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Ligand Effect and Oxygen Tolerance Studies in Photochemically Induced Copper Mediated Reversible Deactivation Radical Polymerization of Methyl Methacrylate in Dimethyl Sulfoxide

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Well-defined poly(methyl methacrylate) was prepared by a photochemically induced reversible deactivation radical polymerization using 50−200 ppm of copper catalyst in dimethyl sulfoxide under both an inert atmosphere and in the presence of limited amount of air. Effect of the ligand structure and concentration on kinetics and polymerization control was investigated. Under inert atmosphere, equimolar amount of the ligand, such as tris(2-pyridylmethyl)amine (TPMA) or *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA), was sufficient to achieve well-controlled polymerization of MMA. In the presence of air, a well-controlled polymerization started just after some induction time, which was dependent on the concentration of TPMA ligand. Irradiation at λ > 350 nm provided both a photochemical reduction of an initially-added copper(II) catalyst, which complexed with either PMDETA or TPMA ligand, to a copper(I) activator, and photochemical regeneration of the copper(I) activator after its oxidation by oxygen. Successful chain-extension polymerization performed without degassing of the polymerization mixture confirmed the high degree of livingness of the photopolymerization system even in the presence of limited amount of air.

Introduction

Atom transfer radical polymerization (ATRP) is one of the most powerful reversible deactivation radical polymerization (RDRP) techniques. In recent years, many variations of ATRP have been developed.[1-4] ATRP with activators generated by electron transfer (AGET) enables the use of air stable forms of catalyst complexes, which are reduced *in situ* to their respective activators by various reducing agents.[1, 2] This principle was found to also be applicable for systems with diminished metal catalyst concentrations as low as 10 ppm in activators regenerated by electron transfer (ARGET) or initiators for continuous activator regeneration (ICAR) ATRP.[3-5] These systems are conducted in the presence of an excess amount of reducing agent such that metal activators are continuously regenerated from metals in higher oxidation state deactivators. RDRP has also been performed in the presence of elemental metals such as copper or iron in polar solvents such as dimethyl sulfoxide (DMSO) or water. In the presence of elemental copper in polar solvents, two mechanisms have been proposed.[6] The first one, called single electron transfer living radical polymerization (SET-LRP), takes Cu^0 as a major activator of alkyl halides and Cu^{II} as a major deactivator, whereas formed Cu^I rapidly disproportionates to Cu^0 and Cu^{II}. The second proposed mechanism, called supplemental activator and reducing agent (SARA) ATRP, identifies Cu^I and Cu^{II} as the major activator and deactivator, respectively, and Cu^0 as a supplemental activator and reducing agent for Cu^{II}. Regardless of which mechanism is correct, RDRP in the presence of elemental metals provides high polymerization rates with high monomer conversions even at room temperature.

Recently, various stimuli to activate dormant species in RDRP, such as thermal, photochemical and chemical, have been developed. Photochemical stimuli in polymerization have some particular advantages, such as an extremely fast photochemical process, minimal to no released volatile organic compounds, low activation energy of photochemical initiation, a more specified course of polymerization at lower temperatures, etc.[7, 8] In the past only a few studies have investigated photochemically initiated ATRP. As a first, Qin et al. reported a photo ATRP-initiating system consisting of 2,2-dimethoxy-2-phenylacetophenone (DMPA)/ferric tri(*N,N*-diethyldithiocarbamate) [$Fe(dtc)_3$] for polymerization of methyl methacrylate (MMA).[9] A similar approach of using dithiocarbamates, but in combination with a copper catalyst, was used in photoATRP of MMA and *t*-butyl methacrylate (BMA) by Kwak et al[10] and Ishizu et al.[11]

A photoATRP system without photolabile dithiocarbamates was for the first time reported by the Yagci group.[12, 13] An *in situ* photochemical reduction of an air stable $CuBr_2$/PMDETA catalyst to a CuBr/PMDETA activator was used, which subsequently activated an R-Br initiator and started the polymerization of MMA at ambient temperature. In addition, the polymerization was found to accelerate under irradiation.[13, 14] This group also used the same system in combination with various photoinitiators.[15] In all of these studies, however, the copper catalyst and the initiator were used in equimolar amounts. Recently we reported photochemicaly mediated ATRP of MMA with $CuBr_2$/L catalyst amounts of 50-100 ppm while preserving good control over the molar mass and narrow dispersity.[16] Later the Matyjaszewski group extended this work by investigation of photoATRP of various monomers under irradiation at several wavelengths in the visible light region.[17] Groups of Hawker and Boyer published photoRDRP of various vinyl monomers mediated by iridium-based photoredox catalyst.[18-20] Very recently, the photoRDRP of various acrylates mediated by copper bromide catalyst was performed in DMSO, and it was shown that an excess amount of the ligand is needed to proceed successfully the polymerization.[21-23]

Here we showed that unlike in the case of acrylates, the equimolar amount of ligand to copper bromide is sufficient to proceed successfully of photoRDRP of MMA in DMSO. Moreover, in the second part of the manuscript we showed for the first time that the copper mediated photoRDRP of MMA in DMSO can be performed also in the presence of a limited amount of air, while PMMA with well controlled molar mass, narrow dispersity and high chain-end livingness can be obtained.

Experimental

Materials.

