

Visible Light-Driven MADIX Polymerisation via a Reusable, Low-Cost and Non-Toxic Bismuth Oxide Photocatalyst

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Abstract: The continuous amalgamation of photocatalysis into existing reversible deactivation radical polymerisation processes has initiated a rapidly propagating area of polymer research in recent years. We introduce bismuth oxide (Bi₂O₃) as a heterogeneous photocatalyst for polymerisations, operating at room temperature with visible light. We demonstrate formidable control over degenerative chain-transfer polymerisations, such as macromolecular design by interchange of xanthate (MADIX) and reversible addition-fragmentation chain transfer (RAFT) polymerisation. We achieved narrow molecular weight distributions and attribute the excellent temporal control to a photo-induced electron transfer (PET) process. This methodology was employed to synthesise diblock copolymers combining differently activated monomers. The Bi₂O₃ catalyst system has the additional benefits of low toxicity, reusability, low-cost, and ease of removal from the reaction mixture.

The impact of photochemistry on the field of polymer science has progressively extended the toolbox by which we can control polymerisations.[1] Most significantly, this has allowed for precise spatiotemporal control.[2] The seamless incorporation of photoinduced reactions into existing radical polymerisation protocols based on thermal initiation, now offer a low-cost and energy-efficient approach to initiate and control various types of polymerisation and processes.[2b, 3] A shift of the wavelength regime by which to induce photo-polymerisations (originally predominately limited to UV) has been accomplished, having reached the visible and near-infrared wavelength range in recent years.[4] This has led to the circumvention of thermal initiators and activators in polymer synthesis and allowed their replacement by stoichiometric photo-reagents and photocatalysts. In the field of reversible deactivation radical polymerisation (RDRP), such as reversible addition-fragmentation chain-transfer (RAFT) polymerisation and atomic transfer radical polymerisation (ATRP), the introduction of light as reaction stimulus has led to new modes of reactivity, such as photoiniferter[5] and photoinduced single electron transfer (PET) processes.[6] RAFT polymerisation in particular has been explored with the incorporation of mild light sources into the process to avoid excessive heating or irradiation with ultraviolet light.[5b, 7] Inspiration has been taken from living systems where ambient light is capable to drive radical reactions under physiological conditions.[8]

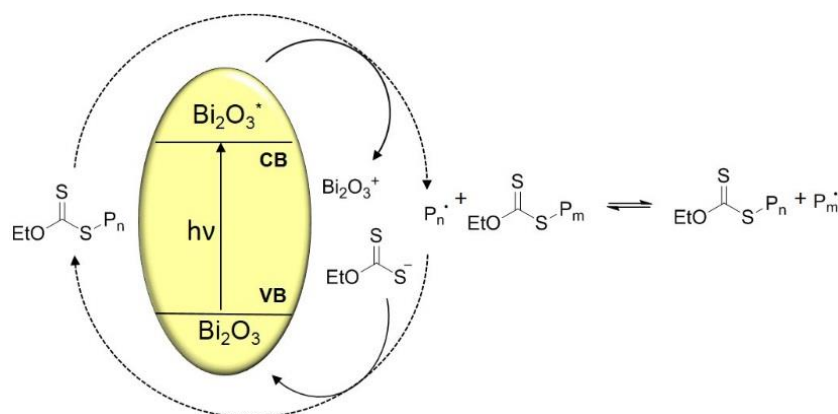
Regarding photoinitiated RAFT processes, Otsu and others found that many trithiocarbonates and dithiobenzoates can be directly photoexcited by light of a specific wavelength leading to photolysis, and initiating the polymerisation.[5a, 9] This so-called photoiniferter process, where the chain transfer agent (CTA) serves simultaneously as the initiator, transfer, and terminating agent, respectively, works well for a broad range of monomers including for less-activated (typically electron rich) monomers when a xanthate is excited under UV and purple light.[10]

In contrast, the pioneering work by Fors and Hawker investigated RDRP mediated by photoredox catalysis upon irradiation with visible light.[11] This concept has since been adopted and used for both metal-mediated and metal-free radical polymerisations.[12] Similarly, in RAFT polymerisation, Boyer and coworkers found that the CTA can generate an initiating species after undergoing an electron transfer from a photoredox catalyst.[13] The so-called PET-RAFT process has since been continuously improved,[2c, 7b] using new photocatalysts and a variety of monomers and CTAs, and exploring a bathochromic shift,[14] biocompatible polymerisation,[15] catalysts recyclability,[16] oxygen tolerance,[13, 17] reactions in flow,[18] and wavelength orthogonality.[19] From the first PET-RAFT photo-catalysts based on transition metal complexes such as iridium bipyridyls,[7a] different systems have been employed such as metalloporphyrins,[20] dyes,[15] and carbonyl photosensitizers.[21] Careful selection of photo-catalysts broadened the wavelength range of the PET-RAFT process, which now comprises the visible and near-infrared, and hence avoids an irradiation with high energetic light.[7b]

