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Tertiary Amine Catalyzed Photo-induced Controlled Radical Polymerization of Methacrylates

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A novel tertiary amine catalyst (TAC) and trithiocarbonate (TTC) synergistic photo-induced controlled radical polymerization of methacrylates in the *absence* of conventional photo-initiators, metal-catalysts, or dye sensitizers, has been realized under mild UV irradiation ($\lambda_{max} \approx 365$ nm), yielding polymethacrylates with low molecular weight distributions and excellent end-group fidelity (> 95%).

Since the discovery of reversible deactivation radical polymerization (RDRP) techniques including nitroxide-mediated polymerization (NMP),[1] atom-transfer radical polymerization (ATRP),[2] single electron transfer-living radical polymerization (SET-LRP),[3] and reversible addition-fragmentation chain transfer (RAFT) polymerization[4] there have been extensive efforts to exert control over such RDRPs through various physical and chemical stimuli.[5] Of the many possible external activation sources light is perhaps the most ideal, as it is inherently spatiotemporally-controllable, abundant and easily accessible, as well as being environmentally benign or "green".[6-12] In addition to reversibly switching the polymerization reaction by simply turning the light "on" or "off", light can further facilitate precise control over reaction kinetics by modulating the intensity of irradiation.[7] Numerous examples of photo-induced (Pi) polymerizations exist in the literature. For example, Hawker *et al.* developed an ATRP process controlled by visible light using a photoredox catalyst.[7] Boyer *et al.* reported a new photochemically mediated RAFT polymerization using a similar iridium/ruthenium-complex photocatalysts.[9, 13, 14] Haddleton *et al.* recently reported a photo-induced RDRP in the presence of copper(II) bromide and an aliphatic tertiary amine ligand.[6] Additionally, Matyjaszewski and co-workers have also demonstrated the polymerization of photochemically mediated ATRP.[8]

Among the existing Pi-RDRP techniques, RAFT polymerization is one of the most versatile, as it is tolerant to a wide variety of reaction conditions and chemical functionalities, and can also be performed on existing conventional free-radical polymerization set-ups.[4] Because of the low dissociation energy of the C-S bond, various thiocarbonylthio compounds can be readily used as photoinitiators of living radical reactions, including not only photoiniferters such as dithiocarbamates[15] but also RAFT/MADIX agents such as xanthates,[16] trithiocarbonates (TTC)[17, 18] and dithioesters.[19, 20] In 2002, Rizzardo *et al.* reported on the RAFT polymerization of methyl methacrylate (MMA) under UV irradiation using dithioesters as the radical source as well as the chain transfer agents (CTAs).[19] At low conversions (< 20%), the polymerization was well controlled, however upon reaching relatively high conversions (> 30%) the control was significantly reduced. It has been demonstrated that common RAFT/MADIX agents are strongly sensitive to UV irradiation.[21] The photolysis of the RAFT agents at relatively high conversions or long irradiation time has been suggested to lead to irreversible decomposition of the CTAs, resulting in the unavoidable loss of end-group fidelity and therefore the "living" character. In order to suppress the photolysis of CTAs under UV irradiation, Cai *et al.* chose long-wavelength UV (365-405 nm, cutting off the short-wavelength UV light) as an irradiation source and employing a suitable photoinitiator, achieving a well-controlled RAFT polymerization of methyl acrylate (MA).[22] Recently, Bai and

co-workers also reported a controlled radical polymerization of MA mediated by TTC under UV irradiation in high conversions.[17] Despite some success in the suppression of photolysis of the CTA in the RAFT polymerization of MA, the mechanism for the "living" character is not yet well understood. Moreover, maintaining a narrow molecular weight distribution for methacrylate-type monomers at high monomer conversions is still not achievable. More recently, Johnson *et al.* have developed a photopolymerization system employing a TTC iniferter relying on the utilization of an organic photoredox catalyst.[23] They proposed that electron transfer from a photoexcited catalyst to the TTC can activate the TTC and lead to the generation of a radical for propagation or degenerative chain transfer (*i.e.* RAFT process). The catalyst system enabled the synthesis of high molecular weight polymers as well as triblock copolymers. We have recently reported on the photopolymerization of acrylates/acrylamides with both visible light and under UV irradiation.[24] During our studies, we found that direct photolysis of TTCs allowed for excellent control over these monomers with both irradiation sources. However, utilizing this system for methacrylate monomers resulted in a significant loss of control, in agreement with previous reports.[19] Indeed, there is still a research gap in the literature concerning well-controlled photo-induced RAFT polymerizations of methacrylates, particularly at high monomer conversions. Inspired by the abovementioned works, and in conjunction with our own findings, we discovered that the addition of tertiary amines to the UV activated photopolymerization of methacrylate monomers improved the control of the system dramatically.

