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Microporous Thioxanthone Polymers as Heterogeneous Photoinitiators for Visible Light Induced Free Radical and Cationic Polymerizations

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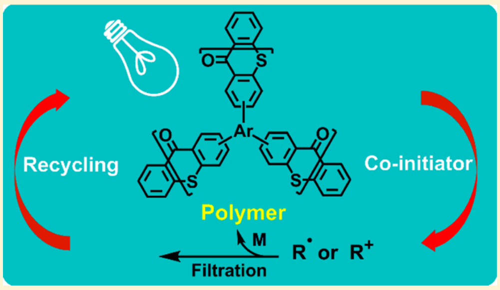
Supporting Information

ABSTRACT: Conjugated microporous polymeric networks possessing thioxanthone groups were reported to initiate free radical and cationic polymerizations of vinyl monomers and cyclic ethers, respectively, under visible light irradiation. These new classes of *Type II* macrophotoinitiators with high porosity having large BET surface area of 500−750 m^2 g^{-1} were prepared through different cross-coupling processes. Polymerizations are successfully achieved in conjunction with several co-initiators benefiting from hydrogen abstraction or electron transfer reactions stimulated by either visible light or natural sunlight irradiation. Photopolymerizations conducted by using knitted photoinitiators show better conversion and rate of polymerization than those obtained via Sonogashira−Hagihara coupling. The heterogeneous nature of the photoinitiators makes them easily separable from the media and more importantly reusable for further polymerizations while retaining the photocatalytic activity.



INTRODUCTION

The use of light for green chemistry and energy applications is an intriguing issue in today's world.[1] Thus, researchers are focused on utilization of conversion of solar energy to usable versions like electricity or production of green energy sources like hydrogen via photocatalytic water splitting.[2,3] Furthermore, most of the photochemical reactions are useful to avoid traditional high-energy consuming thermal methods to obtain resulting products in green/sustainable way, which is crucial in industrial scale.[4,5] In this aspect, photopolymerization is a favorable method for low-cost production of polymers in milder conditions and relatively controlled media.[6,7]

Photoinitiators are mainly classified into two categories: *Type I* (also known as α-cleavage) and *Type II* (or hydrogen abstraction type) initiators. Thioxanthone (TX) compounds are well-known as efficient *Type II* photoinitiator in free radical polymerization in conjugation with various hydrogen donor (H-donor) groups.[8] An interesting advantage associated with specially designed TXs is their capability to act as one component initiator if the H-donor group is chemically incorporated into the TX structure. This diminishes any probable problem regarding the use of additional H-donor co-initiators.[9−17]

Regarding this, Yin and co-workers reported various macrophotoinitiators owning both TX and H-donor functionalities.[18−22] Aside from their initiation ability of photopolymerization process, these macrophotoinitiators can be applied to challenge some problems often encountered with the low molecular weight photoinitiators such as migration, high volatility, and strong odor, etc.[23−30] As one step further, heterogeneous semiconductor macrophotoinitiators have recently been reported.[31−36] Porous materials with their high accessible pre/post-functionalized surfaces are mostly used materials in heterogeneous catalysis in wide perspective from water splitting to chiral syntheses.[37−42] With respect to porous metal oxides, porous organic polymers are favorable in this aspect with their ease of functionality and higher surface areas.[43] Furthermore, covalently bonded microporous organic polymers have the advantage of enhanced (hydro)thermal stability in comparison to metal−organic frameworks effecting constancy and reusability as a fundamental matter of heterogeneous catalysis.[44−47]

Herein, we report TX-based microporous organic polymers as heterogeneous macrophotoinitiator for visible light induced free radical and cationic polymerizations. Synthetic methods for the preparation of these macrophotoinitiators were Sonogashira−Hagihara cross-coupling reaction with triethynylbenzene (TX-CMP) in standard route for conjugated microporous polymers (CMPs),[48] and knitted random copolymerization with benzene (TX-Ph) and triphenylmethane (TX-TPM).[49,50]

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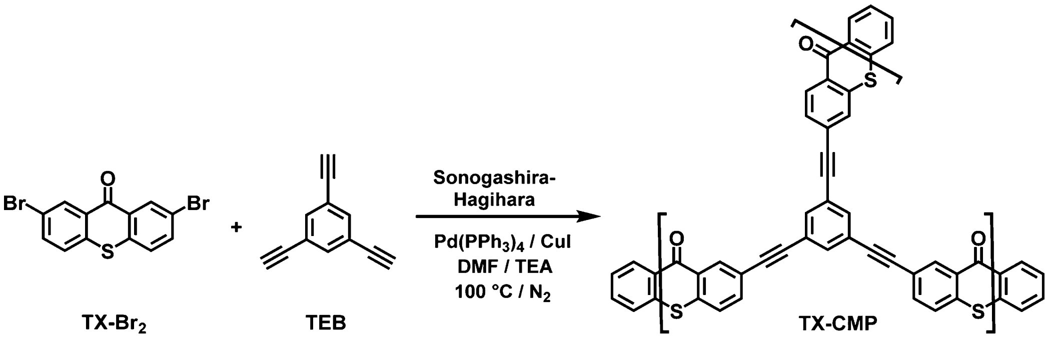
Scheme 1. Synthesis of TX-CMP by Sonogashira–Hagihara Coupling



Resulting polymers exhibited a large specific Brunauer–Emmett–Teller (BET) surface area (500–750 m^2 g^{-1}). The photopolymerization processes were accomplished with H-donor or iodonium salt co-initiators under visible light and also natural sunlight irradiation.

