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Making Invisible Visible: In Situ Monitoring the RAFT Polymerization by Tetraphenylethylene-Containing Agents with Aggregation-Induced Emission Characteristics

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Abstract: Polymerizations are difficult to monitor in real time unless using specific online instruments. In this paper, we demonstrated a facile and efficient approach to visualize the polymerization in situ. A group of tetraphenylethylene (TPE)-containing dithiocarbamates were synthesized and screened as agents for reversible addition fragmentation chain transfer (RAFT) polymerization. The spatialtemporal control characteristics of photochemistry enabled the RAFT polymerizations to be "ON" and "OFF" on demand under alternating visible light irradiation. The emission of TPE is sensitive to the local viscosity change due to its aggregation-induced emission characteristic. Quantitative information could be easily acquired by "naked eyes" without destroying the reaction system. In addition, the versatility of such technique was well demonstrated by 12 different polymerization systems. The present approach thus demonstrated a powerful platform for understanding the controlled living radical polymerization process.

Monitoring and understanding polymerization process in situ are of vital importance in both academic and industrial field, especially for the prevention of explosive reactions.^[1] The diffusion of monomer, initiator and polymer molecules plays an important role in the kinetics of polymerization and also in the properties of the resulting polymers. Various methods such as rheometry, viscometry or dilatometry, have been used to obtain such information.^[2] However, these approaches gain merely insight on the macroscopic viscosity rather than at the molecular level, unless using the specific online instruments.

Fluorescence-based techniques have found promising applications in this field, due to their high sensitivity, large contrast, fast response and non-invasive character.^[3] Fluorescent dves or

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molecular rotors can be used as probes to monitor the local viscosity change^[3a,4]. However, as most of the polymers are inherently non-fluorescent or show very weak fluorescence,[5] external fluorophores are needed to label the polymers. Notably, although facile physical blending method has been developed, the dye only senses the viscosity of the system rather than the segmental motion of the polymer.^[3a] Thus, it is particularly useful to attach dye molecules directly to the polymer chain at specific site such as the chain-end.^[6] This low degree of labeling and the precise location of the dye molecules barely affect the intrinsic property (conformation) of the polymers but make the resulting fluorescent macromolecules promising for applications in optical imaging, (bio)sensing, light-harvesting etc.[3a,7] Generally, dveend-labeled polymers with well-defined architecture and narrow polydispersity index (PDI) are synthesized by controlled polymerization using dye-labeled initiators.^[8] However, the high reaction temperature employed prevents the subsequent in situ tests. Additionally, extra thermal initiators affect the chain fidelity or dye labeling efficiency of the resulting polymers. Fortunately, photochemistry makes us possible to monitor the polymerization process in situ due to its spatial-temporal control characteristics.^[9] It is worth noting that Boyer and Qiao independently reported the direct photoactivation of trithiocarbonate-based agents for reversible addition fragmentation chain transfer (RAFT) polymerization.^[10] This method enables excellent "ON-OFF" control of the chain growth at room temperature, to give polymers with narrow PDI (< 1.15) and high chain fidelity (>95%). Nevertheless, the polymerization suffers from long reaction time of >15 h for complete monomer conversion.[10b]

On the other hand, commonly used dyes, such as pyrene, rhodamines and coumarins, often emit intensely as isolated molecules but experience partial or complete emission quenching when aggregated or clustered.^[3a,3c] Such aggregation-caused quenching (ACQ) effect makes them difficult as tools to visualize the polymerization process. The phenomenon of aggregationinduced emission (AIE) is a unique photophysical process opposite of ACQ.^[11] AIE luminogens (AIEgens) often emit weakly in solution but show strong emission in the aggregated state due to the restriction of intramolecular motion (RIM).^[12] Such mechanism makes the fluorescence of AIEgens highly sensitive to the environmental change to allow them to serve as probes to sense the viscosity change during the polymerization process. AlEgen-based probes have been developed for the direct visualization of gelation process,[13] crystallization process,[14] defect,^[15] microphase separation,^[16] glass transition temperature (T_{α}) ,^[17] interfacial dynamic self-assembly,^[18] and so on. Despite monitoring the step polymerization based on in situ formed

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fluorophore was reported,^[19] direct visualization of the radical polymerization using AIE technology is virtually unexplored.