Herein, we present a Pi-RDRP exploiting photoactivation in the presence of a tertiary amine catalyst (TAC) and TTC (Scheme 1). Near quantitative conversions for methacrylates has been realized upon mild UV irradiation ($\lambda_{max} \approx 365$ nm). The resulting polymers display narrow molecular weight distributions and high end-group fidelity as exemplified by *in situ* chain extension upon sequential monomer addition. Temporal control is illustrated by intermittent light and dark cycles, with polymer growth arrested in the absence of irradiation.
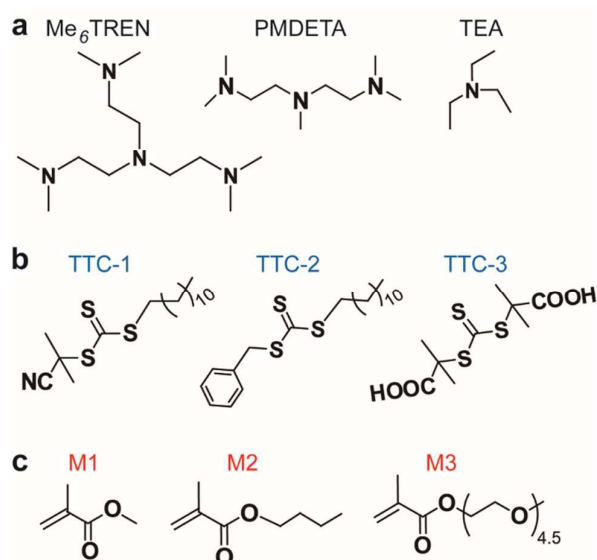
Scheme 1. Chemical structures of compounds investigated in this study. (a) Tertiary amines: tris(2-(dimethylamino)ethyl)amine (Me$_6$TREN), *N,N,N',N'',N''*-pentamethyldiethylenetriamine (PMDETA) and triethylamine (TEA). (b) TTCs: 2-cyano-2-propyl dodecyl trithiocarbonate (TTC-1), benzyl dodecyl trithiocarbonate (TTC-2) and 2,2'-(thiocarbonyl-bis(sulfanediyl))-bis(2-methyl-propanoic acid) (TTC-3). (c) Monomers: methyl methacrylate (MMA, M1), *n*-butyl methacrylate (*n*BuMA, M2) and oligo(ethylene glycol) methacrylate (OEGMA, M3). The UV absorption spectra of TTC-1, TTC-2 and Me$_6$TREN are shown in Figure S1.

Tertiary amines (TAs) are known to readily form amine radical cations by loss of an electron using light-mediated photochemistry,[25, 26] and have been wildly employed in Pi-RDRPs.[27, 28] Lalevée *et al.* proposed a three-component photoredox mechanism for the photo-induced ATRP process as illustrated in Scheme 2a.[29] The three-component catalytic mechanism

(Cu^I/NR_3/P_n-X) under irradiation leads to the formation of an excited state Cu^I*. This transient species is thought to be far more reactive than when in the ground state due to its lower oxidation potential. A fast halogen (X) transfer reaction with the initiator can ensue, resulting in the generation of the propagating radical ($P_n\bullet$) and the complex corresponding to the Cu^{II} oxidation state (Cu^{II}X). Subsequent reaction of this deactivated form of the catalyst with a propagating radical can regenerate the Cu^I complex and produce a dormant species. This results in the progressive establishment of a classical ATRP equilibrium. A faster polymerization can be achieved in the presence of tertiary amine, acting as an additional species that can permit faster regeneration of the Cu^I activator.

In other work, Goto and Kaji have demonstrated a reversible complexation-mediated polymerization (RCMP), where a tertiary amine may play another role in the Pi-RDRP process.[30, 31] Mechanistically, RCMP is based on the reversible activation of a dormant species (P_n-iodine) to a propagating radical species using organic amines as complexing agents to drive the radical-forming step (Scheme 2b). A sufficiently large number of activation-deactivation cycles are required for achieving low molecular weight distribution. An advantage of RCMP is that no special capping agents or metals are used.

