Carbon Quantum Dot-Catalyzed, Highly Efficient Miniemulsion Atom Transfer Radical Polymerization Induced by Visible Light

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Carbon Quantum Dots (CQDs) Catalyzed Highly Efficient Miniemulsion Atom Transfer Radical Polymerization Induced by Visible Light

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Abstract:

Owing to the benefits of using natural or artificial light sources as a stimulus, photo-induced reversible-deactivation radical polymerization (photoRDRP) techniques have been recognized to be a powerful "green" platform for the preparation of well-defined polymers. However, the development of highly efficient visible light-induced photoRDRP processes in aqueous dispersed media remains a challenge due to light scattering and refraction by monomer droplets or colloidal particles. In this work, an efficient green photocatalyst, carbon quantum dots (CQDs), was introduced to visible light-mediated miniemulsion atom transfer radical polymerization (ATRP), leading to highly efficient polymerizations with reaction rates (>80% monomer conversion within 1h) much higher than in previous studies. This heterogeneous photocatalytic system is presumed to involve three catalytic cycles in: i) the aqueous phase, ii) the oil-water interface and iii) the monomer droplets. The effect of different polymerization parameters on the polymerization reaction was investigated, including the amounts of surfactant and CQDs, $CuBr_2$ dosage and solid content. Excellent temporal control of the polymerization was illustrated by "ON/OFF" polymerizations, and natural sunlight was also used as an energy source. This novel CQDs-catalyzed miniemulsion photoATRP process may be easily extended to other aqueous dispersion RDRP systems. As an extension of our previous work (*J. Am. Chem. Soc. 2022, 144, 22, 9817–9826*) we also developed a "one-pot" method for the rapid preparation of heterogeneous hydrogels.

Introduction

According to the principles of green polymerization, the ideal polymerization reaction is one that quantitatively converts monomers into well-defined polymers, with maximize economy and reduce waste.[1,2] In this regard, photomediated reversible-deactivation radical polymerizations (photoRDRP), using in particular visible light as a "green" energy source, have attracted broad research interest.[3,4] In addition, photoRDRP can be carried out in aqueous media, which is particularly relevant from an environmental perspective, offering better temperature control due to easy heat removal, and leading to high solids, low viscosity polymers.[5,6] Polymerizations in aqueous dispersed media encompass a variety of processes including miniemulsion, emulsion, suspension and dispersion polymerization, all of which are used extensively in many applications.[5,7-9]

PhotoRDRP techniques including atom transfer radical polymerization (ATRP) and reversible addition−fragmentation chain transfer (RAFT) have been widely developed in miniemulsion.[10-12] In contrast to the high-energy UV irradiation which may lead to photodegradation of the photoinitiator or to undesirable side reactions, milder visible light is expected to remedy most of these drawbacks.[13,14] The first reported technique for visible light-induced photoRDRP in miniemulsion was photo-induced electron transfer-RAFT (PET-RAFT).[12,15,16] PET-RAFT was used to mediate the controlled polymerization of styrene in an oil-in-water (O/W) miniemulsion by using blue light (λ = 460 nm) as a stimulus and $Ir(ppy)_3$ as photocatalyst. However, depletion of the photocatalyst from the oily monomer droplets during polymerization, led to low

reaction rates and limiting conversions. The same group then developed RAFT iniferter miniemulsion polymerization under green light irradiation (λ = 530 nm), based on light-induced photolysis of the RAFT agent.[16] However, despite obvious progress in RAFT polymerization, UV light still remains the dominant source in the case of miniemulsion photoATRP.[10,11] Matyjaszewski and coworkers reported the UV light-mediated photoATRP of (meth)acrylic monomers in miniemulsion, and demonstrated the efficient control of polymerization through the formation of an ion-pair catalyst by interaction of the Cu/ligand with sodium dodecyl sulfate (SDS).[10] This ion-pair photoATRP catalytic system was next successfully extended to more industrially relevant ab initio emulsion polymerization.[11] However, accessing high reactivity under mild visible light irradiation in aqueous dispersed media remains a challenge in photoATRP. One main reason is the opacity of the aqueous dispersion system, and the light scattering and refraction contribute to radiation attenuation.[17] In this respect, the use of highly efficient photocatalysts appears to be a promising approach to address this problem.

