.1:0.3. Reactions conditions for preparation of PMMA-Br macroinitiator: time 5 h otherwise as for (c).

Previous studies revealed that the characteristic UV spectral absorption bands of Cu^{II}/L complex should be around 250, 300 and 640nm [24, 25] and Yagci et al.[8] used the decrease of the characteristic Cu^{II} d-d ligand field transition around 640 nm to follow the photoredox reaction. The photoinduced $Cu^{II}Br_2/L$ to $Cu^{I}Br/L$ reduction was followed in real time by *in situ* UV-vis spectroscopy using a solution of EBiB (3.1×10^{-2} M), $CuBr_2$ (3.1×10^{-3} M) and PMDETA (9.3×10^{-3} M) in DMF/Methanol (v/v, 2/1). The solution was irradiated in a quartz cell with light of a spectral range from 400-750nm at room temperature and the UV-vis absorption spectra were recorded periodically during 8h.

- **FIGURE 3** -

Fig. 3 *In situ* UV-vis spectroscopy of the Cu$^{I/II}$/L system (EBiB (3.1×10^{-2} M), CuBr$_2$ (3.1×10^{-3} M) and PMDETA (9.3×10^{-3} M) in DMF/Methanol (v/v, 2/1)). a) Spectra recorded during irradiation with visible light (400-750nm) in a quartz cell at room temperature; b) UV/vis spectral changes in the dark.

In Fig. 3a, the spectra are summarized along with inserts of the prominent spectral changes found around 685 and 528 nm. Under irradiation, the UV adsorption around 685 nm steadily decreases simultaneously to systematic spectral changes in the range of 527 - 529 nm. We assign this to the photoreduction of Cu^{II}Br$_2$/L to Cu^{I}Br/L mediated by the ligand PMDETA. Interestingly, as depicted in Fig. 3b, an opposite change of the UV-vis spectra was observed under exclusion of light. Within only 11 min, the Cu^{I}Br/L apparently reoxidizes to Cu^{II}Br$_2$/L in the dark at room temperature. The first spectrum of Fig. 3a and the last of Fig. 3b were found to be identical.

The photoreduction of Cu^{II}/L to Cu^{I}/L along with the fast reoxidation allows to control the ATRP polymerization rate with high precision and was demonstrated by Mosnacek and Ilcikova [10] for irradiation at λ = 366, 405, 408, 436, and 546 nm, and the Yagci group for UV light (λ =320-500 nm) both using PMDETA as the ligand and MMA as the monomer.[9] Here we investigate if the photoinduced ATRP could be "switched on and off" using the light switch for the fluorescence lamp.

Again starting with CuBr$_2$, the monomer, initiator, ligand and solvents ([MMA]:[EBiB]:[CuBr$_2$]: [PMDETA]=100:1:0.1:0.3) were mixed in the absence of light placed between the fluorescent lamps and the light was switched on. After 2 h irradiation, the reaction mixture was stirred for 2 h in the dark followed again by 2 h irradiation a.s.f. The reaction progress was monitored by taking aliquots of the reaction mixture, isolation of polymer product, determination of monomer conversion and analysis of the polymer by GPC. The dark-light phases and resulting products are summarized in Fig. 4.

- FIGURE 4 -

Fig. 4 Photoinduced ATRP performed by light-dark cycles of 2 h each. The stop-and-go characteristics of the polymerization is shown by a) development of the monomer conversion as a function of the irradiation time over 24 h. Narrow dispersity is maintained throughout the experiment. b) Development of M_n of the polymer product sampled at each time point as indicated in a). Reactions were conducted with [MMA]:[EBiB]:[$CuBr_2$]:[PMDETA]=100:1:0.1:0.3 at room temperature using irradiation from two fluorescent lamps at a distance of 10 cm to the reaction vial.