Methyl methacrylate was purchased from Sigma-Aldrich and purified before use by passing through a basic alumina column to remove the inhibitor. 2-Bromopropionitrile (BPN), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA), tris(2-pyridylmethyl)amine (TPMA), ethyl 2-bromoisobutyrate (EBiB), tris[2-(dimethylamino)ethyl]amine (Me_6TREN), 1,1,4,7,10,10-hexamethyltriethylenetetraamine (HMTETA), 4,4′-dinonyl-2,2′-dipyridyl (dNbipy), copper(II) bromide, copper(II) oxide and dimethyl sulfoxide (DMSO) (all from Sigma-Aldrich) were used as received. All other reagents and solvents were purchased from Sigma-Aldrich and used as received, without further purification.

Polymerizations.

Photopolymerization under inert atmosphere. The following procedure for photoRDRP of MMA was used. To a 10-mL Schlenk tube containing $CuBr_2$, evacuated and filled with argon, 1.3 mL of argon purged DMSO containing a dissolved ligand was added under an argon atmosphere. The mixture in the Schlenk tube was sonicated for 5 minutes to form a $CuBr_2$/L complex. Then, 15 µl of BPN and 3.7 mL of MMA purged with argon was added to the Schlenk tube under an argon atmosphere, and the mixture was subsequently degassed by three freeze-pump-thaw cycles and back-filled with argon. Photopolymerization with light of $\lambda > 350$ nm (i.e., irradiation at $\lambda = 366$, 405, 408, 436 and 546 nm) was performed using a medium pressure mercury lamp in a Spectramat apparatus (Ivoclar AG, Liechtenstein, glass filter $\lambda = 350$ to 550 nm). To prevent heating of the sample during irradiation, the Schlenk tube was placed into a double-layer glass tube. In the outer layer of the finger, water thermostated to 25 °C was circulated. With such a cooling system, the temperature of the reaction mixture during the photopolymerization process slightly increased but remained between 30 and 35 °C. The distance of each sample from the arc was approximately 10 cm. The power of the light measured at the sample position was approximately 20 $mW\,cm^{-2}$. In one case of polymerization of methyl acrylate, the UV irradiation was performed using a High-Intensity UV Lamp (EMSdiasum) at $\lambda = 365$ nm on thermostated samples at 25 °C. The distance of the sample from the arc was 20 cm. The power of the light measured at the sample position was 0.9 $mW\cdot cm^{-2}$.

Photopolymerization performed with exact amount of oxygen. The same procedure as for photopolymerization under inert atmosphere was performed, but before starting the irradiation 780 µl of air was added to the polymerization mixture.

Photopolymerization performed without degassing of monomer and solvent. To a 10-mL Schlenk tube containing $CuBr_2$ and TPMA, evacuated and filled with argon, 1.3 mL of DMSO without any previous procedure of removing oxygen (air) was added and the mixture in the Schlenk tube was sonicated for 5 minutes to form a $CuBr_2$/L complex. Then, 15 µl of BPN and 3.7 mL of MMA, without any previous procedure of removing oxygen (air), were added and irradiation was started.

Chain Extension polymerization in the presence of air. A PMMA-Br macroinitiator was prepared using similar procedures to those without degassing of monomer and solvent, with an MMA/BPN/$CuBr_2$/TPMA ratio of 100/1/0.04/0.16, while 1.8 mL of MMA and 0.7 mL of DMSO was used. After 5 h of irradiation (65 % MMA conversion, GPC of PMMA: M_n of 7500 g/mol and an M_w/M_n of 1.22) another 1.8 mL of MMA and 0.7 mL of DMSO without degassing was added to the polymerization mixture and the mixture was homogenized by stirring in the dark overnight at room temperature. After 5.5 hours of chain extension the polymerization was stopped at 88 % of MMA conversion.

Analysis.

The molecular weights and molecular weight distributions of the polymers were analyzed using gel permeation chromatography (GPC); the set-up consisted of a Waters 515 pump, two PPS SDV 5-µm columns (d = 8 mm, l = 300 mm; 500 Å + 10^5 Å) and a Waters 410 differential refractive index detector with THF as an eluent at a flow rate of 1.0 mL/min. Poly(methyl methacrylate) and polystyrene calibration was used for determination of molar masses and dispersity of poly(methyl methacrylates) and poly(methyl acrylates), respectively. Monomer conversions were determined by ^{1}H NMR on a 400 MHz VNMRS Varian NMR spectrometer equipped with a 5-mm 1H-19F/15N-31P PFG AutoX DB NB probe at 25 °C in deuterated chloroform as the solvent.

Results and discussion

Effect of ligand structure and concentration under inert atmosphere.