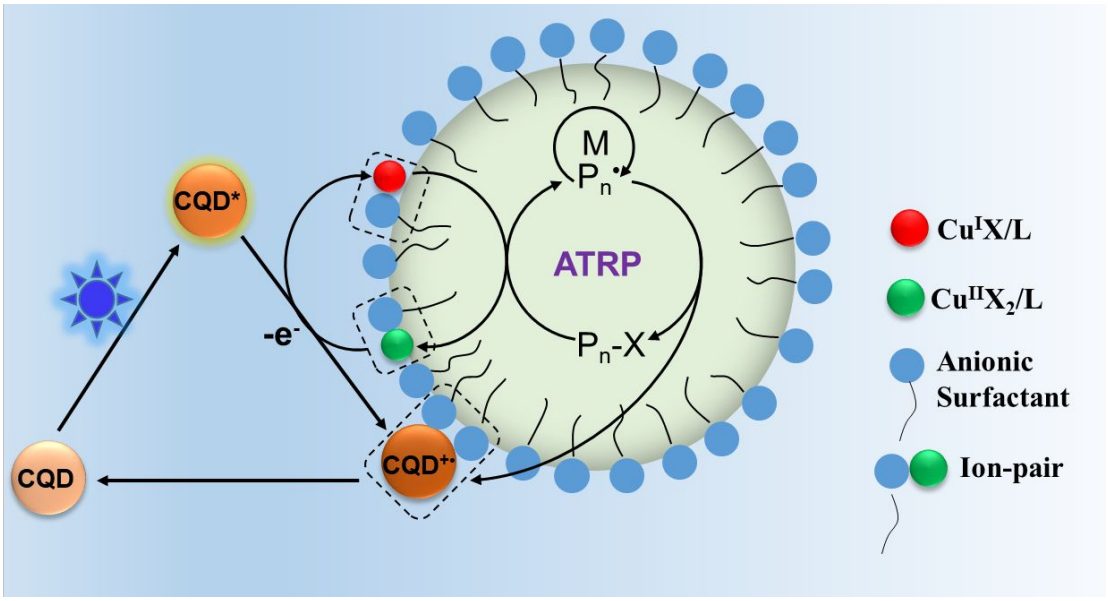
In this paper, a highly efficient visible light-induced miniemulsion ATRP system is developed for the first time by using pyridine nitrogen-doped carbon dot (CQDs) as photocatalyst. Higher than 80% monomer conversion could be achieved within 1h, with a good control of polymer molecular weights and low dispersities (M_w/M_n < 1.20). Several parameters were explored, including the concentrations of surfactant, copper catalyst and CQDs as well as the solids content. In addition, the temporal control of polymerization was achieved by switching the blue light “ON” and “OFF”,

and polymerization could also be carried out with natural sunlight. As an extension of our previous work, [16] we also developed a "one-pot" method for the rapid preparation of heterogeneous hydrogels.

Results and discussion

Due to their low toxicity, easy preparation, sustainability of raw materials, stable optical properties and other advantages, CQDs have been recently reported to be ideal green photocatalysts for both photoATRP and PET-RAFT.[18-21] Notably, our group developed an ultrafast visible light-induced ATRP system in aqueous media with 100% pyridine nitrogen-doped CQDs as the catalyst, which can be further applied for digital light processing 3D printing.[18,21] The ultrafast polymerization rate was attributed to the combination of excellent catalytic capacity, a high equilibrium constant, K_{ATRP}, for Cu-catalyzed ATRP and a high rate of electron transfer in aqueous media.[22,23] Additionally, the abundant surface groups enabled CQDs to be well dispersed in aqueous media and the large surface area enhanced contact between CQDs and the $Cu^{II}X/L$ complex.[24] According to this, we anticipate that N-doped CQDs may be a suitable heterogeneous photocatalyst for miniemulsion photoATRP. The photocatalyst is expected to work in synergy with the ATRP ion-pair catalyst, provoking a cascade of photocatalytic reactions taking place in the water phase, the oil-water interface and the monomer droplets, respectively. As described in Scheme 1, the formed monomer droplets after ultra-sonicating are stabilized by the anionic surfactant SDS. According to pioneer works,[10,25] the $Cu^{II}X_2/L$ complex can form ion-pair with the surfactant molecules at the oil-water interface. Upon visible light

irradiation, CQDs in the water phase can form electron−hole pairs and act as excellent electron donors.[18,26] With the help of water, which can stabilize the charge separated species, electrons can quickly transfer from excited CD* to the $Cu^{II}X_2$/L complex resulting in the formation of Cu^{I}X/L complex. The resulting hydrophobic Cu^{I}X/L/SDS ion pair complex later can then enter the monomer droplets and undergo a catalytic ATRP cycle with the alkyl bromide as the initiator. The CQDs that lose electrons have a positive surface charge ($CD^{\bullet+}$), and can thus adsorb onto the negatively charged monomer droplets by electrostatic interaction. As an electron acceptor, the oxidized $CD^{\bullet+}$ can be involved in promoting dormancy of living polymer chains,[20,21] and go back to the ground state, CD, which may escape to the water phase from the oil/water interface (Scheme 1).



