Solution [2 + 2] photopolymerization of biomass-derived nonrigid monomers enabled by energy transfer catalysis

Yu Jiang,^a Qiang Ma,^a Xun Zhang,^a Junfang Li,^b and Saihu Liao^{a,c,*}

The [2 + 2] photopolymerization has been known for more than fifty years and widely applied in many fields. However, this process was typically conducted in solid state, while the corresponding [2 + 2] photopolymerization of simple non-rigid diolefinic monomers were rarely achieved in solution under visible light, owing to the lack of monomer preassembly and low/no absorption of visible light. In fact, the [2 + 2] photopolymerization of simple biscinnamate monomers remains an unsolved problem. Here, we demonstrate that energy transfer catalysis could overcome the low efficiency in the intersystem crossing to triplet states of monomers, and enable the [2 + 2] photopolymerization of biomass-derived biscinnamate monomers in solution for the first time. As no preassembly is required, this solution polymerization protocol is applicable to biscinnamate monomers with different linker structures, and allows copolymerization between different biscinnamate monomers to regulate polymer mechanical properties. A series of cyclobutane-imbedded polyesters(M_w ranged from 25.3 kDa to 61.3 kDa) become accessible, which shown excellent solubility in organic solvents and good processability, in sharp contrast to the properties of the biscinnamate polymers obtained before via the solid state photopolymerization methods.

Introduction

Since the pioneering study on topochemistry by Schmidt and coworkers in the 1960s,¹ the potential of solid state [2 + 2] photocycloaddition for the preparation of organic polymers has immediately drawn the attention of polymer chemists.²⁻¹⁷ However, conventional [2 + 2] photopolymerization were often conducted in solid state under ultraviolet irradiation rather than in solution,¹⁻³ as a pre-organization of diolefinic monomers in a close sliding stacking fashion is critical to achieve polymerization by repeating [2 + 2] photocycloaddition. In contrast, the face to face stacking only leads to the cyclic dimer formation (Fig. 1a), while a longer distance of the orbital overlapping between the two C-C double bond than 4.2 Å will prevent the [2 + 2] cycloaddition.^{1,18-22} Accordingly, a small change on the diolefinic monomer structures (e.g. the length of the linker) could result in an ineffective monomer stacking, and thus lead to the failure of polymerization. In particular, due to the lack of this monomer preorganization, [2 + 2] photopolymerization of simple non-rigid monomers has proved to be very challenging and few examples have been achieved in solution.¹⁹⁻²⁹ For example, Yagci et al. reported the successful photopolymerization of bis-dibenzazepine, a monomer with a cyclic rigid structure, in solution.²⁶ Very recently, Barner-Kowollik et al. disclosed an interesting wavelength-gated topology control over а catalyst-free [2 + 21 photopolymerization of bis(styrylpyrene) with a polyethylene glycol (PEG) diester linker under visible light, in which a



Fig.1 Comparison of [2 + 2] photopolymerization of bis(cinnamate)s in solid state (previous work) and in solvent (this work).

prearrangement of the styrylpyrene units in THF favoured by the dispersion interactions between the large aromatic systems was proposed.^{27,28} However, in contrast, the [2 + 2] photopolymerization of simple non-rigid biscinnamate monomers were inefficient and failed to afford any polymer products in solution, which, to the best of our known, remains unsolved to date,²³⁻²⁵ though the corresponding solid state polymerization was known over 50 years ago.²³ Therefore, for the [2 + 2] polymerization of these nonrigid monomers in solution, an effective and general approach remains to be developed.²³⁻³⁰

^a Key Laboratory of Molecule Synthesis and Function Discovery (Fujian Province University), State Key Laboratory of Photocatalysis on Energy and Environment, College of Chemistry, Fuzhou University, Fuzhou 350108, China.

^b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, University of Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, China.

^c Beijing National Laboratory of Molecular Science (BNLMS), Beijing 100190, China. *Email: shliao@fzu.edu.cn