TPMA is a commonly used ligand when ATRP is performed in the presence of ppm amounts of a copper catalyst.[4, 5] It was successfully used also in photoATRP of various (meth)acrylates in anisole,[16] therefore it was primarily chosen here for photoRDRP of MMA in DMSO. Control experiments with the pure MMA/DMSO and MMA/DMSO mixtures in the

Table 1. Results of photochemically induced reversible deactivation radical polymerization of methyl methacrylate (MMA)[a] and methyl acrylate (MA)[b]

Entry	Initiator[d]	Ligand[d]	$CuBr_2$ [ppm]	$CuBr_2$/L ratio	Time [h]	Conv.[e] [%]	$M_{n,\ theor}$ [g/mol]	$M_{n,\ exp.}$ [g/mol]	M_w/M_n
1[a]	-	-	-	-	3	-	-	-	-
2[a]	-	TPMA	-	-	3	-	-	-	-
3[a]	BPN	-	-	-	3	-	-	-	-
4[a]	BPN	TPMA	-	-	3	8	1730	284,000	2.38
5[a]	-	TPMA	100	1/1	3	5	NA	65,500	2.00
6[a]	BPN	TPMA	100	1/1	5	73	14,730	17,700	1.14
7[a]	BPN	TPMA	100	1/4	5	79	15,930	20,400	1.10
8[a]	BPN	Me_6TREN	100	1/1	7.5	45	9130	11,300	1.37
9[a]	BPN	PMDETA	100	1/1	5	71	14,330	18,900	1.20
10[a]	BPN	HMTETA	100	1/1	7	24	4930	13,500	1.30
11[a]	BPN	dNbipy	100	1/1	9.5	< 2	530	NA	NA
12[a]	BPN	TPMA	50	1/4	7	65	13,130	17,500	1.27
13[a]	BPN	TPMA	200	1/4	5	74	14,930	14,800	1.15
14[a]	EBiB	Me_6TREN	100	1/1	5	48	9800	16,050	1.31
15[a]	EBiB	Me_6TREN	150	1.5/1	5	39	8000	14,500	1.47
16[b]	EBiB	Me_6TREN	100	1/1	6	46	13,850	10,500	1.11
17[b,c]	EBiB	Me_6TREN	100	1/1	8	-	-	-	-

[a]Polymerizations were performed in 26 vol % DMSO at 35 °C with an MMA/L ratio of 200/1, concentration of $CuBr_2$ in ppm is related to monomer, where L stays for ligand; $\lambda > 350$ nm, P = 20 mW cm^{-2}. [b]Polymerizations were performed in 26 vol % DMSO at 35 °C with an MA/EBiB ratio of 345/1, concentration of $CuBr_2$ in ppm is related to monomer; $\lambda > 350$ nm, P = 20 mW cm^{-2}. [c]Light with wavelength $\lambda = 365$ nm was used, the power of the light in the sample position was P = 0.9 mW/cm^2. [d]BPN, EBiB, TPMA, Me_6TREN, PMDETA, HMTETA and dNbipy stay for 2-bromopropionitrile, ethyl 2-bromoisobutyrate, tris(2-pyridylmethyl)amine, tris[2-(dimethylamino)ethyl]amine, *N,N,N',N'',N''*-pentamethyldiethylenetriamine, 1,1,4,7,10,10-hexamethyltriethylenetetraamine and 4,4′-dinonyl-2,2′-dipyridyl, respectively. [e]Based on ^1H NMR spectra.

presence of either only TPMA as the ligand or BPN as an initiator did not lead to the formation of any polymer after 3 h of irradiation (Table 1, Entries 1-3). When combinations of TPMA with BPN or TPMA with $CuBr_2$ were added to the MMA/DMSO mixture a polymers with a molar masses of 284,000 g/mol and 65,500 g/mol, respectively, and broad dispersities of above 2 were obtained after 3 h of irradiation; meanwhile, conversion of MMA, as determined by NMR, were only 8 and 5 %, respectively (Table 1, Entries 4 and 5).

After irradiation for 5 hours, the MMA/DMSO mixture in the presence of BPN as an initiator and a 100 ppm $CuBr_2$/TPMA catalytic system, a polymer with molar mass of 17,700 g/mol and narrow dispersity of 1.14 was obtained, while the monomer conversion was 73 % (Table 1, Entry 6). Comparison of kinetic plots of the polymerization carried out in DMSO, and with previously reported polymerization performed under the same conditions but in anisole as a solvent, showed that polymerization was significantly faster in DMSO (Figure 1). On the other hand, even though in both solvents the dispersities were almost the same, slightly higher molar masses than the theoretical ones were obtained in DMSO. In order to improve the control over the molar masses, the photoRDRP in DMSO was investigated using various conditions, i.e. using an excess of ligand, various types of ligands, and various concentrations of the catalytic system.