Scheme 1. Proposed mechanism for CQDs-catalyzed visible light-induced miniemulsion ATRP.

Table 1. Experimental conditions and results of CQDs-catalyzed photoinduced miniemulsion ATRP reactions performed in this study.[a]

Entry	$[M]_0$:$[RX]_0$:$[Cu]_0$:$[L]_0$	SDS (wt%)	CQDs (mg/mL)	Cu concentration (ppm)	Solids content (wt%)	Time (min)	α (%)	$M_{n,th}$ [b]	$M_{n,SEC}$ [c]	M_w/M_n [c]	$Z_{av.}$ (nm) [d]	PDI
1	200:1:0.06:0.36	2.5	0.4	300	20	60	48	12500	12780	1.54	190	0.06
2	200:1:0.06:0.36	5.0	0.4	300	20	60	72	18600	15100	1.21	160	0.04
3	200:1:0.06:0.36	10.0	0.4	300	20	60	81	21000	21000	1.21	104	0.07
4	200:1:0.02:0.12	10.0	0.4	100	20	60	84	21700	19100	1.33	109	0.06
5	200:1:0.12:0.72	10.0	0.4	600	20	60	69	17960	15630	1.17	104	0.08
6	200:1:0.06:0.36	10.0	0.2	300	20	60	72	18700	17300	1.19	106	0.05
7	200:1:0.06:0.36	10.0	0.8	300	20	60	77	19980	20100	1.20	92	0.05
8	200:1:0.06:0.36	10.0	0.4	300	10	60	71	18300	16530	1.23	103	0.04
9	200:1:0.06:0.36	10.0	0.4	300	30	60	72	18580	15210	1.20	95	0.06
10[e]	200:1:0.06:0.36	10.0	0.4	300	20	60	89	25500	22580	1.38	108	0.09

[a]Reaction conditions: [M]/[RX]/[Cu]/[L] = [BA]/[EBiB]/[$CuBr_2$]/[TPMA], 460 nm irradiation (6W) at room temperature. V_{tot} = 5 mL. Stirring rate = 500 rpm. [b]Theoretical molecular weight calculated according to: $M_{n,th.} = [M]_0/[RX]_0 \times MW^M \times \alpha + MW^{RX}$, where $[M]_0$, $[RX]_0$, MW^M, α, and MW^{RX} correspond to initial monomer concentration, initial RX concentration, molar mass of monomer, conversion determined by gravimetric analysis, and molar mass of alkyl halide. [c]Number average molecular weight and dispersity determined by SEC analysis (DMF as eluent) calibrated with polystyrene standard. [d]Final average hydrodynamic particle diameter determined by DLS. [e]Monomer = BMA.

The polymerization of *n*-butyl acrylate (BA) was initially investigated to test the efficiency of our visible light-mediated miniemulsion ATRP process, using blue light (λ = 460 nm, 2mW/cm^2) as the irradiation. Pyridine nitrogen-doped CQDs were prepared as reported previously.[18,21] In a typical reaction (Table S1), ethyl α-bromoisobutyrate (EBiB) was used as alkyl halide initiator together with ppm level of the $CuBr_2$/tris(2-pyridylmethyl)amine (TPMA) complex ([$CuBr_2$]:[TPMA] = 1:6). As listed in Table 1 (entries 1-3), the amount of SDS was varied from 2.5 to 10.0 wt% based on monomer, while the CQD and copper salt concentrations were held constant (0.4 mM and 300 ppm, respectively). Notably, the polymerization performed using 10 wt% of SDS achieved 81% monomer conversion within 1h, which polymerization rate is significantly higher than in previous reports (see Table S2 in the Supporting Information). In addition, molecular weights were in very good agreement with the theoretical values while SEC analysis indicated a narrow molecular weight distribution ($Đ$ = 1.21, entry 3 in Table 1) suggesting a good level of control. In contrast, lower amounts of SDS led to lower monomer conversions within the same reaction period, and to larger particles (Table 1 and Figure S1). Moreover, a relatively higher polydispersity ($Đ$ = 1.54) was observed for the reaction performed using 2.5 wt% of SDS. As increasing SDS concentration resulted in smaller (and therefore larger number concentration) monomer droplets, a higher polymerization rate was achieved in agreement with the so-called segregation effect (compartimentalization) that is well documented in the case of miniemulsion RDPR, leading to a reduction in the rate of bimolecular termination.[27] Moreover, the decrease of SDS concentration