Scheme 2c illustrates a typical Pi-RAFT process. UV irradiation induces the homolytic cleavage of the C-S bond in the TTC, generating a propagating radical ($P_n\bullet$) and a sulphur radical ($\bullet$S-C(=S)-S-Z). However, it is believed that the resulting sulphur radical may not be stable under these conditions and can undergo subsequent fragmentation reactions to produce CS_2 and a Z group radical, resulting in poor control of the Pi-RAFT polymerization.[17, 32]

Differing from a conventional Pi-RAFT process, the tertiary amine/TTC two-component system developed in this study is thought to operate according to a photoredox process (Scheme 2d). The photo-irradiation induces an electron transfer from the tertiary amine to the TTC, leading to the generation of a TTC radical anion ([P_n-S-C(=S)-S-Z]$\bullet^-$) and an amine radical cation ([NR_3]$\bullet^+$). Subsequently, the TTC radical anion reversibly cleaves to generate a reactive carbon-centered radical ($P_n\bullet$), as well as a resonance-stabilized TTC anion ([S-C(=S)-S-Z]$^-$). The improved control observed in this tertiary amine catalyzed (TAC) Pi-RDRP of MMA *vs.* conventional Pi-RAFT process (TTC itself) is thought to result from the additional electron transfer process, which avoids the formation of the neutral TTC radical species and thus limits this degradation.
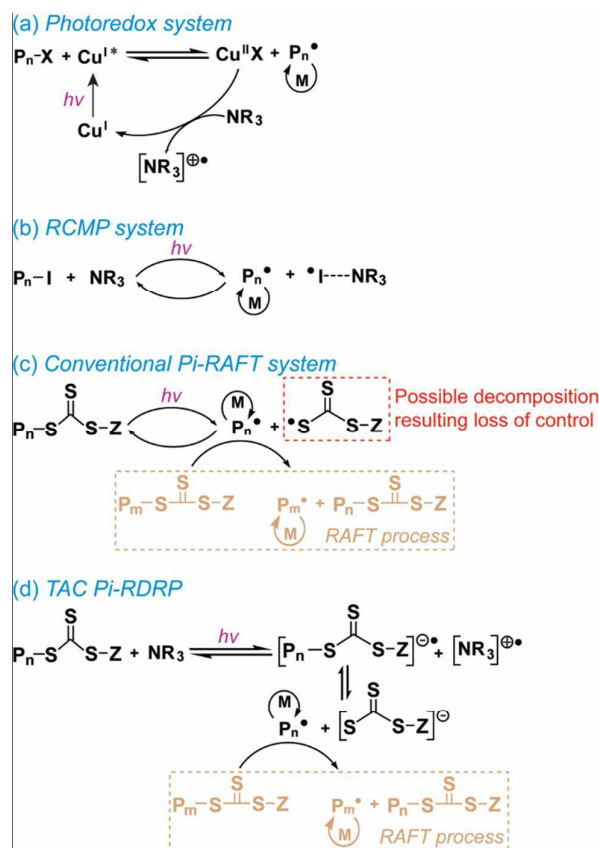
Scheme 2. The comparison of amine assisted Pi-RDRP systems with conventional Pi-RAFT process: (a) typical photoredox system, (b) typical RCMP, (c) typical Pi-RAFT polymerization and (d) proposed mechanism of the tertiary amine catalyzed photo-induced RDRP (TAC Pi-RDRP).