Change of $CuBr_2$/TPMA ratio from 1/1 to 1/4 did not lead to any change in either the rate of polymerization or development of molar masses and dispersities with monomer conversion (Table 1, Entries 6 and 7; Figure 2). This is in contrast with recent works of Ribelli et al.[21] and Anastasaki et al.,[22] who needed an excess of ligand in comparison to $CuBr_2$ because no polymer was formed when the $CuBr_2$/ligand ratio of 1/1 was used during photoRDRP of (meth)acrylates in DMSO. In that work Me_6TREN was used as a ligand. Therefore, we further studied effect of ligand structure on photoRDRP of MMA in DMSO (Table 1, Entries 8 – 11; Figure 3). Totally, five various ligands with various activity in ATRP were studied. Using Me_6TREN, as the only studied ligand with higher activity in ATRP than TPMA,[24] led to formation of polymer with similar control of molar masses but with significantly broader dispersity. In addition, the rate of polymerization was decreasing with polymerization time, suggesting progressive termination reactions due to too high concentration of active macroradicals in the polymerization mixture (see Figure 3). Thus for photoRDRP of MMA in DMSO the $CuBr_2$/Me_6TREN complex is not an efficient enough deactivator to shift sufficiently the equilibrium toward the dormant species. PMDETA is known as a less active ligand in ATRP than TPMA.[24] In the recent work of photoATRP in anisole, however, it was found that the polymerization was faster in the case of PMDETA than in the case of TPMA, due to possible different redox potentials of copper/ligand complexes in basic and excited states.[16] Nevertheless, in photoRDRP of MMA in DMSO the kinetics of polymerization with PMDETA and TPMA were the same (Figure 3). The control over the molar masses and dispersities were also almost the same for both ligands. For further invetigations, HMTETA and dNbipy were selected as slightly less active ligands in ATRP than PMDETA.[24] PhotoRDRP in the presence of HMTETA led to a polymer with dispersities approximately of 1.3 but significantly higher molar masses than the theoretical ones (see Figure 3). In addition, slow polymerization with nonlinear behavior in first order kinetic plots was observed and polymerization was stopped at 24 % monomer conversion. In this case, the photochemical reduction of a $CuBr_2$/HMTETA complex seemed to be very slow. Contrary to this, no polymerization was observed even after 9.5 h of irradiation in the case of dNbipy, which contained only aromatic nitrogens (Table 1, Entry 11).

Furthermore, an effect of copper catalyst concentration was

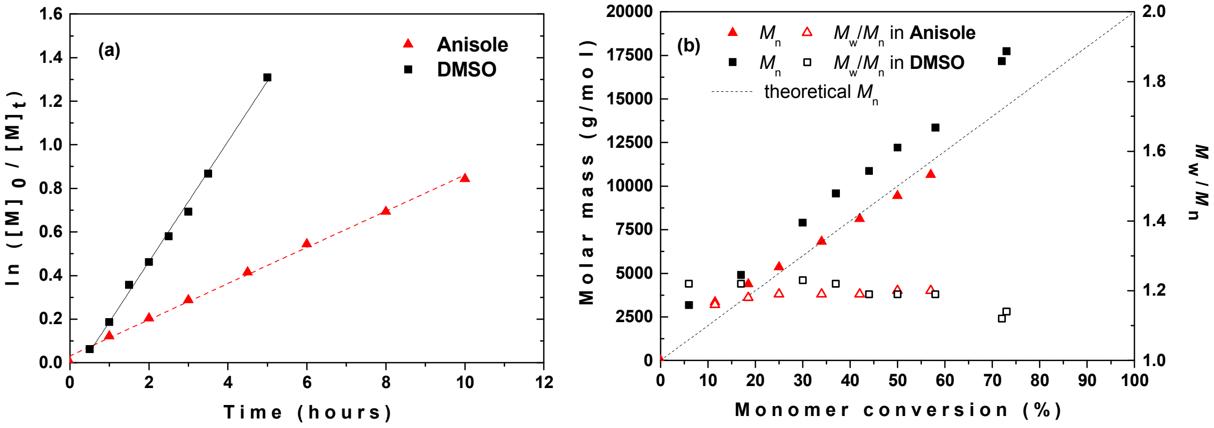


Figure 1. (a) Kinetic plots and (b) evolution of the molar mass and dispersity with the converstion of MMA during photoRDRP either in anisole or DMSO. Experimental conditions: MMA/BPN/$CuBr_2$/TPMA 200/1/0.02/0.02; [MMA] = 6.9 M; T = 35 °C, 26 vol % DMSO; λ > 350 nm.

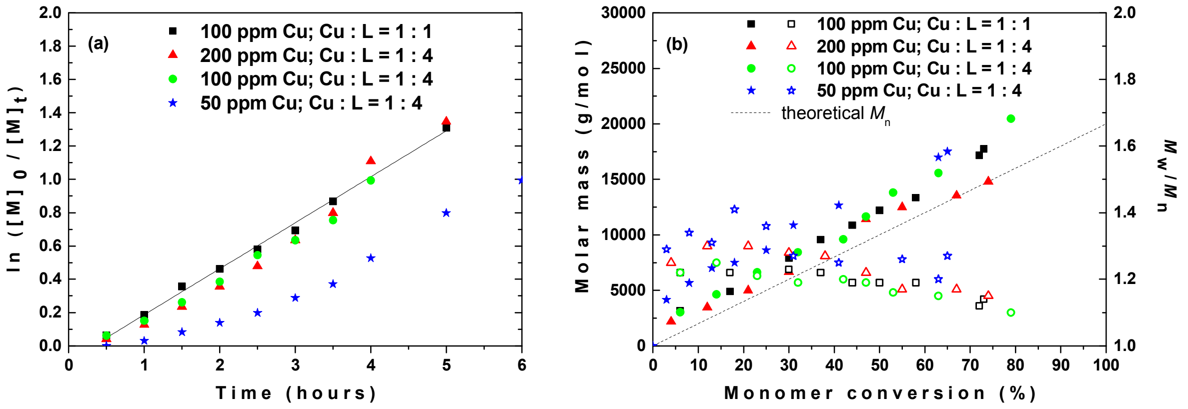


Figure 2. (a) Kinetic plots and (b) evolution of the molar mass and dispersity with the converstion of MMA during photoRDRP at varius copper catalyst and ligand concentrations. Experimental conditions: MMA/BPN/CuBr2/TPMA = 200/1/X/Y; [MMA] = 6.9 M; T = 35 °C, 26 vol % DMSO; λ > 350 nm.