resulted in low concentration of $Cu^{II}X_2$/L/SDS ion pair complex, and reduced the copper catalyst involved in ATRP. Together with the so-called confined space effect (compartimentalization), [27] the larger size of droplets (or particles) induced by much lower SDS concentration would result in the loss control of polydispersity.

For all three SDS concentrations, the corresponding semi-logarithmic plot of $Ln([M]_0/[M]_t)$ versus time indicates two distinct linear regimes (see Figure 1a). The first regime corresponds to a "fast" polymerization followed by a decrease in reaction rate. According to the interfacial "ion-pair catalysis" mechanism of Scheme 1, one possible explanation for this "two stages" kinetic behavior is the drastic change of the internal viscosity of the monomer droplets with time. The viscosity inside the monomer droplets or latex particles increases with increasing monomer conversion and molecular weights, which may limit the rotation and movement of the dormant chains (P_n-X) and propagating radicals ($P_n^{\cdot}$). According to the RDRP polymerization mechanism, most of the polymer chains should be in a dormant state to achieve the controlled growth of polymer chains. The contact between $Cu^{I}X$/L complex and P_n-X likely became difficult as diffusion was hindered due to the high viscosity for high monomer conversions, leading to a decrease in the concentration of propagating radicals (Figures 1b and 1c). A closer observation showed that $M_{n,\,SEC}$ became slightly lower than the theoretical value for high monomer conversion with less SDS concentrations (Figure 1b). Although the overall concentration of propagating radicals was decreased for high viscosity, the activation period of propagating radicals may increase in limited region, due to the limitation of dormancy and termination which

also controlled by diffusion. Degradation reaction may occur in such limited region, resulting in a slightly lower molecular weight of the polymer than the theoretical value. In view of the confined space effect, the system with higher SDS content and small particle size may reduce the occur probability of degradation reaction.[27] Nonetheless, all SEC traces were unimodal and shifted toward higher molecular weights with increasing monomer conversion, indicating reasonably good control over the polymerization up to high conversions (Figure S2).