In this work, we endowed RAFT initiators with AIE characteristics and applied them for in situ visualization of the polymerization process. Based on understanding of the catalytic mechanism (Scheme S1 in the supporting information), a series of dithiocarbamate-based RAFT agents with stabilizing units (Z functionality) and fragmenting (R group) units were designed to optimize the controlled radical polymerization (Scheme 1).^[9a,20] Notably, tetraphenylethylene (TPE), an archetypal AIEgen, was incorporated into their structures to make them AIE-active. Benzyl-based group was selected as R group because of the lesser side reactions under visible light initiation.^[21] UV-vis analysis indicated that the *N*-cyclic dithiocarbamates **2a–d** exhibited absorption at 400–500 nm (Figure S1), which well overlapped with the emission of blue light-emitting diode (~460 nm).^[10b]



Scheme 1. Chemical structures of dithiocarbamates developed in this work.

Table 1. Photopolymerization of MA in toluene in the presence of different dithiocarbamates under blue LED light irradiation.^[a]

Entry	Initiator	T (h)	Conv. ^[b] (%)	<i>M</i> _{n,th} ^[c] (kg mol ⁻¹)	M _{n, GPC} ^[d] (kg mol ⁻¹)	PDI ^[d]
1 ^[e]	2a	24	0	-	-	-
2 ^[f]	-	24	0	-	-	-
3	2a	2.1	91	16.5	20.2	1.10
4	2b	2.5	91	16.1	19.6	1.16
5	2c	5	94	16.6	21.3	1.07
6	2d	11	82	14.7	19.2	1.12
7	2e	10	81	14.5	16.6	1.30
8	2f	11	71	12.8	13.5	1.35
9	3	3.2	90	15.8	19.2	1.21
10	4	11	88	15.3	17.5	1.06

[a] Polymerization conditions referred to supporting information. [b] Monomer conversion was determined by ¹H NMR spectroscopy. [c] Theoretical molecular wight ($M_{n,th}$) (see supporting information). [d] Determined by GPC analysis. [e] The polymerization was performed at 60 °C without light. [f] The polymerization was carried out with blue light irradiation in the absence of initiator.

Blue light-induced polymerizations using methyl acrylate (MA) as monomer were carried out in toluene as shown in Table 1. The control experiments shown in entry 1 and 2 excluded the possibility of occurrence of thermal or self-induced polymerization. The polymerization rate increased remarkably by gradually increasing the electron-withdrawing ability of Z group from diphenylamine (2f) to imidazole (2a), as the reaction time for nearly complete conversion was significantly decreased from 11 h to 2.1 h (entry 3-8). These results indicated the significant effect of Z group on the photo-induced radical polymerization, and were different from those initiated by heating.^[22] By changing the R group from phenyl ring of initiator 3 to TPE unit of 2a, the polymerization proceeded faster (entry 3 and 9) and the PDI (1.09 vs 1.21) became narrower (Figure S2). Density functional theory calculations indicated a much lower energy band gap of 2a (2.88 eV) than that of 3 (3.66 eV) (Figure S3), suggesting that TPE was beneficial for controlling and accelerating the polymerization. Kinetic study indicated a *pseudo*-living polymerization behaviors of initiators 2a-2e (Figure S4).^[10b] Notably, 2a showed the highest propagation rate constant (k_p^{app}) of 0.067 min⁻¹, which was substantially higher than that achieved by commercial initiator 4 $(k_{\rm p}^{\rm app} = 0.009 \text{ min}^{-1})$ under similar conditions.^[10a]

The spatial-temporal control enables workers to reinitiate a reaction on demand and is critical for in situ monitoring.^[23] As expected, the polymerizations initiated by **2a-2e** displayed excellent "ON-OFF" control under alternating light "ON" and "OFF" environment (Figure S5-S9). In addition, the resulting TPE-labelled polymethyl acrylate (PMA) displayed high chain fidelity (Figure S10-S15). Compound **2a** also worked for the polymerization of other monomers (Figure S16). Among them, **2a** displayed higher catalytic activity for acrylate monomers than styrene.



Figure 1. RIM mechanism. (A) Schematic illustration of fluorescence process during the polymerization. (B) Fluorescence of PMA derived from **2a** (M_n = 1.5 × 10⁴ g mol⁻¹, 20 mg in 1 mL THF) with different amount of PS (Mw = 2.8 × 10⁵ g mol⁻¹). (C) Plot of relative PL intensity (III_0) versus the PS concentration, where I_0 is the PL intensity in pure THF.