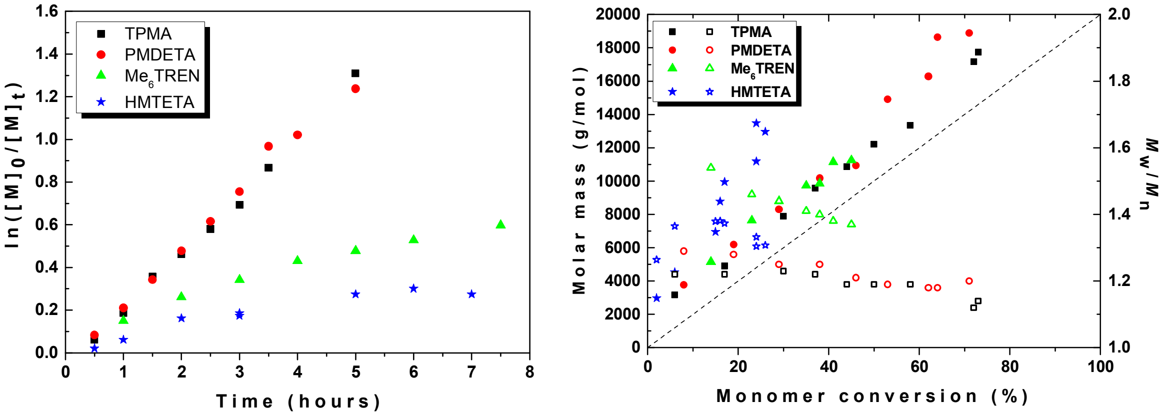


Figure 3. (a) Kinetic plots and (b) evolution of the molar mass and dispersity with the converstion of MMA during photoRDRP using various ligands. Experimental conditions: MMA/BPN/$CuBr_2$/L = 200/1/0.02/0.02; [MMA] = 6.9, T = 35 °C, 26 vol % DMSO; λ > 350 nm.

studied (Table 1, Entries 12 and 13; Figure 2). Decrease of the copper catalyst concentration down to 50 ppm led to a decrease in rate of polymerization, while polymers with higher molar masses and slightly broader dispersities in comparison to polymerizations with 100 ppm of catalyst were obtained. Surprisingly, when a 200 ppm copper catalyst was used the kinetics of the polymerization was almost the same as in the case of 100 ppm of catalyst. However, unlike previous examples, the molar masses of the obtained polymers fitted well the theoretical molar masses when 200 ppm of catalyst was used, while dispersities were as narrow as in the case of 100 ppm of catalyst.

The possibility of “on/off” temporal control during photoRDRP of MMA in DMSO was investigated by alternating light and dark exposure for 30 minute periods. As shown in Figure 4, in all cycles, the polymerization took place during irradiation and almost stopped when the polymerization mixture was placed in the dark. Thus, the irradiation dramatically accelerated the rate of RDRP of MMA with low copper catalyst concentration and without any other reducing agent. The reason could be different activation and deactivation constants for CuBr/L and $CuBr_2$/L, respectively, in their basic and excited state.[16]

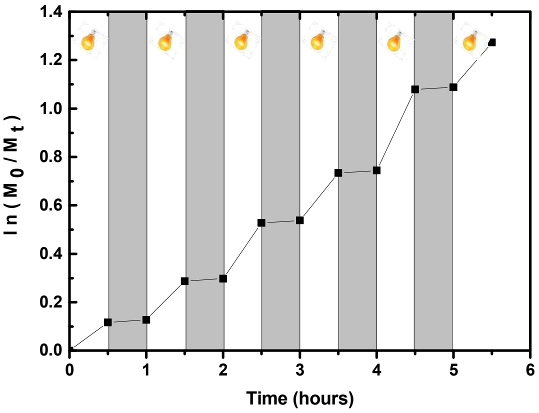


Figure 4. Kinetic plot of RDRP of MMA during irradiation at λ > 350 nm and no irradiation cycles. Experimental conditions: MMA/BPN/$CuBr_2$/TPMA = 200/1/0.02/0.02; [MMA] = 6.9, T = 35 °C, 26 vol % DMSO.

As seen from the experiments reported above, unlike in the case of photoRDRP of acrylates reported by Ribelli[21] and Anastasaki[22], the equimolar amount of ligand to copper bromide was sufficient to proceed successfully of photoRDRP of MMA in DMSO. In order to investigate a possible reason of the difference between the photoRDRP of MMA and acrylates, some additional experiments using the same initiator and catalytic system as described previously for acrylates, were performed. Thus EBiB as an initiator and Me_6TREN as a ligand were used and photoRDRP of MMA and MA was studied. Using $CuBr_2$/Me_6TREN ratio of 1/1 in photoRDRP of MMA led to 48 % conversion after 5 hours of irradiation (Table 1, Entry 14). The molar mass was, however, much higher than the theoretical one and the dispersity was 1.31 as a result of slower activation of EBiB in comparison with PMMA-Br.[16] The polymerization was repeated using $CuBr_2$/Me_6TREN ratio of 1.5/1, in order to ensure that not even slight excess of ligand is present in the system due to either inaccuracy of preparation of mixture or photochemical decomposition of catalyst complex. Similarly to the previous experiment, 39 % conversion was achieved after 5 h of irradiation (Table 1, Entry 15). It should be also mentioned that in both cases a short induction period was observed and the polymerization started just after 1.5 h of irradiation indicating slower initiation in the case of EBiB compared to BPN.