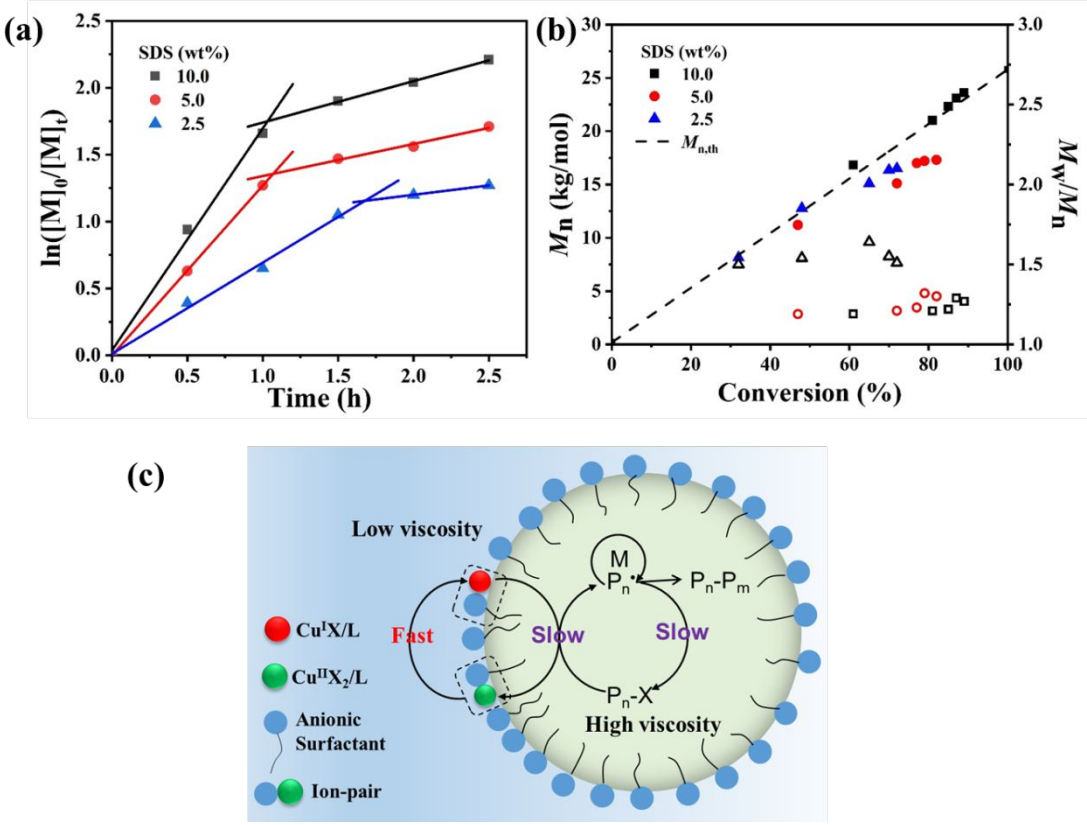


Figure 1. Influence of the SDS concentration on the CQDs-catalyzed miniemulsion photoATRP of BA. a) Kinetic plot of $\ln([M]_0/[M]_t)$ versus exposure time, b) evolution of M_n and M_w/M_n with conversion and c) proposed reaction mechanism. Reaction conditions: BA = 1 mL (20 vol %), [BA]/[EBiB]/[$CuBr_2$]/[TPMA] = 200/1/0.06/0.36, [HD] = 10 wt% relative to BA, [SDS] = 2.5–10.0 wt % relative to BA, CQDs = 0.4 mg/mL, blue LED irradiation (6 W, λ_{max} = 460 nm, 2 mW cm^{-2}), room temperature.

As shown in Figures 2a and 2b, the polymerization rate decreased with increasing

$CuBr_2$/TPMA catalyst loading (entries 4, 3 and 5 in Table 1) due to the increased number of dormant active species. The quality of the control was therefore improved, as attested by the decrease of the molecular weight distributions. By comparison, the other parameters had a relatively minor effect on the polymerization rate as shown in Table 1 and Figure 2c-f. Indeed the droplet or particle sizes were only little influenced by the amount of CQDs or solids content (Table 1, Figure S4 and S6).[28,29]