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The TPE-based RAFT agents were non-emissive both in solution or solid state due to the quenching effect of the carbonyl sulfur group.^[24] However, the polymers derived from them exhibited strong photoluminescence (PL) with AIE characteristics (Figure S17). Although the polymers contained the same TPE fluorophore, their emission intensity and wavelength differed due to the variation of the Z group (Figure S18). From above, we chose **2a** as initiator to visualize the polymerization reaction.

The mechanism of visualization of the polymerization process was illustrated in Figure 1. With an increase of viscosity of the local environment by adding almost non-emissive polystyrene (PS), the polymerization mixture showed significant viscosity-dependent fluorescence with a "turn-on" character as a result of RIM of TPE rotor (Figure 1A and B).^[25] The progressive increase of emission intensity laid the foundation for visualizing the polymerization process (Figure 1C).



Figure 2. Visualization of visible light-induced RAFT polymerization of MMA in the presence of **2a**. (A) Schematic illustration of the reaction process. (B). Fluorescent photos of the polymer solutions at different conversion taken under 365 nm UV irradiation from a hand-held UV lamp. (C) PL spectra of the polymerization mixtures at different conversion. (D) The exponential relationship of conversion and M_n with PL intensity.

The photo-induced polymerization was performed in a 4 mL glass vial with a rubber septum suitable for direct PL measurement. To exclude the effect of UV light (340 nm) on the polymerization during the PL measurement, the excitation and emission slit was fixed at 2 mm. Methyl methacrylate (MMA) was a commonly used monomer and was first used to verify the feasibility of present method (Figure 2A). Clear and high-contrast fluorescent photos of the polymerization mixtures were observed by naked eyes with gradual increased emission intensity (Figure 2B). This result was consistent with the PL results (Figure 2C). At a conversion of below *ca* 34%, the system was nearly nonemissive because the intramolecular motion of the TPE unit was still active in such low viscous medium to nonradiatively dissipate the exciton energy. Between *ca* 47% and 84% conversion, the PL

intensity rose rapidly due to the significant enhancement in viscosity. At conversion higher than 84%, the rate of PL enhancement slowed down and the intensity tended to reach constant, suggestive of an almost constant viscosity (Figure 2D). This phenomenon was in well agreement with the results from fluorescence lifetime.^[4] Notably, we found that M_n of the resulting PMMA had an exponential function with PL intensity (Figure 2D). This aspect is important to obtain the polymerization information without destroying the reaction system.



Figure 3. Visualization of visible light-induced RAFT polymerization of representative types of monomers: (A) MA, (B) HMA, (C) tBA, (D) MEO₂MA, (E) HEA and MBAA, and (F) HEA.

To demonstrate the versatility of this technique, polymerizations using other types of monomers were conducted. We first studied the polymerization of less steric acrylate monomers. In MA system, the polymer molecular weight increased exponentially with the PL intensity (Figure 3A) due to the similar variation trend between the PL intensity and the monomer conversion (Figure S19). The slow increase of viscosity of the polymerization mixture made MA distinctly different from that of MMA system, as reflected by their different T_g and plot of PL intensity versus their M_h shown in Figure S20. Polymerization using butyl acrylate (BA) and isooctyl acrylate (IOA) were also explored and the exponential increase of PL intensity with M_h was observed (Figure S21 and S22). Despite low viscosity at low

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conversion, elongation of side chain of the monomer helped increase the PL of the polymerization system (Figure S23).

To further enhance the viscosity at low conversion, bulky monomers such as methacrylate could be employed. In hexyl methacrylate (HMA) system, the PL intensity increased exponentially with the monomer conversion (Figure S24). Meanwhile, the M_n of the resulting PHMA could be facilely obtained from the PL intensity (Figure 3B). To further increase the steric hindrance, *tert*-butyl methacrylate (tBMA) and benzyl methacrylate (BzMA) systems were used. The same exponential relationship could be easily drawn between M_n and PL intensity (Figure S25 and S26). Again, the PL intensity of the system was proved to be associated with the T_g of the resulting polymer (Figure S27).