When photoRDRP of MA was performed under the same conditions, the polymerization started after 4 h of irradiation reaching conversion of 46 % after 6 h of irradiation, while the molar mass of PMA fitted quite well the theoretical one and the dispersity was 1.11 (Table 1, Entry 16). This result is really surprising since, as already mentioned above, in previous works of Ribelli[21] and Anastasaki[22] polymerization was observed using the same initiator and catalytic system. Only difference was power (source) of the light. While in our case the power of the light in the sample position was 20 mW/cm^2, Ribelli[21] reported the power of the light of 0.9 mW/cm^2. Therefore, we decided to repeat the polymerization with different source of light, which enabled us to adjust the power of the light. Thus repeating of the polymerization with power of the light of 0.9 mW/cm^2 gave no polymerization of MA even after 8 hours of irradiation (Table 1, Entry 17). The results showed that the power of the light is very important at least for the successful and fast initiation when equimolar ratio of copper catalyst and ligand is used in photoRDRP. However, to better understand the effect of the light power and the mechanism, more experiments are needed.

Tolerance of photoRDRP of MMA to presence of oxygen.

It is known that in ARGET ATRP the polymerization can proceed in the presence of a limited amount of oxygen. CuBr, after its oxidationby oxygen, can be continuously regenerated *in situ* by reducing agents until all oxygen in the system is not consumed; polymerization can then proceed under typical ATRP conditions.[25] We were curious during photoRDRP if the CuBr can also be photochemically regenerated in the presence of a limited amount of oxygen. The polymerization of MMA was performed similar to previous cases using a $CuBr_2$/TPMA 1/1 catalytic system and BPN as an initiator in DMSO; however, after all degassing steps, an exact amount of air was added to the polymerization mixture. The amount of air was calculated to achieve a $CuBr_2/O_2$ molar ratio in the system of approximately 1/1. After addition of air, the irradiation was started to initiate the reduction of $CuBr_2$. As shown in Figure 5, no polymerization was observed before 4 hours of irradiation. After 4 hours the polymerization of MMA started and followed first order kinetics. The polymerization led to PMMA formation with a molar mass fitting well with theoretical cases and a dispersity of approximately 1.2. Also, when the polymerization was performed under the same conditions, i.e., in the presence of equimolar ratio of oxygen to copper but with a 4-fold excess of TPMA used, the induction period was dramatically decreased as shown in Figure 5. The polymerization started almost immediately after the start of irradiation, and the rate of polymerization was approximately 3 times higher than in the case of an equimolar ratio of ligand to copper. This was quite surprising, because, as discussed above, when no oxygen was added to the polymerization system, no difference in kinetics was observed regardless of whether the $CuBr_2$/TPMA ratio of 1/1 or 1/4 was used (see Figure 2a). The TPMA ligand unambiguosly participates in the photochemical reduction of oxidized copper(II) species. In an effort to confirm that TPMA alone does not act as a reducing agent in the used system, it should be noted here that no polymerization was observed after 19 hours of stirring the polymerization mixture containing a 4-fold excess of TPMA in the dark.

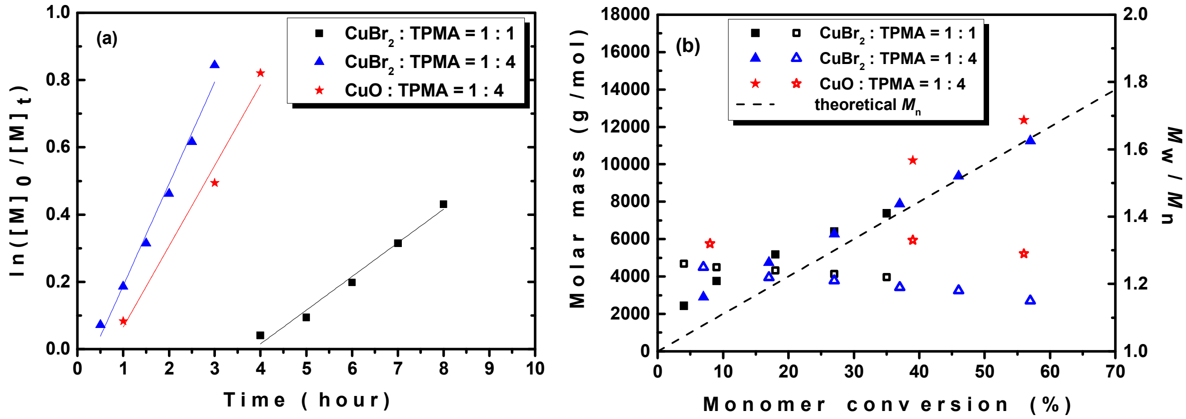


Figure 5. (a) Kinetic plots and (b) evolution of the molar mass and dispersity with the converstion of MMA during photoRDRP performed with addition of exact amount of oxygen (air) to degassed polymerization mixture. $CuBr_2$/TPMA ratios of 1/1 or 1/4 or using CuO, instead of $CuBr_2$, with CuO/TPMA ratio of 1/4 were used. Experimental conditions: MMA/BPN/Cu^{II}/TPMA/O_2 = 200/1/0.04/X/0.04; [MMA] = 6.9, T = 35 °C, 26 vol % DMSO; $\lambda > 350$ nm.