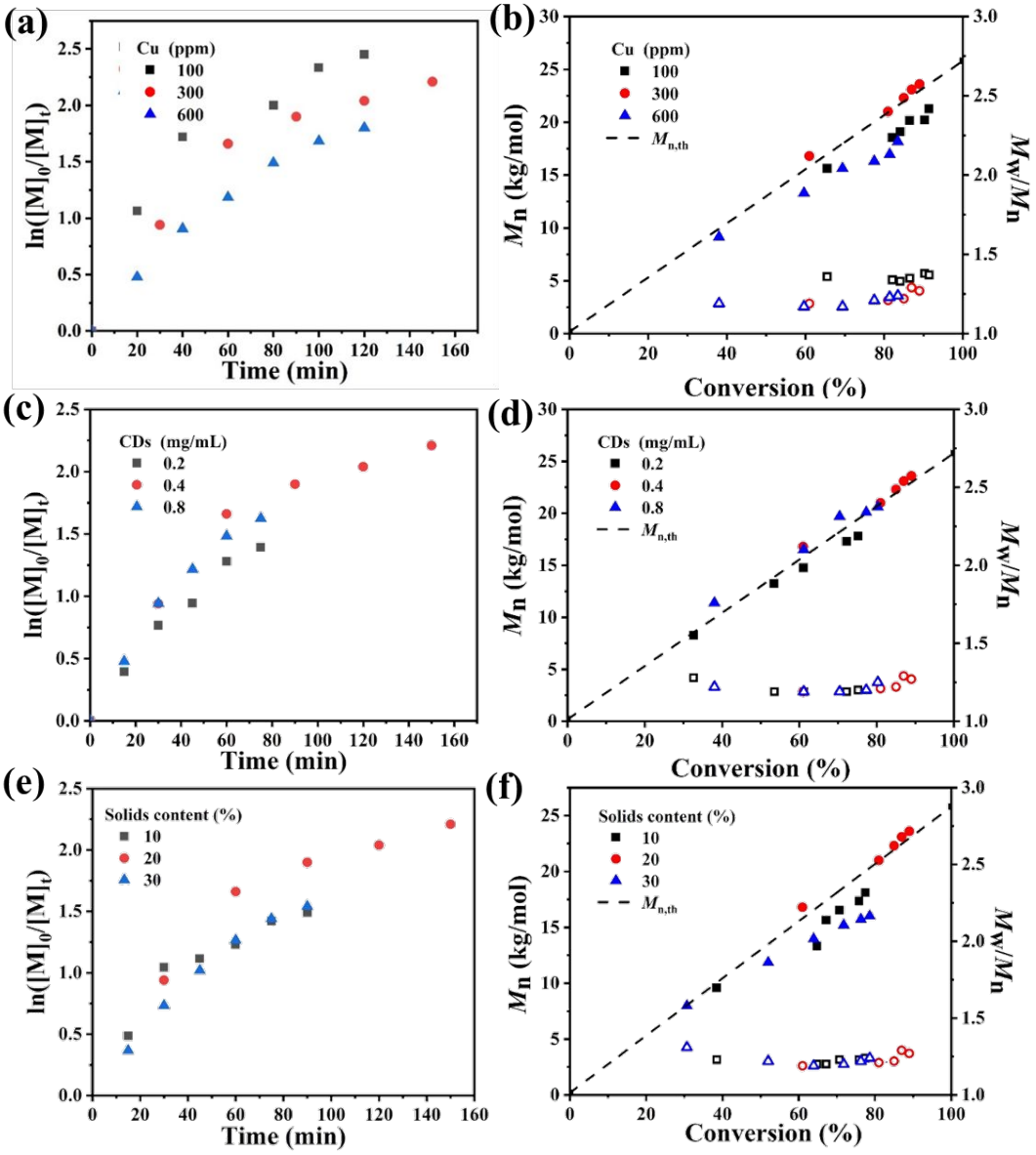


Figure 2. Effects of copper, CD and solids contents on CQDs-catalyzed miniemulsion photoATRP

of BA under blue LED irradiation (6 W, λmax = 460 nm, 2 mW cm^{-2}) at room temperature. BA = 1 mL (20 vol %), [BA]/[EBiB] = 200/1, [HD] = 10 wt % relative to BA, [SDS] = 10.0 wt % relative to BA. (a, c, e) Kinetic plot of $\ln([M]_0/[M]_t)$ versus exposure time and (b, d, f) Evolutions of M_n and M_w/M_n with monomer conversion.

Subsequently, the experimental conditions of entry 1 in Table 1 were used to assess the temporal control of CQDs-catalyzed miniemulsion photoATRP under blue LED irradiation, by switching the light source "ON" and "OFF" with 15 min intervals (Figure 3a). As expected, the polymerization stopped quickly when the light was turned "OFF", and recovered rapidly after switching it "ON". The molar mass ($M_{n.SEC}$) did not change much during the "OFF" period, and increased after the light has been switched "ON" to reach a value in good agreement with the theoretical molecular weight ($M_{n.th}$). The total exposure time was 45 min and a final PBA polymer with a molar mass of 19900 g mol^{-1} and a low dispersity (M_w/M_n = 1.19) could be succesfully obtained. A purified PBA macroinitiator (M_n = 8500, M_w/M_n = 1.22) obtained through miniemulsion photoATRP was applied in another miniemulsion photoATRP to confirm the chain-end fidelity. The PBA macroinitiator was chain extended after well dissolved in BA monomer. As shown in Figure 3c, well-defined PBA-*b*-PBA (M_n = 22500, M_w/M_n = 1.19) was achieved, evidenced by a clear shift of the monomodal GPC traces toward higher molecular weights. The polymerization was also carried on under natural sunlight as shown in Figure 3d. After 1.5h, the monomer conversion reached 92% leading to stable PBA latex

particles with a molar mass of 18700 g mol^{-1} and again a narrow molecular weight distribution (M_w/M_n = 1.20). Therefore, it can be concluded that the CQDs-catalyzed miniemulsion photoATRP maintains high polymerization efficiency, polymerization stability and good controllability even under natural sunlight source. BMA was also tested as another monomer in the same conditions (entry 10 in Table 1, Figure S7) leading to high monomer conversion (~89%) within 1h, and reasonably good control illustrating the robustness and versatility of the process.