The monomer conversion by photoinduced ATRP could be directly controlled by the irradiation time and no monomer conversion was detectable during the dark periods. The polymerization was essentially intercepted in the absence of light, because of the fast oxidation of Cu^I/L, the negligible concentration of radicals and the apparently slow intermediate fragmentation reaction. In each irradiation phase, the polymerization proceeds with nearly the same kinetics (within the experimental error) (Fig. 4a). Again, low dispersity ($Đ \leqq 1.2$) was maintained throughout the entire experiment in a course of 24 h and M_n increased progressively with monomer conversion (here to 89%) without a detectable trace of low molar mass products (Fig. 4b). Basically, each on-off cycle had the same characteristics as the chain extension experiment using a PMMA-Br macroinitiator as described above and during the dark phases the molar mass was unchanged (see: Fig. 4b e.g. GPC traces for 2 h *vs.* 4 h or 10 h *vs.* 12 h).

2. Photoinduced surface-initiated ATRP (PSI-ATRP)

The use of light to trigger a controlled polymerization and to perform consecutive polymerization steps is especially intriguing for the fabrication of polymer brushes by surface-initiated polymerization. Besides surface-initiated living ionic polymerizations,[26-28] surface-initiated controlled radical polymerization techniques such as SI-ATRP are very versatile to prepare defined polymer brushes for a multitude of applications.[29-32] Only recently, Zhou et al.[18] reported on the use of UV-light (λ = 330 nm at 0.5 or 1.25 mW/cm^2) and TiO_2 particles as the photosensitizer for the photoinduced surface-initiated ATRP (PSI-ATRP) of different methacrylates from self-assembled monolayers (SAMs) on TiO_2 or gold. However, as thiols are prone to photooxidation by exposure to UV light,[33] it would be beneficial to conduct PSI-ATRP with light in the visible range and without addition of particles that might irreversibly contaminate the surfaces. Hence, we performed PSI-ATRP analog to the reactions described above but using a SAM as the ATRP-initiator bound to silicon dioxide surface as outlined in Fig. 5. Additionally, we performed PSI-ATRP on patterned initiator-SAMs. Although various possibilities are feasible for the synthesis of patterned polymer brushes,[34] we selected the simplest technique and prepared patterned SAMs by UV-photolithography. Finally, consecutive PSI-ATRP, with MMA and *tert*-butyl methacrylate (tBMA) as the second monomer was performed to realize block copolymer brushes.

- FIGURE 5 -

Fig. 5 Photoinduced surface-initiated ATRP (PSI-ATRP) of MMA on a SAM of APTES-BIBB on silicon dioxide. The initiator-SAM was prepared as reported by Wang et al.[20] Patterned polymer brushes were prepared form photopatterned initiator-SAMs and block copolymer brushes by consecutive PSI-ATRP. The photograph in the lower left corner shows the experimental setup.

Under light exclusion, the functionalized silicon substrates were immerged in the reaction solution as described above for ATRP in solution and PSI-ATRP was performed for 5 h. After cleaning, the substrates were investigated by atomic force microscopy (AFM). The PSI-ATRP resulted in the formation of homogeneous PMMA brushes without detectable defects. Measurements at an implied scratch revealed a brush thickness of d = 14.5 ± 0.5 nm (Fig. 6a,c). With the same substrate, a consecutive PSI-ATRP with tBMA resulted in a P(MMA-*b*-tBMA) copolymer brush of d = 20.3 ± 1.2 nm thickness in the collapsed state (Fig. 5b,c). Again, the polymer brush surface appeared homogeneous as determined by random sampling with the AFM and the thickness increase was found to be nearly identical at different locations at the edge. Patterned PMMA brushes were readily obtained by PSI-ATRP from micropatterned SAM-initiators. Different patterns were produced and two are displayed in Fig. 6d) and e). The brush thicknesses were very similar (d ~ 12 nm) and the PSI-ATRP selectively transformed the initiator pattern to the pattern brush. No polymer grafting was observable on unmodified substrate areas.

- FIGURE 6 -

Fig. 6 AFM scans at an inflicted scratch of a) PMMA brush and b) P(MMA-*b*-tBMA) block copolymer brush prepared by consecutive PSI-ATRP. c) Cross section analysis along the dashed lines in a) and b) indicating the thickness increase. d) and c) AFM scans of micropatterned PMMA brushes prepared from patterned SAM-initiators. Reaction time 5 h, scale bar in all scans is 20 µm.