To examine our hypothesis, TAC Pi-RDRP of MMA was carried out in the presence of Me_6TREN under mild UV irradiation (Figure 1a, broad emission, $\lambda_{max} \sim 365$ nm). In a typical experiment, a 25 mL Schlenk tube was charged with MMA (100 eqv.), TTC-1 (1.0 eqv.), Me_6TREN (0.25 eqv.) and DMSO (50 vol% w.r.t monomer). After 4 hours of irradiation, poly(methyl methacrylate) (PMMA) polymers were obtained with relatively good control of the molecular weights and low molecular weight distributions (M_w/M_n) at high MMA conversion (~80 %, Figure 1b and Table S1). The results show the characteristics of a typical "living" polymerization: namely, first-order kinetics with regards to monomer conversion (Figure 1c), and molecular weights increasing linearly accompanied by decreasing molecular weight distributions as a function of monomer conversion (Figure 1d). The molecular weight values obtained from the GPC DRI chromatograms were in close agreement with theoretical values based on ^{1}H NMR analysis. A fundamental key to the success of any RDRP is chain-end fidelity. Achieving high chain-end fidelity allows for effective block copolymer formation, chain-end functionalization, and the successful synthesis of a wide variety of well-defined macromolecules. It was therefore critical to determine chain-end fidelity in the TAC Pi-RAFT reactions. Using the described system the synthesized PMMA displayed excellent retention of α and ω end-groups even at high monomer conversions, as evidenced by MALDI-ToF MS (Figure 1e-f) and ^{1}H NMR analysis (Figure S2). The MALDI-ToF MS show a single monomodal series and is in good agreement between expected mass ($M_{n,exp}$) and observed mass ($M_{n,obs}$), providing strong evidence for the near-quantitative retention of α and ω end-group fidelities at high monomer conversion. In addition, TAC Pi-RDRPs of MMA were carried out using a

lower [M]/[TTC] ratio of 20 (Figure S3). The results also demonstrated the "livingness" of the present RDRP during the polymerization process.
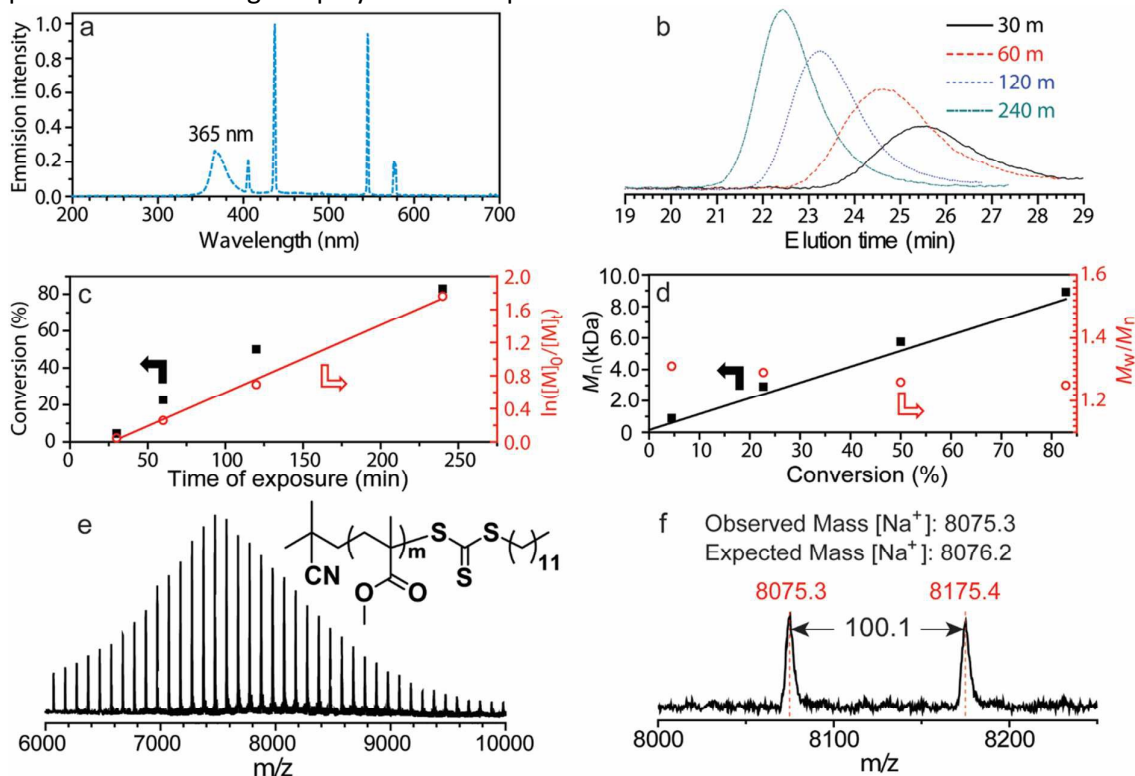

Figure 1. (a) UV light source emission. And characterization on PMMA prepared by a TAC Pi-RDRP process in the presence of Me$_6$TREN: (b) GPC evaluation, (c) kinetic study, (d) molecular weight/molecular weight distribution date and (e-f) MALDI-ToF-MS.