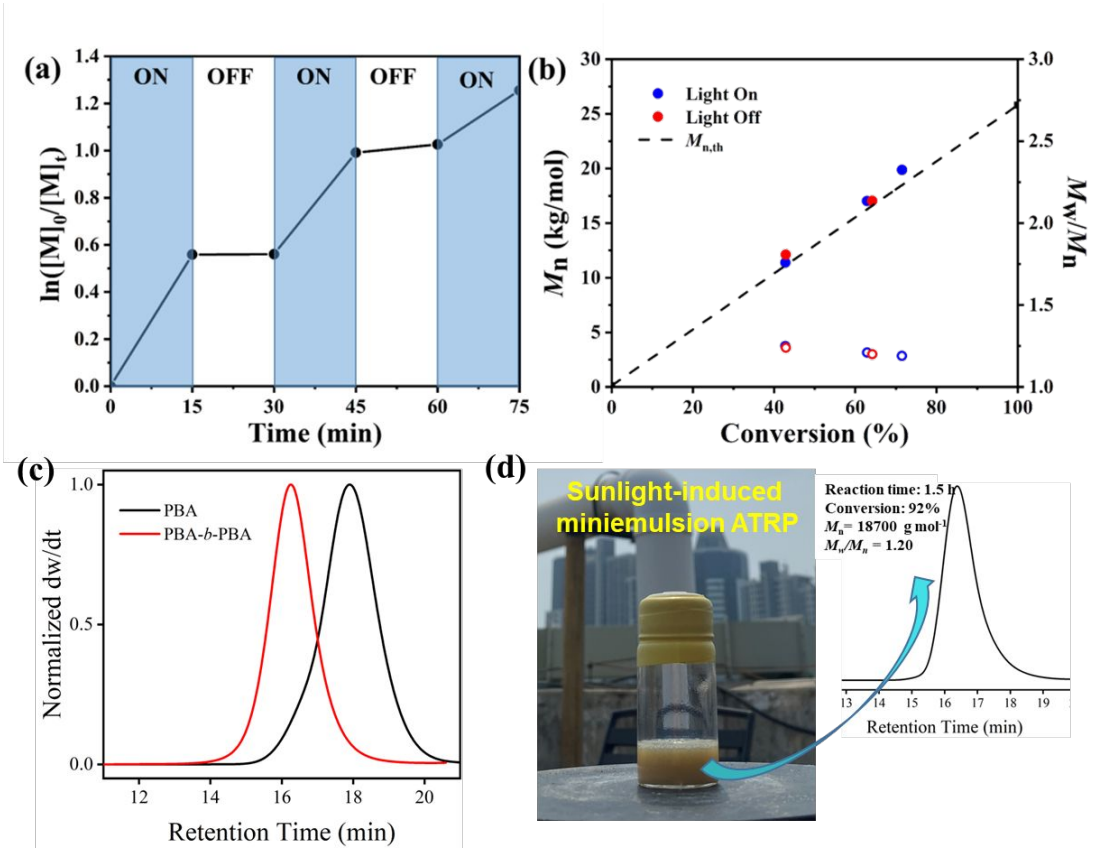


Figure 3. Temporal control of miniemulsion photoATRP. (a) Kinetic plot of ln([M]$_0$/[M]$_t$) versus exposure time during "ON" and "OFF" periods and (b) M_n and M_w/M_n plots versus conversion during "ON" and "OFF" periods. (c) Chain extension of PBA macroinitiator with BA in miniemulsion. (d) Photo of sunlight-induced miniemulsion ATRP and SEC chromatrogram of the final polymer. Reaction conditions: BA 1 mL (20 vol %), [BA]/[EBiB]/[CuBr2]/[TPMA] = 200/1/0.06/0.36, [HD] = 10 wt% relative to BA, [SDS] = 10 wt% relative to BA, CQDs = 0.4

mg/mL, blue LED irradiation (6 W, λmax = 460 nm, 2 mW cm^{-2}), room temperature.

We also developed a "one-pot" method for rapid preparation of heterogeneous hydrogels. The application of RDRP in preparation of polymer networks can not only bring more homogenous network, but also enable the production of "living" materials containing dormant reactivatable species which can be used for post functionlization.[30] The miniemulsion was prepared as described above using BA as hydrophobic monomer. After ultrasonic treatment, an hydrophilic monomer (HEA), a crosslinker polyethylene glycol diacrylate (PEGDA) and HEBiB initiator were added to the miniemulsion, followed by the addition of $CuBr_2$/TPMA and CQDs. PhotoATRP was performed simultaneously in the aqueous phase and within the hydrophobic monomer droplets under blue LED irradiation leading to an heterogeneous hydrogel composed of polymer particles embedded in a crosslinked water-swollen polymer network (Figure 4a). A digital image of the resulting heterogeneous hydrogel is depicted in Figure 4b (right) and compared to that of an homogeneous gel (left side of the Figure) obtained in similar conditions, using pure water as reaction medium instead of the miniemulsion. As expected, the heterogeneous hydrogel was less transparent due to light scattering by the PBA latex particles. In addition, the CQDs-containing hydrogel was endowed with photoluminescence characteristics.