As the PSI-ATRP is depending on constant light irradiation and is independent from an additional reducing agent, this technique offers great potential for the fabrication of very complex polymer brushes such as gradient, binary, (multi)block copolymer brushes in a simple fashion. Related experiments are currently ongoing in our laboratories.

Conclusion

We showed a simple and low-cost technique to perform photoinduced ATRP with common, cheap fluorescent lamps as the light source. The control and efficiency of ATRP is similar to earlier reports using light in the UV range or specific lasers. The stop-and-go characteristics of the ATRP kinetics allows for consecutive polymerization steps without apparent change of the active chain concentration. The photoinduced ATRP can easily be adapted to surface-initiated polymerization for the fabrication of polymer brushes, block copolymer brushes and patterned polymer brushes by photoinduced surface-initiated ATRP (PSI-ATRP). As the used fluorescent lamps are also commonly used to illuminate chemical hoods, these results are of relevance for all experimentalists performing ATRP in a standard hood. As many copper complexes are known to be light sensitive and/or mediate photoredox reactions [35-38] it most probably will make a difference if one is performing an ATRP reaction with the hood lights on or off.

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Figure 1

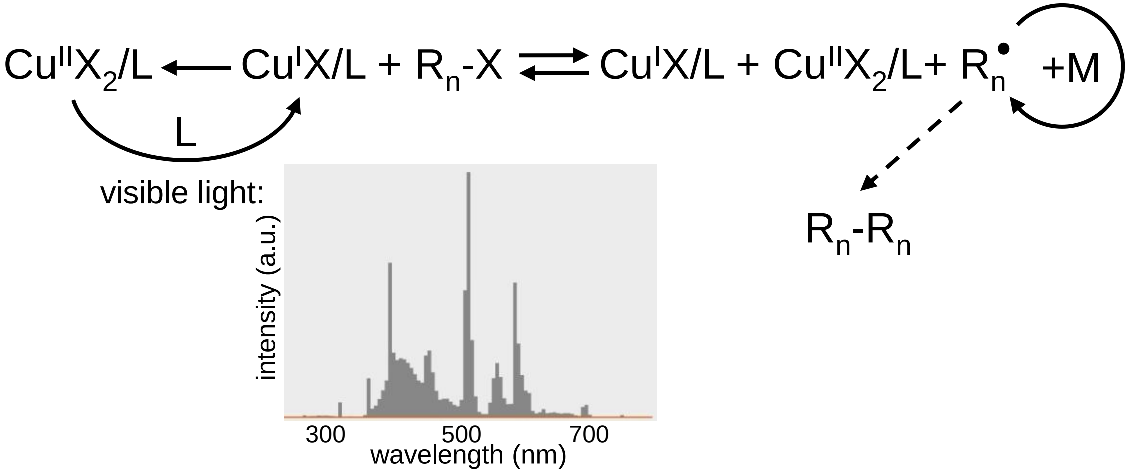

$Cu^{II}X_2/L$
$Cu^{I}X/L + R_n\text{-}X$
$Cu^{I}X/L + Cu^{II}X_2/L + R_n^{\bullet}$
+M
L
visible light:
$R_n\text{-}R_n$
intensity (a.u.)
300
500
700
wavelength (nm)