Control experiments were performed in which amine or light was selectively omitted (Table 1). Polymerization did not occur without UV irradiation (Entry-1 and Figure S4a). It should be noted that for the case in which the reaction mixture contained the TTC but no amine catalyst, polymerization still occurs, however the product is of high molecular weight distribution (M_w/M_n >1.8) indicating that the polymerization is not well controlled (Entry-2 and Figure S4b). This is in agreement with previous reports at high monomer conversion for methacrylate monomers.[19] The reason for the loss of controllability is potentially a result of the photo-induced irreversible decomposition of the TTC (Scheme 2c). In contrast, the PMMA obtained from the amine/TTC system has a much lower molecular weight distribution of 1.25 (Table S1), indicating good controllability over the TAC Pi-RDRP process. This is thought to be due to the formation of amine radical cations and TTC radical anions, providing an alternative and beneficial pathway compared with direct photolysis (Scheme 2d). Based on these results we can conclude that the amine catalyzed system (with an additional electron transfer process) allows for good control over the PMMA chain-growth process, enabling the preparation of PMMA with precise molecular weight and low molecular weight distribution.

The electron transfer from amine to TTC is a key step in our proposed TAC Pi-process. In a recent publication focused on elucidating the mechanism of Cu-based Pi-RDRP it was illustrated that electron transfer from an amine ligand identical to the amine employed in this study (*i.e.* Me$_6$TREN) can occur in such systems. Moreover, it was pointed out that enhanced electron transfer of amine/carbonyl combinations under photoirradiation is classically understood to be due to a realignment of the respective molecular energy levels.[33] Additionally, electrochemical studies have shown RAFT agents similar to those employed herein (*i.e.* TTCs) to be easily reduced in solution,

indicating their ability to act as electron acceptors.[9] These independent investigations provide support for the proposed mechanism for activation in this study.

Table 1 summarizes the characterization data of the prepared polymethacrylates using Me_6TREN and different TTCs (Scheme 1). We obtained hydrophobic (Entry 3-5, Figure S4c-e) and hydrophilic (Entry 6, Figure S4f) polymers with low molecular weight distribution (M_w/M_n ~ 1.3) at quantitative conversion (> 99 %). The GPC plot of POEGMA (Figure S3f) shows an asymmetric curve and a small tail at the low molecular weight region. This phenomenon is known to be due to the strong interaction between polyethylene glycol chains and the chromatography column (THF as mobile phase).[34] We also studied the polymerization behaviour of methyl acrylate (MA), styrene (St) and *N*-isopropylacrylamide (NIPAM) using TTC-2 (Figure S5-8). The addition of TAC in the Pi-RDRP of these monomers appears to have a negligible effect on these polymerizations, in agreement with previous reports.[17, 24, 35]

Table 1: Summary of GPC and ^{1}H NMR data of the polymers synthesized in this study.

Entry[a]	Solvent	TTC	Monomer	Ratio [TTC]:[M]	Catalyst	Conversion[c] (%)	$M_{n, th}$[c] (Da)	$M_{n, GPC}$[d] (Da)	M_w/M_n[d]
1[b]	DMSO	TTC-1	MMA	1:100	Me_6TREN	-	-	-	-
2	DMSO	TTC-1	MMA	1:100	N/A	> 99	10,400	33,100	1.82
3	DMSO	TTC-1	MMA	1:100	Me_6TRE	> 99	10,400	11,700	1.30
4	DMSO	TTC-1	EMA	1:100	Me_6TRE	> 99	11,700	12,400	1.28
5	DMSO	TTC-1	BuMA	1:100	Me_6TRE	> 99	14,360	15,500	1.26
6	H_2O	TTC-3	OEGMA	1:200	Me_6TRE	> 99	74,500	82,700	1.31

[a] The reactions were performed in solvents for 8 hrs at room temperature using UV lamp (λ_{max} = 365 nm) as light source. [b] For Entry 1, the reaction was performed in dark box WITHOUT UV irradiation. [c] Monomer conversion and theoretical molecular weight determined by ^{1}H NMR spectroscopy. [d] Molecular weight and molecular weight distribution determined by GPC analysis.