For the [2 + 2] photocycloaddition of non-biased olefinic monomers, a triplet excitation state is normally required.⁴ In the solid states, molecular move and vibration can be suppressed, which could thus enhance the intersystem crossing (ISC) to triplet state.^{4,19,20} However, the intersystem crossings of nonrigid monomers were usually inefficient in solution.4,31,32 For example, Lewis and Schneider reported the intersystem crossing of methyl cinnamate from S₁ (n, π^*) to either T₁ (π , π^*) or T_2 (n, $\pi^*)$ was expected to be very slow (< $10^9~s^{-1}).^{32}$ Nevertheless, if the solution [2 + 2] photopolymerization of biscinnamates can be realized, several advantages can be expected: (1) solution polymerizations could avoid the need for a precise monomer preorganization, and thus expand the monomer scope and facilitate the synthesis of polymers with structural variation and diversity; (2) solution polymerizations may afford polymer products with different structures and properties, and hopefully with a better processability than that of solid-state polymerization products;²³⁻²⁵ (3) further, solution polymerizations are normally more convenient to conduct in comparison to solid state polymerizations. Given the recent advancement on the photocatalytic intermolecular [2 + 2] cycloaddition,³³⁻⁴⁰ we conceived visible light triplet energy transfer catalysis^{41,42} could probably overcome the challenging issues like low efficiency in intersystem crossing, 19-22, 31, 32 thus bringing in the opportunity to establish a visible light-regulated [2 + 2] photopolymerization of non-rigid biscinnamate monomers in solution. Moreover, after several years of our exploration on photo-controlled polymerizations based on the excited state electron-transfer43,44 and proton-transfer45,46 mechanisms, we became interested in the application of energy-transfer catalysis to polymerization, an approach that has not been well appreciated in the development of photocatalytic polymerizations so far.47-53 Here, we wish to report our efforts toward this goal, and the development of an approach based on visible light-mediated energy-transfer catalysis, which allows for the [2 + 2] photopolymerization of cinnamic acid-derived monomers in solution for the first time.54-⁵⁶ A series of polyesters with imbedded cyclobutane on the main chains can be prepared with this new method, and the polymer products possess a different structure, good solubility and processablity, in sharp contrast to the biscinnamate polymers obtained before^{23,24} via solid state photopolymerization (Fig. 1b).

Results and discussion



Scheme 1 photocatalytic [2 + 2] solution polymerization

Initially, biomass-based ethylene glycol dicinnamate (EDC) was selected as the monomer for photocatalyst searching (Scheme 1 & Fig. 2). As cinnamates are known difficult to be activated through an electron transfer mechanism, owing to their high



Fig. 2 Photocatalyst Screening of [2 + 2] Polymerization in Solvent: (a) Percentage conversion of C=C bonds at 60 min and 300 min with different photocatalyst. (b) GPC traces of crude samples from polymerizations (300 min) with photocatalyst PC 5-11.

reduction potential,^{33,38} we thus mainly focused on the photocatalysts capable to excite the EDC monomers (ca. E_T = 54.8 kcal/mol for methyl cinnamate) via triplet energy transfer.^{31,32} A series of photocatalysts with different triplet state energy was examined in the [2 + 2] polymerization of EDC in DMF (0.5 M) under the irradiation of blue LEDs (Fig. 2). ¹H NMR was employed to monitor the conversion of the monomer C=C bonds (for the calculating method, please see Fig. S1) and GPC for polymer analysis. As indicted by Fig. 2a, the consumption of C=C bonds and the formation of fourmembered carbocycles were observed in most cases after irradiation under blue light for 60 min, except the polymerizations with Methylene Blue (PC 1, E_T = 32.0 kcal/mol),⁴¹ Rose Bengal (**PC 2**, E_T = 43.5 kcal/mol),⁵⁷ Eosin Y (**PC 3**, E_T = 44.9 kcal/mol),⁵⁸ and [Ru(bpy)₃]Cl₂ (**PC 4**, E_T = 46.0 kcal/mol). To our delight, iridium catalysts (PC 5-10) were found efficient in general, with fac-[Ir(ppy)₃] (**PC 8**, E_T = 58.1 kcal/mol) giving the highest conversion after 60 min. [Ir(ppy)₂bpy]PF₆ (PC **6**, E_T = 53.1 kcal/mol) and 4Cz-IPN (**PC 11**, E_T = 60.1 kcal/mol) afforded a relatively slower reaction, probably due to the energy match and also their shorter triplet lifetimes (280 ns and 13 ns at 298K, respectively, versus 1900 ns for PC 8). 41,42,59 The GPC traces of aliquots from each polymerization with PC 5-11 (300 min) were overlaid with THF as a reference as shown in Figure 2B.⁶⁰ In comparison, fac-[Ir(ppy)₃] (PC 8) also afforded the polymers with higher molar mass than those with the other four [Ir] photocatalyst: **PC 5** (E_T = 49.2 kcal/mol), **PC 7** (E_T = 54.2 kcal/mol), PC 9 (E_T = 60.4 kcal/mol), and PC 10 (E_T = 61.8 kcal/mol).41,42,61 Of note, as control experiment, polymerizations in solution without a photocatalyst under direct excitation of blue light (465 nm) or even UV light (310 nm) were not productive, giving no any detectable polymer or oligomer formation.