Figure 2

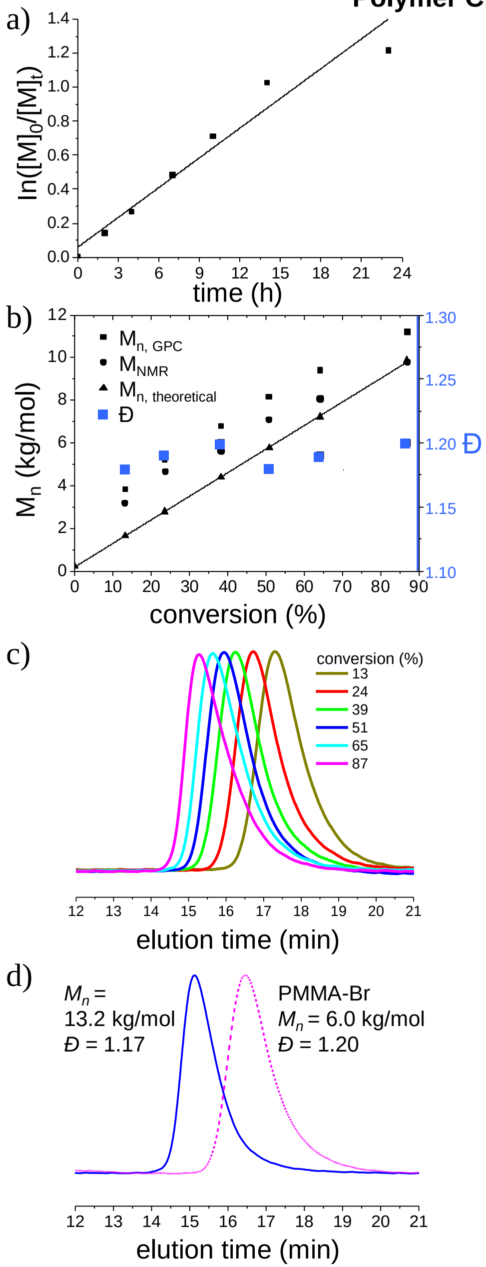
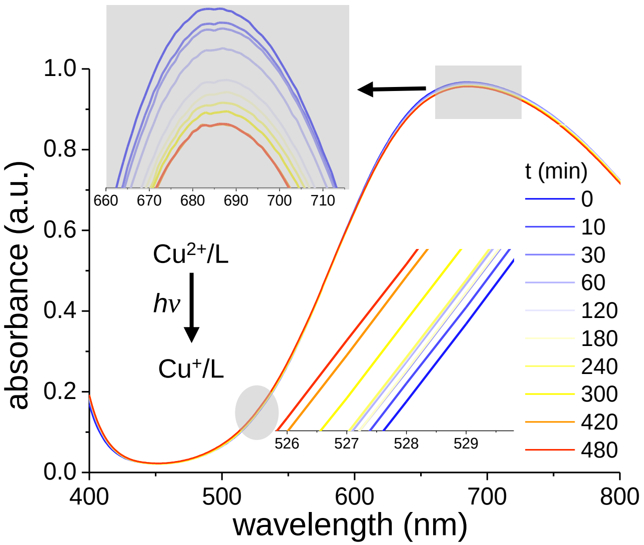

a)
ln([M]0/[M]t)
0.0
0.2
0.4
0.6
0.8
1.0
1.2
1.4
0
3
6
9
12
15
18
21
24
time (h)
b)
Mn (kg/mol)
0
2
4
6
8
10
12
Mn, GPC
MNMR
Mn, theoretical
Đ
1.10
1.15
1.20
1.25
1.30
Đ
0
10
20
30
40
50
60
70
80
90
conversion (%)
c)
conversion (%)
13
24
39
51
65
87
12
13
14
15
16
17
18
19
20
21
elution time (min)
d)
Mn =
13.2 kg/mol
Đ = 1.17
PMMA-Br
Mn = 6.0 kg/mol
Đ = 1.20
12
13
14
15
16
17
18
19
20
21
elution time (min)