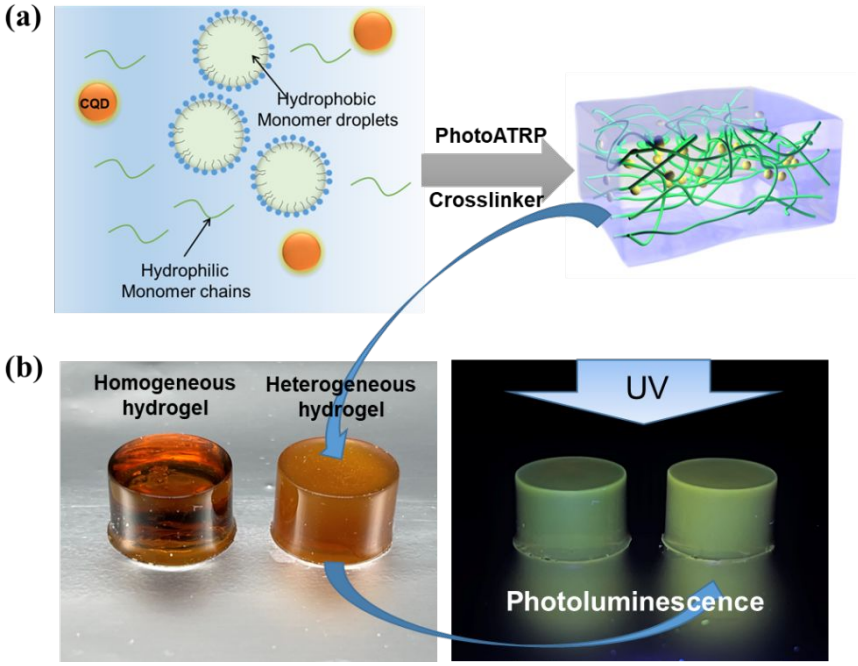


Figure 4. (a) Scheme for the preparation of heterogeneous hydrogels through CQDs-catalyzed photoATRP. (b) Digital photographs of homogeneous and heterogeneous hydrogels exposed to natural and UV light irradiations, respectively. Reaction conditions: BA 1 mL (20 vol %), [BA]/[EBiB]/[$CuBr_2$]/[TPMA] = 200/1/0.06/0.36, [HD] = 10 wt % relative to BA, [SDS] = 10 wt % relative to BA, CQDs = 0.4 mg/mL, [HEA]/[PEGDA]/[HEBiB]/[$CuBr_2$]/[TPMA]=90/10/1/0.03/0.18, blue LED irradiation (6 W, λmax = 460 nm, 2 mW cm^{-2}), room temperature.

Conclusions

In summary, we have shown that pyridine N-doped CQDs are excellent photocatalysts for visible light-induced miniemulsion ATRP, and are able to address the low efficiency problem of photoATRP in aqueous dispersed systems. The experimental results presented here suggest a heterogeneous interfacial photocatalytic mechanism involving three catalytic cycles in the water phase, the oil-water interface and the monomer droplets. In addition to the good control of polymerization, this novel CQDs-catalyzed miniemulsion photoATRP process allowed to reach very high

monomer conversions (>80%) within 1h, which represents a significant advance in the field. Excellent temporal control of the polymerization was illustrated by "ON/OFF" polymerization, and natural sunlight was also exploited as harmful power source. Moreover, photoATRP was successfully carried out simultaneously in an aqueous phase and hydrophobic monomer droplets to prepare a heterogeneous hydrogel in "one-pot". Such hydrogels may find great potential as drug delivery systems for biomedical applications. Owing to it efficiency and robustness, this new CQDs-based photocatalytic platform should be suitable for other photoRDRP systems opening the route to the synthesis of new particles and/or materials with obvious economic and environmental benefits.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website, including brief description of materials, equipment used throughout the experiment, experimental procedures for preparation and characterization of all compounds.

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Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

The work was financially supported by National Science Foundation of China (Grant No.51973201, U1804128, 52173209), the National Science Foundation for Young Scientists of China (Grant No. 22105179) and Scientific & technological research projects in Henan Province (Grant No. 222102520009).

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