The first attempts of heterogeneous catalysis in PET-RDRP demonstrated its utility. While still in its infancy, heterogenous catalysis offers multiple benefits which overcome known drawbacks of homogeneous catalysts. The latter are often expensive, toxic, strongly coloured and/or laborious to separate after polymerisation. Recent work explored heterogeneous catalysis in polymerisations as a means of avoiding the tedious removal of photocatalysts, and promoting their recycling. Examples include works by the Qiao group on gC₃N₄ (graphitic carbon nitride) photoexcited by UV light,[22] the Zhu group on magnetic nanoparticles photoexcited by ambient light,[16a] and the Boyer group on the extension of their previous work on eosin Y photocatalysis by conjugating the dye onto silica nanoparticles.[23] The Matyjaszewski group have also used carbon quantum dots photoexcited by visible light,[24] while others tried TiO₂ and ZnO excited by UV light.[25] Despite recent progress in these endeavours, PET catalysts often remain commercially inaccessible, require UV-initiation, have compromised performance, and/or are toxic.

A recent report using narrow band gap semiconductors, such as bismuth derivatives, has shown that visible-light-driven photocatalysis is feasible.[26] In this study, we present a PET-RAFT/MADIX process driven by Bi₂O₃. This system combines the advantages of a heterogenous photocatalysis with an inexpensive catalyst (i.e. commercially available Bi₂O₃), and features recyclability and non-toxicity. Plain white light (a household light bulb) readily activates the photocatalyst and the system inherently does not require high energy radiation. The versatility of our approach is unambiguously high, as it allows the employment of differently activated monomers, the synthesis of block copolymers, and can be run in a variety of solvents, including water, and at larger scale.

Scheme 1. PET mechanism for MADIX in the presence of Bi2O3



To fundamentally study the PET-MADIX polymerisation with commercial Bi₂O₃ as the heterogeneous catalyst, the polymerisation of vinyl acetate (VAc) was selected as a model system. We used 2-(ethoxycarbonothioyl) sulfanyl propanoic acid (EtPAX) as our CTA-of-choice (Supporting Information S1). VAc polymerisations are well-studied and show excellent compatibility with xanthates. However, the use of xanthates in a PET-MADIX process remains underexplored[7a] despite PET remaining the necessary mode of reactivity under visible light for common derivatives and despite their demonstrated importance in the production of non-toxic, industrially important polymers. The PET-MADIX polymerisations were conducted at room temperature upon irradiation with a common fluorescent white light bulb in combination with different solvents (Figure 1A), in the presence of commercially available Bi₂O₃ powder (i.e. a mixture of α-Bi₂O₃ and β-Bi₂O₃; see Supporting Information S2 for characterisation). The polymerisation kinetics were investigated in various solvents, such as DMSO, dioxane, and hexafluoroisopropanol (HFIP). Figure 1B details an example of the uniform molecular weight evolution and dispersity control in DMSO. Pseudo first-order kinetics were established in all solvents (Figure 1C), whereas the polymers dispersity \bar{D} varied depending on the solvent choice (Figure S3-1).

To confirm that the catalyst reacts exclusively with the CTA (i.e. without any photoiniferter or monomer reduction by the catalyst), control experiments without CTA or catalyst were performed, respectively. These control experiments did not show substantial monomer conversions according to proton nuclear magnetic resonance (¹H NMR) and size exclusion chromatography (SEC) data (Table 1, entry 2 and 3). We consider that the electron richness of the alkene (i.e. its high reduction potential) hinders a free-radical polymerisation in the 'no CTA' control experiment.