The polymerization of *tert*-butyl acrylate (tBA) was hard to trace by ¹H NMR spectroscopy due to the overlapping of proton signals. To our delight, the present method could visualize the polymerization clearly with gradual increased emission intensity (Figure S28). In addition, the M_n of the polymer was in excellent linear relationship with the PL intensity (Figure 3C). The different emission behavior of tBA and MA was probably due to the diversity in polymerization kinetics and the steric hindrance of monomers (Figure S29).

Diethylene glycol monomethyl ester methacrylate (MEO_2MA) based polymers have found many applications in biological field.^[26] Monitoring the polymerization process of this functional monomer is thus of interest. The PL intensity increased gradually with the conversion (Figure S30) and a linear relationship between the monomer conversion and the PL intensity was obtained at conversion < 50% (Figure 3D).

Porous hydrophilic monocliths have received considerable attention for their uses in electrophoretic separation and identification of biological molecules.^[27] However, their formation process remains obscure due to their high degree of crosslinking. To make progress in this direction, the present approach was used to visualize their formation using 2-hydroxyethyl acrylate (HEA) and N,N-methylenebisacrylamide (MBAA) as monomers. The system became increasingly emissive with the reaction time accompanied by the 'frozen' of the reaction system (Figure S31). This again suggested that TPE was very sensitive to the change of the surrounding microenvironment. Despite the solidification of the reaction system, the PL intensity was still increased by up to 12 h and then became steady afterward. To further exploit their relationship, the gel content of the resulting materials was measured.^[28] Excitedly, the PL intensity was correlated with the gel content (60~95%) in a linear manner (Figure 3E). This meant that we could easily recognize the gel content by measuring the fluorescence intensity in a non-invasive method.

Self-condensing vinyl polymerization (SCVP) has emerged as a new approach for preparation of cross-linked polymers.^[29] The common used monomers are 2-hydroxyethyl acrylate (HEA) or 2hydroxyethyl methacrylate (HEMA), which contains pendant reactive group in addition to double bond. By using the present approach, the SCVP process of these two monomers could be facilely visualized (Figure S32 and S33). Interestingly, the gel content increased exponentially with the PL intensity (Figure 3F). Moreover, the PL intensity was found to be more sensitive to the gel content in HEA system than in HEMA (Figure S34). To prove the superiority of the chemically-linked method in monitoring the polymerization process, physical blending experiment was conducted as control. Initiator **3** and free TPE were employed for monitoring the polymerization of tBA (Figure S35). Unlike the linear relationship in chemical bonding system, the PL intensity increased in an irregular way with the M_n of the polymer (Figure 4A). Furthermore, TPE showed less sensitivity to the viscosity change in the physical blending system. We reasoned that the physical blending method merely sensed the change of microenvironment without direct interaction with the polymer segments. On the contrary, in chemically-linked system, the intramolecular motion of TPE is restricted to some extent because it is knitted and embedded in the rigid polymer matrix. Therefore, the chemically-linked method was more sensitive and accurate than the physical blending one.



Figure 4. Visualization of the polymerization process by physical blending method. (A) Dependence of the PL intensity on the polymer M_h in chemical bonding and physical blending systems. (B) PL change at 0 and 100% monomer conversion in pyrene system.

To demonstrate the advantage of AIE over ACQ dyes, polymerization using pyrene, a typical ACQ luminophore, was conducted (Figure S36). Results showed that small PL intensity difference was observed at 0 and 100% conversion (Figure 4B). Moreover, it was hard to differentiate the variation by naked eyes. These results indicated that the luminescence of planar pyrene molecule was less sensitive to the viscosity change and was not suitable for monitoring the polymerization process.

In summary, we have demonstrated a facile approach to in situ visualize the polymerization process by combination of photochemistry and AIE technology. Compared to the physical blending or ACQ system, the chemical bonding method sensed the viscosity change of both the polymer segments and the surrounding environment to result in high sensitivity and accuracy. Thus, the polymerizations of 12 different monomers, including less steric, bulky, NMR-untraceable, functional and bi-functional, were well monitored based on the specific relationship between the monomer conversion or gel content with the PL intensity. This emerging approach thus provided a powerful platform for studying the polymerization process.

Experimental Section

Experimental details please see supporting information.

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Acknowledgements

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By judicious combination of photochemistry and AIE technique, in situ visualization of RAFT polymerization was realized. This approach sensed not only the local viscosity of the system, but also the segmental motion of the polymer, which was important for understanding and monitoring polymerization mechanism.



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