Figure 3

a) Light



b) Dark

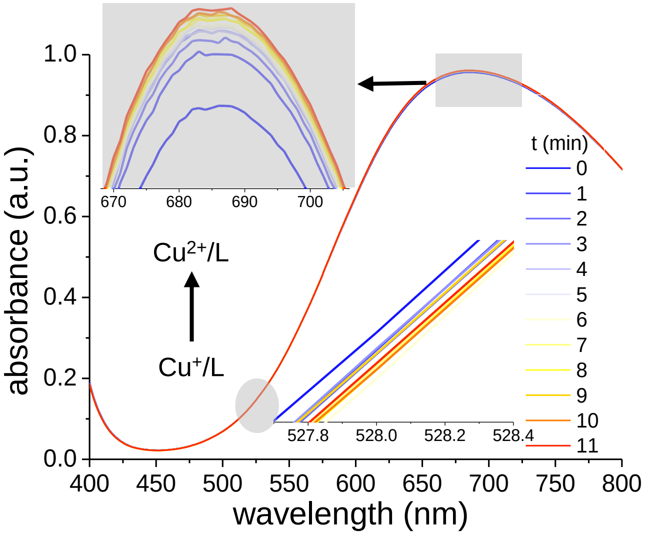


Figure 4

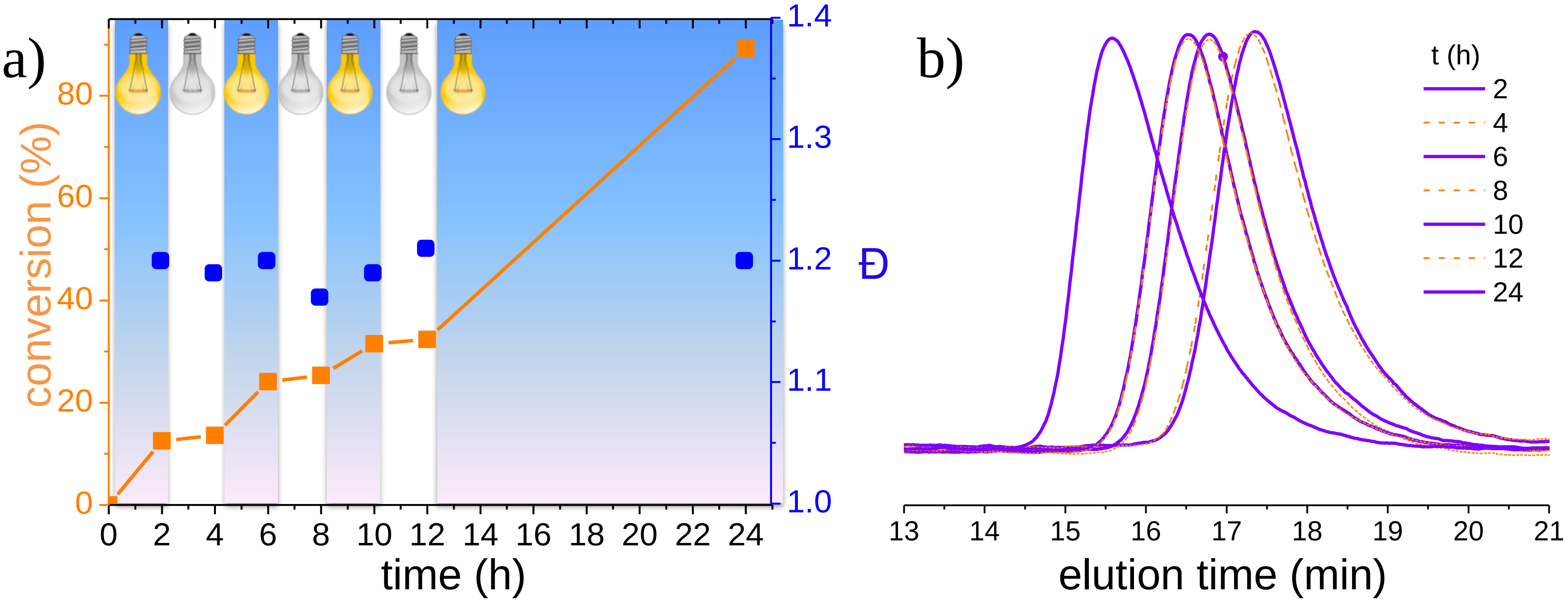

a)
conversion (%)
0
20
40
60
80
time (h)
0
2
4
6
8
10
12
14
16
18
20
22
24
Đ
1.0
1.1
1.2
1.3
1.4
b)
t (h)
2
4
6
8
10
12
24
elution time (min)
13
14
15
16
17
18
19
20
21