The lack of any reaction in the dark suggested that the polymerization could be activated/deactivated by UV light leading to controlled regulation of the polymerization process externally. To investigate this responsive nature, Me_6TREN was combined with the TTC-1 and MMA. The mixture was exposed to 365 nm UV light, reaching ~24 % conversion for TAC within 1 hour. After removal of the light source, nearly *complete* cessation was observed over a further 1 hour period; however, re-exposure with UV light led to resumed polymerization. This cycle could be repeated several times up to high conversions (~70 %), indicating efficient activation and deactivation of the polymerization process (Figure 2a). A bit of conversion during the "dark" cycles is observed. This is suggestively attributed to the RAFT process (as illustrated in Scheme 2d), which has no temporal control resulting in a small amount of conversion during the "dark" cycles. Similar results have been observed in the PET-RAFT polymerizations.[9] Significantly, a linear increase in $\ln([M]_0/[M]_t)$ *vs.* reaction time is obtained even with multiple "ON-OFF" light switching cycles, and the observation of first order kinetics through the course of the reaction demonstrated a controlled polymerization process (Figure 2b). In analogy with traditional RAFT processes, this data indicates that when light is removed from the system the TTC is oxidized to the stable and dormant state and upon re-exposure to light, in the presence of the TAC, the TTC is able to efficiently and reversibly generate propagating radicals (Table S2).
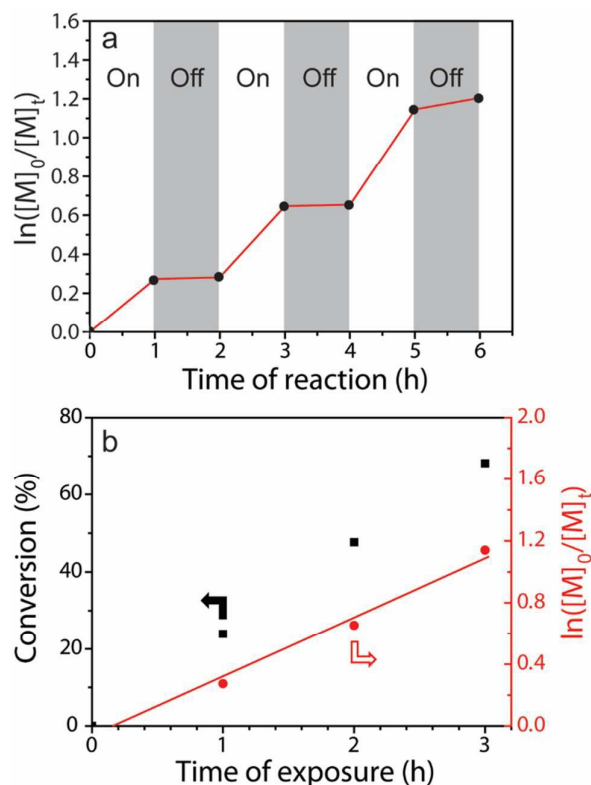
Figure 2. Polymerization of MMA using TTC-1 and Me$_6$TREN with repeated "ON-OFF" cycling of the reaction to 365 nm UV light.