With *fac*-[Ir(ppy)₃] as the photocatalyst at different monomer concentration (0.5 M, 1.0 M, 1.5 M, and 2.0 M), over 97% conversion of C=C bonds can be reached in 270 min in all cases (Fig. 3a). However, overlaying GPC traces of the four samples showed a dependence of polymer molar mass on concentration (Fig. 3b, overlaying GPC traces at different time intervals (from 30-270 min) in different monomer concentration was displayed in Fig. S2); higher monomer concentrations favoured the formation of polymers with higher molar mass. As gelation was sometimes observed at 2.0 M when prolonging the reaction



Fig. 3 The Study for Procedure of [2 + 2] Solution Polymerization: (a) Optimization of monomer concentration in polymerization. (b) GPC traces of aliquots (270 min) at different concentration. (c) Optimization of catalyst loading (1%, 0.1%, 0.01%) in polymerization. (d) GPC traces of aliquots from polymerizations (270 min) at different catalyst loadings. (e) Light "on-off" experiment. (f) GPC traces of aliquots at different polymerization time.

time, a concentration of 1.5 M was adopted for the investigation on the influence of catalyst loading. As shown in Fig. 3c, reducing the catalyst loading to 0.1 mol% could almost maintain the reaction rate and reach over 95% conversion of C=C bonds after 270 min. The catalyst loading also affects the molecular mass distribution (Fig. 3d, overlaying GPC traces at different time intervals (from 30-270 min) in different catalyst dosage was displayed in Fig. S3), with oligomer predominating the distribution when only 0.01 mol% catalyst was used. It is worth mentioning that the photocatalyst is crucial to the polymerization, no conversion was observed without photocatalyst, neither any detectable Z/E isomerization of EDC. In fact, under the solution polymerization conditions without a photocatalyst, no any detectable polymers even dimer formation was observed even under the irradiation of UV light (310 nm). As demonstrated in the light "on-off" experiment, the polymerization can be strictly controlled by light (Fig. 3e).47 Polymerization only proceeded in the presence of light, and stopped immediately when the light was turned off. Once put back to the light irradiation, the polymerization could restart

again. The light "on-off" can be repeated many times until a high conversion was achieved (Fig. 3e). By overlaying the GPC traces (Fig. 3f), we could see monomer rapidly dimerized and trimerized in the initial stage (0-1 h). After 8 h, over 97% conversion of double bonds has been achieved, while the portion of high molecular weight polymers continues to increase, in accordance with a step-growth polymerization kinetics.⁶²⁻⁶⁵ In the end, a portion of oligomer remains in the reaction system, even if the reaction time was prolonged to 72h (see Fig. S4 and S5), suggesting the rest unconverted oligomers were probably cyclic ones, which lack a C-C double bond to participate in further [2 + 2] photocycloaddition.

Importantly, the polymer products (PEDC) can be isolated by precipitation in methanol to remove oligomer, the GPC traces of isolated PEDC (supplemental information S19) indicated the purity of polymer. The polymers showed a good solubility in



Fig. 4 Structure Characterization of Cyclobutane-containing Polymer the stacking ¹H-NMR spectra of (a) Ethylene glycol dicinnamate; (b) Ethyl truxinates (trans and cis) dimerized from ethyl cinnamates; (c) Isolated polymer (PEDC) from polymerized in standard condition; (d) FT-IR spectra of ethylene glycol dicinnamates (EDC) and isolated polymer (PEDC).

common organic solvents (e.g. acetone, acetonitrile, ethyl acetate, toluene, DCM, THF, DMF, DMSO etc.), in sharp contrast to the polymers of biscinnamates obtained via solid state polymerization which are hardly soluble in organic solvents.²³⁻²⁵ ¹H NMR spectra of the monomer (EDC, Fig. 4a), dimer (Figure 4b, six cyclobutane was observed in GC-MS spectra, see Fig. S6, the respective content was showed in Table S3), and polymer (PEDC, Fig. 4c) are compared in Fig. 4. For PEDC, the broad peaks at 6.80, 7.00, 7.18 ppm can be assigned to the protons of the phenyl groups (A + B + C), while signals at 3.41-4.25 ppm belong