To probe whether Bi₂O₃ is acting as the catalyst and not a stoichiometric reagent, catalyst loadings were varied within a range of 50–1000 ppm. Despite a successive reduction of catalyst loading, comparable monomer conversion and dispersity was obtained (Figure S4, Table 1). A decrease in the rate of polymerisation (i.e. gradient of the linear fit) (Figure 1D) was observed as the CTA loading increased (i.e. lower target molecular weight). We observed an eventual plateau of conversion over time, which has also been reported before for polymerisations of vinyl acetate.[27]

Two key features of heterogeneous photocatalysis are the reusability/recyclability of the catalyst and a temporal control of the monomer conversion. To confirm temporal control, polymerisations were conducted by interrupting the light irradiation for a certain time period. No change in conversion was observed during the period where the light was switched off, as shown by the

unchanged conversion at the beginning and end of the 'OFF' period (Figure 1E). To highlight the reusability of our catalyst system, we recovered the catalyst after the polymerisation by centrifugation. The recycled Bi₂O₃ was then deployed in PET-MADIX polymerisations for three more cycles (Figure 2A, 2B). In comparison, the four cycles showed negligible reduction in catalytic performance, as shown by the similar degrees of polymerisations determined by both NMR and SEC analysis (Table 1, entry 6-8 and Figure S4 respectively). Thermogravimetric analysis of the recovered catalyst showed minimal remains of organic material (< 3 wt.-%, Figure S5); therefore, we do not expect polymer grafting on the Bi₂O₃ surface.

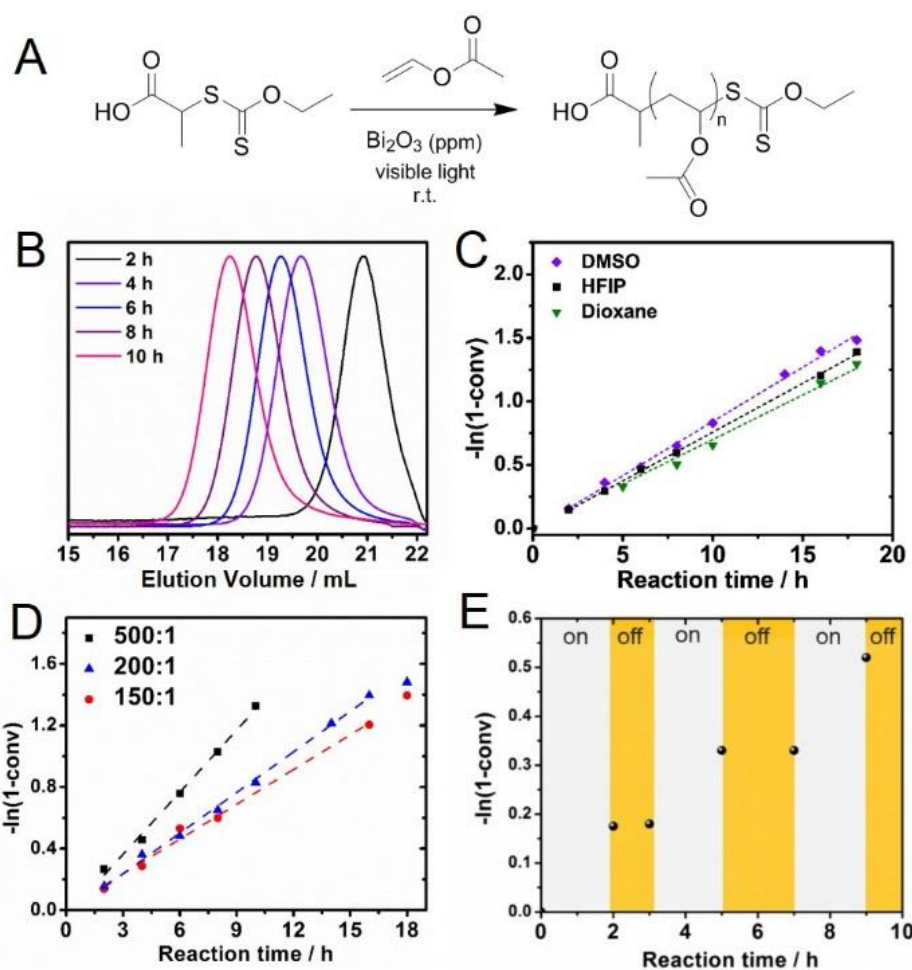


Figure 1. A) Reaction scheme of the PET-MADIX polymerisation of VAc using EtPAX as the CTA; B) SEC traces of the molecular weight evolution of a VAc polymerisation conducted in DMSO, ([VAc]:[CTA]:[Bi₂O₃] = 200:1:0.2; [CTA]₀ = 0.05 M). C) Kinetic plot of the polymerisation of VAc in different solvents, ([VAc]:[CTA]:[Bi₂O₃] = 200: 1: 0.2; [CTA]₀ = 0.05 M); D) Kinetic plot in DMSO with varying CTA to catalyst ratio; E) ON/OFF kinetic plot demonstrating the temporal control of the PET-MADIX polymerisation.