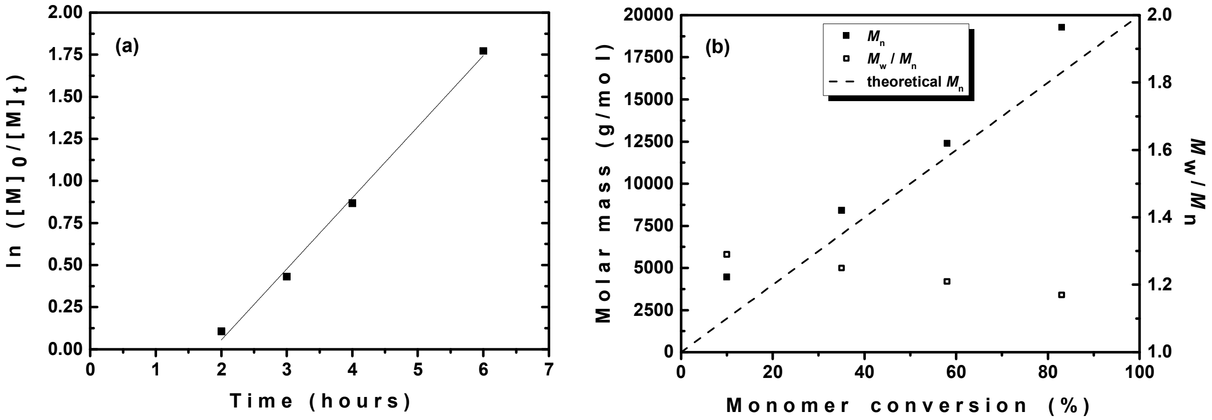


Figure 6. (a) Kinetic plot and (b) evolution of the molar mass and dispersity with the converstion of MMA during photoRDRP performed without degassing of monomer and solvent. Experimental conditions: MMA/BPN/$CuBr_2$/TPMA/O_2 = 200/1/0.04/0.16/X; [MMA] = 6.9, T = 35 °C, 26 vol % DMSO; $\lambda > 350$ nm.

Since it was shown that CuBr can be photochemically regenerated after its oxidation in the presence of oxygen, we were curious if the polymerization can be performed when CuO is used instead of $CuBr_2$. Thus the photoRDRP of MMA was performed using 200 ppm of CuO and a 4-fold excess of TPMA. As shown in Figure 5, the polymerization started after 1 hour of irradiation, i.e., only after very short induction period. The kinetics of the polymerization was very similar to that one with $CuBr_2$ with a 4-fold excess of TPMA and added an equimolar molar ratio of oxygen to copper. Very recently we showed that, regardless whether $CuBr_2$ or $CuSO_4.5H_2O$ or various organic copper salts were used, the kinetic of polymerization of MMA was the same due to *in situ* formation of $CuBr_2$ by reaction of reduced copper compounds with an alkyl bromide initiator.[26] In the case of CuO, after its photochemical reduction, it can therefore be expected that the polymerization will be controlled by an *in situ* formed CuBr/$CuBr_2$ equilibrium. Logically, the molar mass and dispersity of the polymers are slightly higher for the CuO in comparison with polymerization started with $CuBr_2$ because in the first case there is no $CuBr_2$ deactivator present in the polymerization mixture in the first stage of polymerization.

In previous experiments we removed all oxygen from the polymerization mixture by degassing both monomer and solvent by four freeze-pump-thaw cycles and then added an exact amount of air to the mixture before starting the irradiation. From the industrial point of view it would be comfortable to use the monomers and solvents without need of their degassing and performing freeze-pump-thaw cycles. Therefore, we investigated the photoRDRP of MMA without any complicated purification steps. Thus all components were added to an argon filled reaction tube without any processes commonly used for removing oxygen from either MMA or DMSO, and subsequently irradiation of the polymerization mixture was performed. As shown in Figure 6, the polymerization was started after an induction period of 2 hours and the first order kinetic was followed until a high monomer conversion. The molar mass fitted quite well with the theoretical one and the dispersity of the final polymer was below 1.2.

The living character of the photoRDRP under presence of air was demonstrated by a chain extension experiment. The MMA was first polymerized using photoRDPR under similar conditions like in the previous experiment, i.e., whithout degassing of monomer and solvent. After 5 hours of polymerization (monomer conversion of 65 %, M_n = 7500 g/mol and M_w/M_n = 1.22), a further non-degassed monomer and solvent were added and the polymerization mixture was stirred in the dark overnight to homogenize the mixture. No change in molar mass or dispersity was observed during the stirring overnight. The polymerization was re-initiated by irradiation and stopped after 5.5 hours (totally 10.5 hours of irradiation; total monomer conversion was 88 %). As observed from GPC traces (see Figure 7), the molar mass clearly increased after chain extention and chain extended PMMA with narrow dispersity was obtained. The chain extention confirmed that the most of the PMMA-Br macroinitiators were terminated by a living bromine and only negligible low molecular weight tail indicating some small extent of premature termination was observed.