Apart from MALDI-ToF MS and NMR measurements that have demonstrated the high α and ω chain-end fidelity, further successful block copolymerization was carried out to provide solid evidence that a controlled polymerization system with high end-group retention has been achieved. Firstly, the polymerizations of MMA were conducted to give starting PMMA homopolymers (Figure 3a) using a Me$_6$TREN/TTC-1 system. Without any purification, the resultant PMMA was utilized as macro-TTCs for *in situ* chain extension experiments by adding another 100 eqv. MMA, leading to well-defined PMMA-*b*-PMMA *pseudo*-diblock copolymers (Figure 3b). ^{1}H NMR analysis also indicates that high conversions (> 90 %) are achieved in the preparation of starting PMMAs as well as the *pseudo*-diblocks (Table S3, Figure S9-10). The GPC profiles of the chain-extended products (blue trace) clearly shows a shift to higher molecular weight species with little tailing in the homopolymer region, again revealing good chain-end fidelity in the PMMA macro-TTCs and a high reinitiation efficiency in the present TAC Pi-RDRP system.
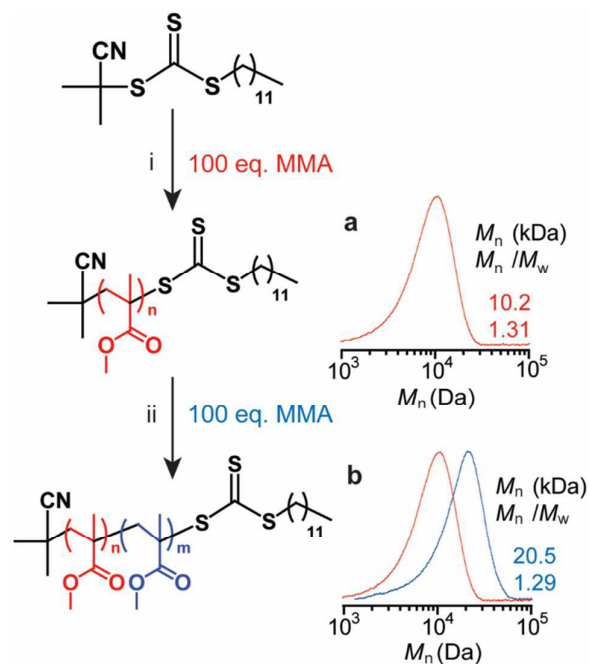
Figure 3. Synthesis of PMMA-*b*-PMMA *pseudo*-diblock copolymers and accompanying GPC traces of the resultant polymers using Me$_6$TREN/TTC-1 system. (Red trace: 1st block PMMA; blue trace: *pseudo*-diblock copolymers, PMMA-*b*-PMMA).

The choice of TTC and solvent in RAFT polymerization is crucial.[32] Similar to typical RAFT polymerization, the TTC molecular structure has a significant effect on the polymerization rate of MMA. For instance, TTCs with different R group leaving abilities (relating to the structure of TTC) were employed to conduct TAC Pi-RDRP of MMA (Figure 4a). TTC-1 has a strong R group ((CH$_3$)$_2$CCN-) leaving ability, which can be activated more readily to generate initiating radical (R•) compared to the R group (PhCH$_2$-) of TTC-2 by photo-irradiation and hence resulting in a faster polymerization rate (R_p). In addition, we observed that the control of PMMA using TTC-2 was significantly reduced in comparison with TTC-1. This result is in good agreement with a recent review by Moad *et al.*, whereby TTC-1 is highly recommended for the RAFT polymerization of MMA.[36] As the initial studies were conducted using a polar organic solvent (DMSO), it was of interest to ascertain if the system is as effective in other solvents. Dioxane and toluene, both with a lower solvent polarity index (SPI) values (4.8 and 2.4, respectively) were tried and shown to be suitable for the polymerization of MMA (Figure 4b). However, the differences in SPI appear to have significant effect on the R_p, while the molecular weight distributions of the furnished PMMA products are almost identical (Table S4). Namely, by using the non-polar solvent toluene (SPI = 2.4), we have demonstrated the preparation of PMMA, following a longer induction period. Monomer conversion reaches 40 % after 4 hours of irradiation, with M_w/M_n of 1.26. When increasing the SPI to 4.8 (dioxane), a faster polymerization rate and shorter induction period were observed, indicating the significant effect of SPI on R_p. This result also supports our hypothesis, whereby electron transfer to generate the ion-pair prior to fragmentation of the TTC radical anion would be enhanced by the stabilizing effect a polar solvent would have on the ionic species in solution.

The nature of the TAC was subsequently investigated. Difference in TAC molecular structure appears to have negligible effect on the polymerization rate. This is unlike metal-complex catalyzed RDRPs where the reactivity of the catalyst complex differs significantly depending on the chemical structure of the amine ligand employed. The polymerization rate and molecular weight distributions of the furnished PMMA products are almost identical (Figure 4c and Table S4). For example, by using an inexpensive TAC like triethylamine (TEA), we have also demonstrated the successful preparation of PMMA (M_w/M_n = 1.26). The advantage to perform the TAC Pi-RDRP using inexpensive TACs opens avenues for the large-