to the protons on the four-membered carbocycles (D + E) and the ethylene linker (F). The dimers obtained under the photocatalytic conditions were mainly a mixture (ca. 8:1) of δ ethyl truxinate (trans) and β -ethyl truxinate (cis).^{36,37,56} Comparing with the peak ratios (3.41-4.25 ppm) of dimers and polymers, the four-membered rings in polymers comprise a similar anti-head-to-head configuration, different from the head-to-tail structures often obtained from solid state polymerization.²³ From the FT-IR spectrum of PEDC (Fig. 4d), we could see the disappearance of the bands at 1630 cm⁻¹ belonging to stretching mode of C=C bonds, while the carbonyl band shifted from 1702 to 1729 cm⁻¹, due to the de-conjugation with C-C double bonds.

To our delight, the advantage of this solution [2 + 2] photopolymerization further became manifested in the scope of monomer, when compared with solid-state polymerizations. As shown in Fig. 5, to verify the generality of this photocatalytic solution [2 + 2] photopolymerization, biscinnamate monomers with different linker structures were examined under the standard photocatalytic conditions. Gratifyingly, these biscinnamate monomers can all polymerize in solution via this triplet energy transfer approach, affording the corresponding polymer products with M_w and dispersity ranged from 25.3 kDa, D = 1.84 for 1f to 61.3 kDa, D = 3.16 for 1b.



Fig. 5 Scope of [2 + 2] Solution Polymerization

Variation on linkers includes length from two carbons (1a) to six carbons (1d), branched one (1b), and also functionalized linker (1e). The successful polymerization of the monomers possessing different linkers provide an advantage over the traditional [2 + 2] solid state polymerization (NMR spectra was displayed in supplemental information S17-S27), in which monomers were often limited by the strict geometric criteria. Moreover, in contrast to the biscinnamate polymers prepared via [2 + 2] solid state polymerizations, $^{23-25}$ the polymers obtained with this solution polymerization method exhibited a good solubility in organic solvents, thus allowing for film

preparation through solvent evaporation or hot pressing (see supplemental information S29).

The DSC analysis of the isolated poly(ethylene glycol dicinnamate) (PEDC) did not show a clear melting point, and the glass transition temperature of polymer is around 73 $\,^{\circ}$ C (see Fig. S7), which reveal the polymer is thermoplastic polymer. Characterization by TGA (see Fig. S8) indicated that the polymer has a good thermal stability, starting to decompose around 344 $\,^{\circ}$ C.

As no preassembly is required, this solution polymerization protocol is applicable to copolymerization of different bicinnamate with different linker, and we try to use this strategy to regulate the mechanical properties of the polymer We conducted tensile tests on the macroscopically harder poly(pentylene glycol dicinnamate) (PPDC) and the softer poly(hexylene glycol dicinnamate) (PHDC). The two polymers were synthesized with the addition of 10 mol% monofunctional cinnamate (hexylene glycol cinnamate) to avoid gelation. It was found that PPDC has higher Young's modulus, but lower elongation at break, while PHDC has low Young's modulus and high elongation at break. Nevertheless, copolymerization of pentylene glycol dicinnamate (PDC) and hexylene glycol dicinnamate (HDC) could afford polymers with improved mechanical properties. For example, the Young's modulus and elongation at break of PP2H2DC (copolymer of PDC/HDC 1:1) could reach 29.0MPa and 77.3%, respectively. When the two monomers ratio of PDC and HDC was 1:3, compared with PHDC (E = 16.9MPa, σ_m = 1.4MPa, ϵ_b = 468.8%), similar Young's modulus was observed (15.6MPa), while the yield stress could be improved to 4.5 MPa (for details, please see supplemental information S29-S30).

Conclusions

In summary, a photocatalytic [2 + 2] polymerization of nonrigid biscinnamate monomers has been realized in solution under visible light for the first time. In comparing with the corresponding traditional [2 + 2] photopolymerization in solid states, this photocatalytic polymerization in solution does not require a preassembly of monomer, and features its operation simplicity, controllability, and a general monomer scope. A series of polymers can be prepared via this method from various cinnamic acid-derived diester monomers with M_w and dispersity ranged from 25.3 kDa, D = 1.84 to 61.3 kDa, D = 3.16. It is worth mentioning that this method can adjust the mechanical properties of the four-membered ring polymer through copolymerization. Application and further expansion of this photocatalytic [2 + 2] solution polymerization via triplet energy transfer catalysis can be expected.

Data availability

Data for all compounds in this manuscript are available in the ESI, which includes general information, general procedures, experimental details, and characterisations.

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