To assess the degree of control over the polymerisation, we investigated the end-group fidelity by NMR spectroscopy and electrospray ionisation mass spectrometry (ESI-MS) (see Supporting Information S6 and S7 respectively). Both analyses gave evidence for the integrity of the expected end-groups of the corresponding degree of polymerisation, showing good agreement of the theoretical and observed m/z values.

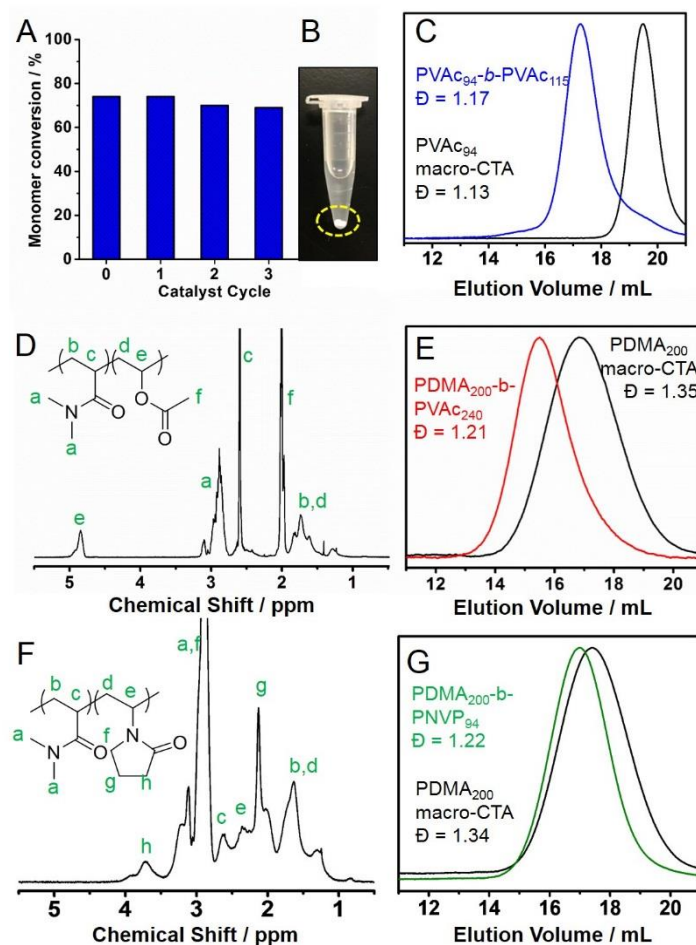


Figure 2. A) Recycling of the Bi_2O_3 catalyst for consecutive VAc polymerisations; reaction time = 16 h. B) Photograph of spun-down catalyst after polymerisation. C) SEC traces of PVAc_{94} macro-CTA (black, $M_{n,\text{SEC}} = 10\,200\text{ gmol}^{-1}$) before and after chain extension with VAc (blue, $M_{n,\text{SEC}} = 21\,700\text{ gmol}^{-1}$). D) NMR of diblock $\text{PDMA}_{200}\text{-}b\text{-PVAc}_{240}$ in CDCl_3 , and E) the corresponding SEC traces of macro-CTA (black, $M_{n,\text{SEC}} = 26\,000\text{ gmol}^{-1}$) and diblock copolymer (red, $M_{n,\text{SEC}} = 63\,600\text{ gmol}^{-1}$). F) NMR of diblock $\text{PDMA}_{200}\text{-}b\text{-PNVP}_{94}$ in CDCl_3 and G) the corresponding SEC traces of macro-CTA (black, $M_{n,\text{SEC}} = 26\,000\text{ gmol}^{-1}$) and diblock copolymer (green, $M_{n,\text{SEC}} = 35\,000\text{ gmol}^{-1}$).

Next, we employed the previously generated polymers as macro-CTAs in chain extension experiments. For the chain extension of PVAc with VAc, we accomplished a significant increase of the molecular weight for the PVAc-block-PVAc polymer, while retaining a low overall dispersity (Figure 2C).

To extend the scope of our approach, vinyl amides and acrylamides were investigated, namely N-vinylpyrrolidone (NVP) and N,N-dimethylacrylamide (DMA). These monomers feature higher degrees of activation. Both can undergo controlled polymerisation in the presence of xanthate CTAs,^[28] and more importantly, their polymerisation can be conducted in aqueous media. In the case of the PET-MADIX polymerisation of NVP in water, a comparatively faster reaction was observed (Table 1 entry 9, Figure S8), with a similar degree of control to VAc. In the case of DMA, the polymerisation proceeded even more rapidly, albeit with a slightly higher dispersity (Table 1 entry 10, Figure S9). However, this polymerisation was able to reach full conversion (> 99%) within 120 min without any loss of control (refer to NMR of reaction mixture in Figure S6-3). By lowering the ratio of monomer

to CTA, the reaction rate increased, contrary to the trend observed for the polymerisation of VAc (Figure S9-1). Using the same setup and to demonstrate the scalability of our approach, we ran a 20-gram DMA polymerisation in water (Table 1, entry 12 and Figure S9-2), producing a 40 wt.-% aqueous solution of PDMA ($M_n, \text{NMR} = 19\,800 \text{ gmol}^{-1}$, $\text{Đ} = 1.38$).