scale preparation of PMMA in practical applications. Investigation into the effect of TAC loading level (using Me_6TREN as model amine) revealed that higher catalyst loadings decreased the R_p (Figure S11). The reason for the slower R_p is still unclear. However it may be ascribed to the ability of the tertiary amine to participate in radical-based termination reactions when high loadings are used, as has been described in the literature. [37]
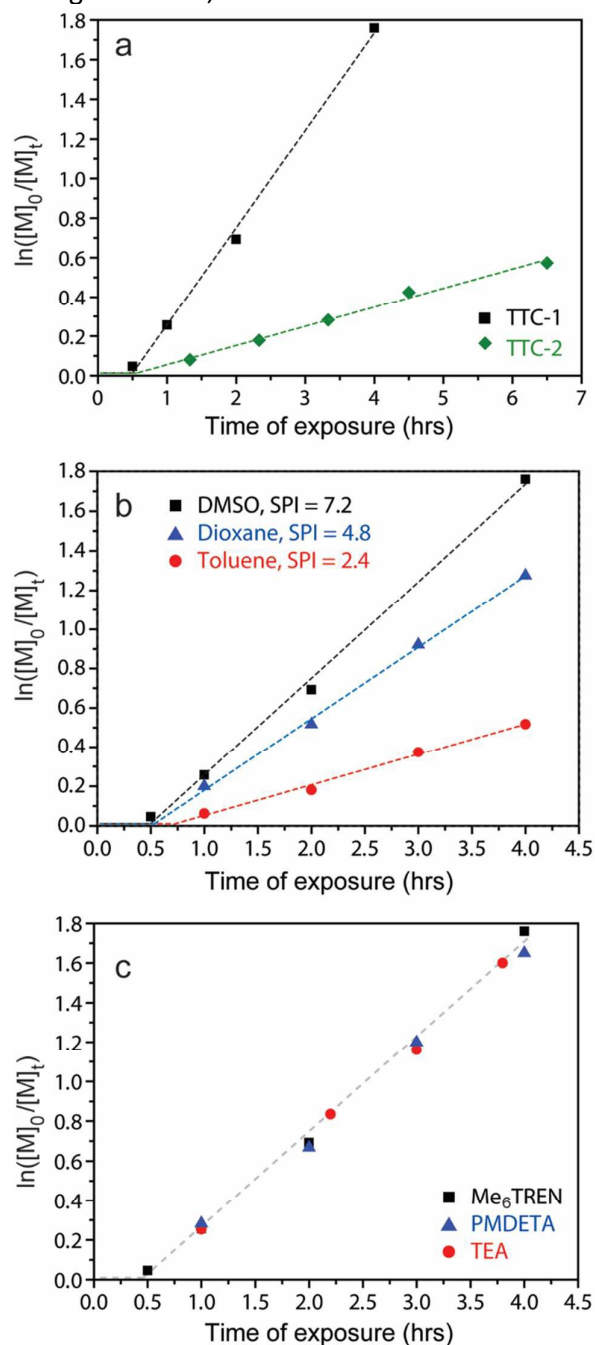

Figure 4. Kinetic plots for the TAC Pi-RDRPs of MMA using (a) different TTCs, (b) various solvents and (c) various TACs under 365 nm UV irradiation. (Note: SPI refers to the Solvent Polarity Index).

Conclusions

We report a synergistic photo-induced RDRP of methacrylates in the presence of tertiary amine catalysts. Polymerizations performed in the absence of the amine additive are uncontrolled and yield only poorly defined polymethacrylates when high monomer conversions are targeted. The tertiary amine catalyst presents advantages over conventional photoinitiators, metal-catalysts, and dye sensitizers, as it is inexpensive, relatively nontoxic, easy to handle, and amenable to a variety of functional groups, monomers and solvents. The polymers synthesized *via* this TAC Pi-RDRP process show narrow molecular weight distributions and excellent end-group fidelity (> 95 %). The accessibility of the end-groups was also confirmed by *in situ* chain extensions to yield *pseudo*-diblock copolymers of high purity. Negligible polymerization in the *absence* of light confers spatiotemporal "ON/OFF" control of the TAC Pi-RDRP process. The properties of this reaction will be important to those in the field of materials science for commercial applications where spatial or temporal control of polymer chain growth is desirable. Further studies investigating the scope for this TAC Pi-RDRP system are in progress.

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TOC

A novel tertiary amine catalyst (TAC) and trithiocarbonate (TTC) synergistic photo-induced controlled radical polymerization of methacrylates in the *absence* of conventional photo-initiators, metal-catalysts, or dye sensitizers, has been realized under mild UV irradiation ($\lambda_{max} \approx 365$ nm), yielding polymethacrylates with low molecular weight distributions and excellent end-group fidelity (> 95%).