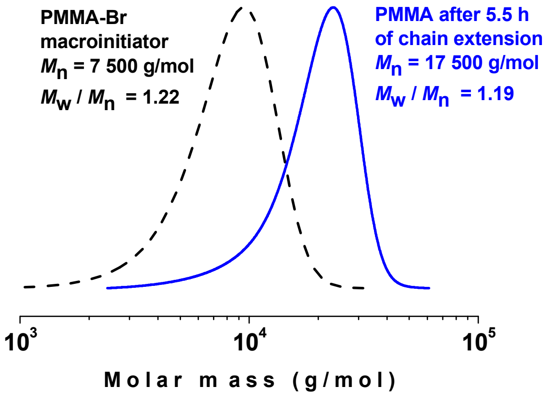
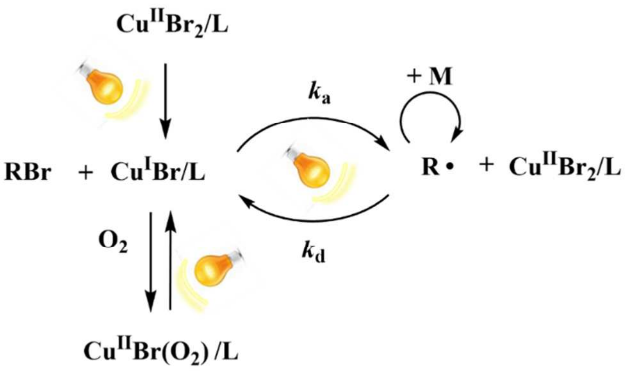


Figure 7. GPC traces from chain extension of PMMA-Br with MMA: (- - -) PMMA-Br macroinitiator and (—) chain extended PMMA after 88% conversion of MMA. Both the preparation of PMMA-Br macroinitiator and the chain extension was performed by photoRDRP without degassing of monomer and solvent, i.e., in the presence of limited amount of oxygen. Experimental conditions: preparation of PMMA-Br: MMA/BPN/$CuBr_2$/TPMA = 100/1/0.04/0.16; chain extension: MMA/PMMA-Br/$CuBr_2$/TPMA = 100/1/0.04/0.16; in both polymerizations: [MMA] = 6.9 M, T = 35 °C, DMSO (26 vol %), irradiation at λ > 350 nm.



Scheme 1. Proposed simplified mechanism of photoRDRP in the presence of oxygen

Scheme 1 presents the proposed simplified mechanism of photoRDRP in the presence of oxygen. The Cu^IBr/L activator is first formed after the photochemical reduction of $Cu^{II}Br_2/L$ by irradiation in the UV-vis region, while probably also bromide radicals are formed. Subsequently, Cu^IBr/L can either activate an RBr initiator to form active radicals and a $Cu^{II}Br_2/L$ deactivator, or more probably is oxidized by present oxygen to $Cu^{II}Br(O_2)$ species. $Cu^{II}Br(O_2)$ can be then photochemically reduced back to Cu^IBr/L. This cycle of oxidation and photochemical regeneration of Cu^IBr/L can proceed until the oxygen is consumed and then a normal photoRDRP equilibrium can be obtained leading to the preparation of a well-defined polymer. As mentioned above, the possible assistance of a free tertiary amine ligand in the photochemical reduction of Cu^{II} spieces, maybe through an electron transfer or forming of radicals, should be considered as well. However, more detailed studies are needed to better understand the mechanism of photochemical reduction of Cu^{II} spieces and O_2 consumption.

Conclusions

In summary, RDRP of MMA employed with ppm amounts of copper catalyst under irradiation at λ > 350 nm in DMSO was reported. The polymerization started after the photochemical reduction of the copper(II) catalyst complex to a copper(I) activator. Among the studied ligands, only TPMA and PMDETA were found to form catalyst complexes enabling preparation of well-defined PMMA. The possibility of using significantly cheaper PMDETA as a ligand has tremendous advantage, especially in view of industrial application. Equilibrium amount of ligand in comparison to copper catalyst was sufficient to obtain PMMA with controlled molar mass and narrow dispersity. The rate of polymerization was significantly higher under irradiation than in the dark, enabling temporal control over switching on/off the polymerization by switching on/off the light. In the case of MA, it was shown that some minimal power of the light is needed to perform successfully pohtoRDRP when equimolar ratio of copper catalyst to ligand is used. It was also proved that photoRDRP of MMA catalyzed by copper catalyst can be performed in the presence of limited amount of air as well. First, there are cycles of oxidation of CuBr/L by reaction with oxygen and photochemical regeneration of CuBr/L. Subsequently after consumption of oxygen in the system the CuBr/L activates the alkyl halide to initiate the polymerization of MMA. The induction period before starting the polymerization could be shortened by using approximately a 4-fold excess of TPMA ligand in respect to the copper catalyst. It was also shown that the photoRDRP of MMA as well as the chain extension polymerization can be successfully performed without necessity of degassing monomer and solvent. In comparison with ARGET or ICAR ATRP, which can also be run under the limited amount of oxygen, the presented photoRDRP does not need additional chemicals such as reducing agents or sources of radicals. The presented photoRDRP system can have tremendous importance from an industrial point of view because costly, time-consuming procedures of removing oxygen from the polymerization mixture can be avoided without losing control over the molecular characteristics of the final PMMA.

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Notes and references

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