Table 1. Optimisation and control studies for PET-MADIX of various monomers

Entry	Monomer	[M]: [CTA]: [Bi ₂ O ₃]	Solvent, concentration	Conversion , time	$\langle MW_{n, \text{NMR}} \rangle$	Đ
1	VAc	200: 1: 0.2	DMSO, 10 M	74%, 16 h	12 900	1.13
2	VAc	200: 1: 0	DMSO, 10 M	8%, 16 h	1 600	1.06
3	VAc	200: 0: 0.2	DMSO, 10 M	2%, 16 h	-	-
4	VAc	200: 1: 0.01	DMSO, 10 M	71%, 16 h	12 400	1.15
5	VAc	200: 1: 0.002	DMSO, 10 M	72%, 16 h	12 600	1.14
6	VAc	200: 1: 0.2 (first recycle)	DMSO, 10 M	74%, 16 h	12 900	1.15
7	VAc	200: 1: 0.2 (second recycle)	DMSO, 10 M	70%, 16 h	12 200	1.16
8	VAc	200: 1: 0.2 (third recycle)	DMSO, 10 M	69%, 16 h	12 100	1.19
9	NVP	200: 1: 0.2	Water, 5 M	80%, 4 h	18 000	1.11
10	DMA	500: 1: 0.2	Water, 2 M	93%, 1 h	46 300	1.30

The ability to polymerise less-activated monomers (LAM) makes MADIX uniquely amenable to block copolymerisation of a wide range of monomers. Building on the success of the polymerisation of a more activated monomer (MAM, in this case DMA), the synthesis of PDMA-block-PVAc was explored. While the copolymerisation of MAM-LAM block copolymers has been previously achieved, it is typically with a short block of MAM (to minimise dispersity) or with tailor-made CTAs.[10a, 29] Using our methodology, we synthesised a narrowly dispersed high molecular weight MAM-LAM diblock copolymer, (PDMA200-b-PVAc240, $M_n, \text{NMR} = 40\,500$; $\text{Đ} = 1.21$) (Figure 2D, 2E, Figure S6-5 and S10-1). In addition, DMA and NVP were employed in a copolymerisation by sequential monomer addition in one pot in water, affording a MAM-LAM diblock copolymer with narrow molecular weight distribution (PDMA200-b-PNVP98, $M_n, \text{NMR} =$

30 300 gmol^{-1} ; $\text{Đ} = 1.22$) (Figure 2F, 2G and Figure S6-6) and formidable control (Figure S10-2). Aside from the excellent control of the homopolymerisation, the ease and feasibility of the block

copolymer syntheses underpins the synthetic potential of employing Bi₂O₃ as a heterogenous photocatalyst for radical polymerisation processes. To further extend the scope of this system, we verified that Bi₂O₃ can also be used with characteristic CTAs, such as trithiocarbonates and dithiobenzoates, for PET-RAFT of methyl (meth)acrylate (Table 1, entries 13 and 14, and Supporting Information S11).

In conclusion, we report the use of Bi₂O₃ as an outstanding catalyst for visible-light driven PET-MADIX polymerisation of various monomers, using only a generic household light bulb. Bi₂O₃ further comprises favorable attributes with regards to low toxicity and ease of handling, its possible recycling and use in various solvents, as well as its commercial availability. This study advances the application of heterogenous photocatalysis in polymer synthesis and highlights the applicability of MADIX polymerisation more generally. The scope of this process (afforded inherently by using a xanthate as CTA) also lends itself to MAM-LAM block copolymerisations. Moreover, the ease of which xanthates can be generally synthesised, and their diverse possibilities for functionalisation at the CTA R- and/or Z-group, makes MADIX uniquely suitable for the synthesis of a wide variety of polymer architectures for future applications. The possibility of scaling polymerisations and applying this catalyst system in characteristic PET-RAFT polymerisations set the foundation for further investigation of heterogeneous metal oxide photocatalysts in RDRP more broadly.

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Keywords: RDRP • block copolymers • photochemistry • PET-RAFT • polymerisation

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