Figure 5

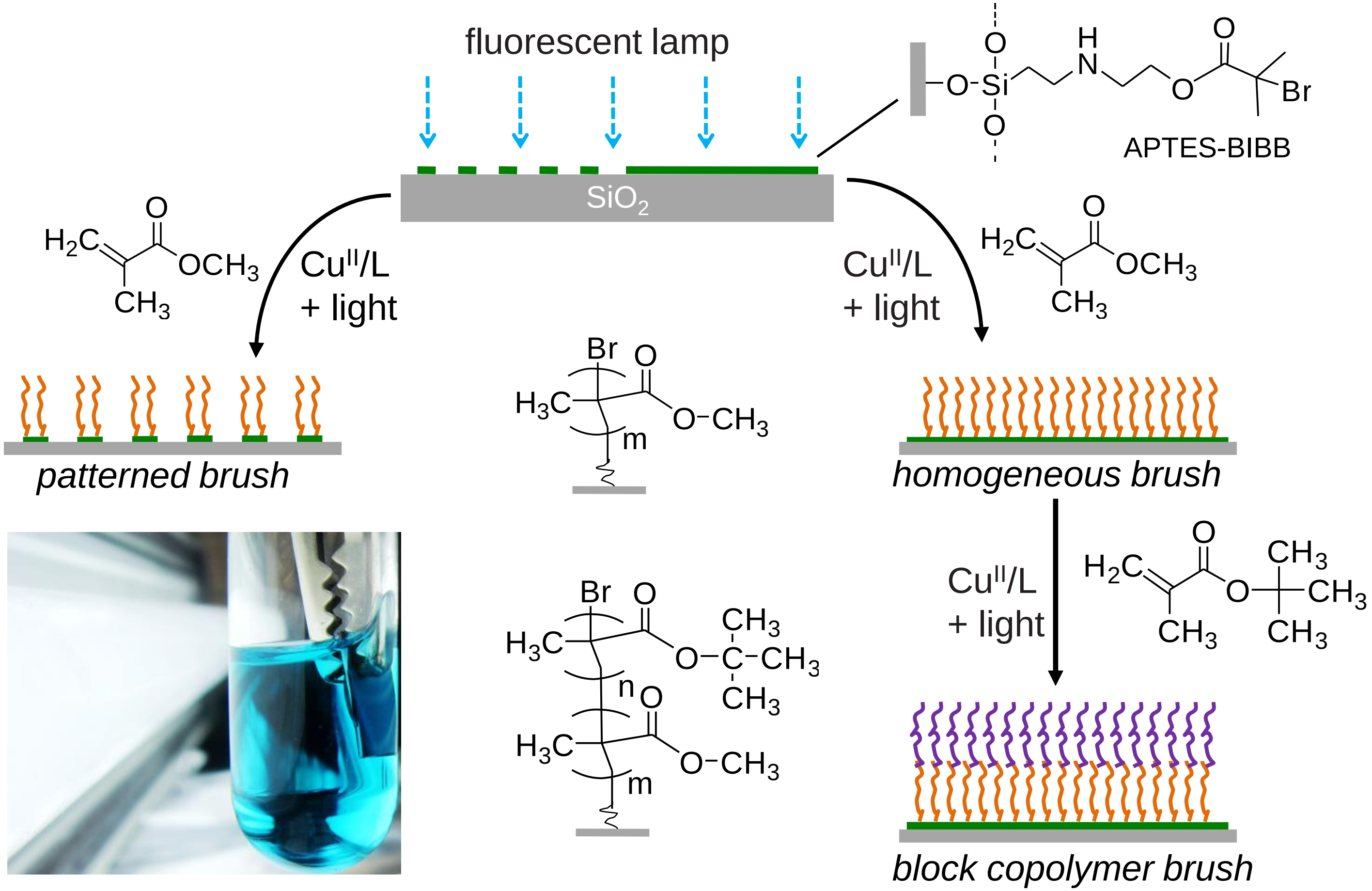
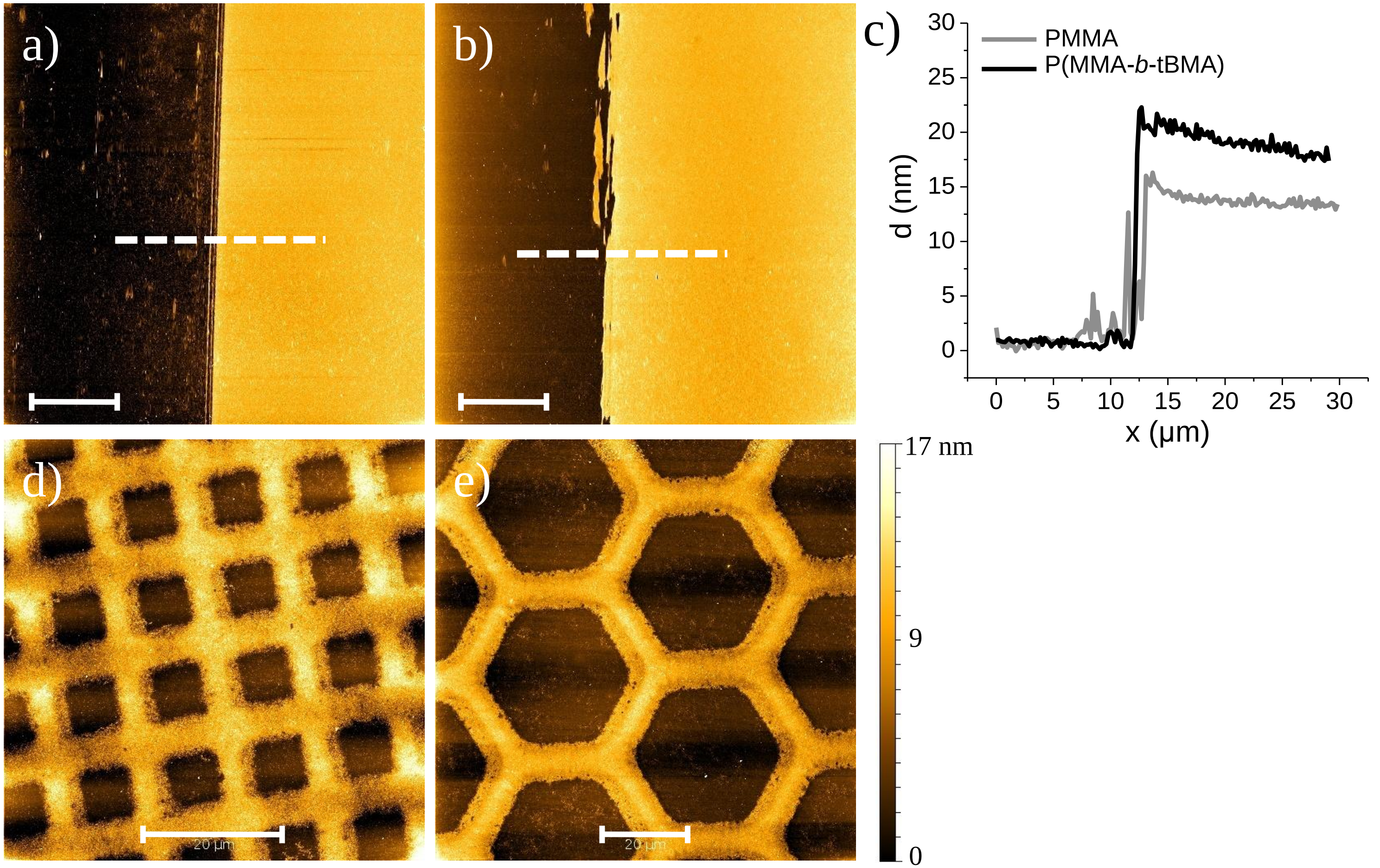
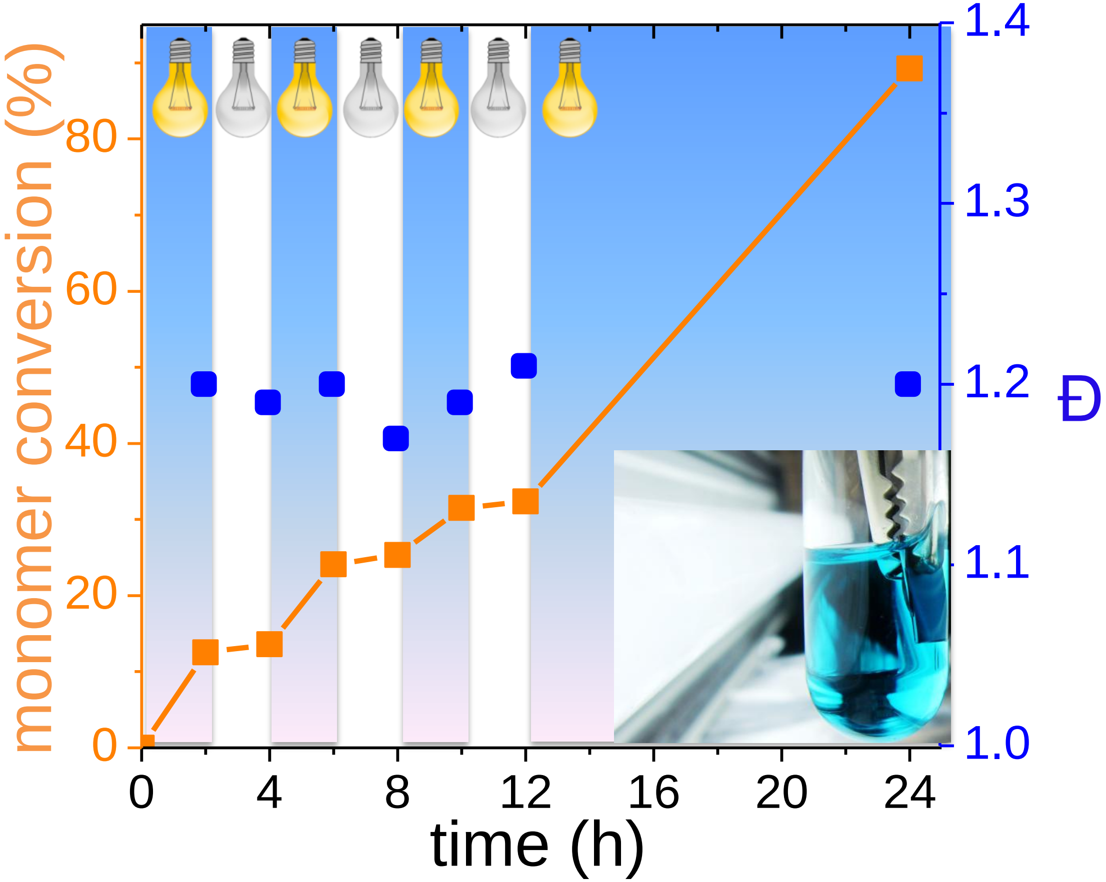

fluorescent lamp
APTES-BIBB
SiO$_2$
Cu^{II}/L
+ light
Cu^{II}/L
+ light
patterned brush
homogeneous brush
Cu^{II}/L
+ light
block copolymer brush
Br
O
H$_3$C
O–CH$_3$
m
n
CH$_3$
O–C–CH$_3$
H$_2$C
OCH$_3$
Si
N
H

Figure 6


a)
b)
c)
PMMA
P(MMA-*b*-tBMA)
d (nm)
30
25
20
15
10
5
0
x (µm)
0
5
10
15
20
25
30
d)
e)
20 µm
20 µm
17 nm
9
0

TOC


monomer conversion (%)
0
20
40
60
80
time (h)
0
4
8
12
16
20
24
Đ
1.0
1.1
1.2
1.3
1.4