■ EXPERIMENTAL SECTION

Materials. Thioxanthone (TX; 97.0%, Aldrich), formaldehyde dimethyl acetal (98%, Alfa Aesar), 1,3,5-triethynylbenzene (TEB; 98%, Alfa Aesar), dimethylformamide (DMF; anhydrous, 99.8%, Aldrich), tetrakis(triphenylphosphine)palladium(0) ($Pd(PPh_3)_4$; 99%, Aldrich), copper(I) iodide (CuI; 99.5%, Aldrich), benzene (99.8%, Aldrich), triphenylmethane (TPM; 99%, Aldrich), iron(III) chloride ($FeCl_3$; 97%, Aldrich), and 1,2-dichloroethane (DCE; 99.8%, Aldrich) were used as received without further purification. Methyl methacrylate (MMA, 99%; Aldrich) was purified by passing through a basic alumina column to remove inhibitor. Cyclohexene oxide (CHO; 98%, Aldrich) was vacuum distilled over calcium hydride. Triethylene glycol dimethacrylate (TEGDA; M_n = 286.32 g mol^{-1}, Aldrich), triethylamine (TEA; 99%, Aldrich), *N*,*N*-dimethylaniline (DMA, Fluka), tetrahydrofuran (THF; 99.9%; Aldrich), diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$; 98%, Alfa Aesar), toluene (Merck), and methanol (MeOH; 99.9%, Merck) were used as received without any further purification.

Instrumentation. Nuclear magnetic resonance (NMR) spectra were obtained from a Bruker Avance II 400 MHz (100.6 MHz for ^{13}C), and Bruker Avance 400 MHz cross-polarization magic-angle spinning (CP/MAS) (100.6 MHz for ^{13}C) for solution and solid state, respectively. Diffuse reflectance UV–vis was recorded on a Varian Cary 300. N_2 gas sorption measurements were performed using a QUADRASORB SI and Autosorb 1-MP. The mass spectra were recorded in Finnigan MAT95S.

Gel permeation chromatography (GPC) measurements were performed on a Viscotek GPC max auto sampler system consisting of a pump, a Viscotek UV detector, and Viscotek a differential refractive index (RI) detector with three ViscoGEL GPC columns (G2000H HR, G3000H HR, and G4000H HR, 7.8 mm internal diameter, 300 mm length) in series. The effective molecular weight ranges were 456–42 800, 1050–107 000, and 10 200–2 890 000, respectively. THF was used as an eluent at flow rate of 1.0 mL min^{-1} at 30 °C. Both detectors were calibrated with PS standards having narrow-molecular-weight distribution. Data were analyzed using ViscotekOmniSEC Omni-01 software.

Fourier transform infrared (FTIR) spectra were recorded on PerkinElmer FTIR Spectrum One spectrometer with an ATR accessory (ZnSe, PikeMiracle accessory) and cadmium telluride (MCT) detector.

Photodifferential scanning calorimetry (photo-DSC) measurements were carried out by means of a modified PerkinElmer Diamond DSC equipped with a Polilight PL400 Forensic Plus light source between 320 and 500 nm. A uniform UV light intensity is delivered across the DSC cell to the sample and reference pans. The intensity of the light was measured as 40 mW cm^{-2} by a UV radiometer covering broad UV range. The measurements were carried out in an isothermal mode at 25 °C with a nitrogen flow of 20 mL min^{-1}.

Synthesis of 2,7-Dibromo-9*H*-thioxanthene-9-one (TX-Br_2).[51] TX (2.5 g, 0.012 mol) was dissolved in 20 mL of acetic acid, and 5 mL of Br_2 was added dropwise at room temperature and heated to 130 °C. After 20 h of reflux, cooled mixture was poured over ice and filtered. The precipitate was washed with saturated solution of $NaHCO_3$, 20% aqueous solution of $NaHSO_3$, and water, subsequently. The solid part was dried in vacuum and recrystallized in toluene. Resulting bright yellow solid was yielded as 2.57 g (59%). ^1H NMR (400 MHz, $CDCl_3$) δ: 8.75 (d, ^4J = 2.34 Hz, 2H), 7.75 (dd, ^3J = 8.60, ^4J = 2.32 Hz, 2H), 7.48 (d, ^3J = 8.60 Hz, 2H) (Figure S1, Supporting Information). EI *m/z* for $[M]^+$ calculated: 367.85006; found: 367.85089.

Synthesis of TX-CMP. TX-Br_2 (0.200 g, 0.54 mmol), TEB (0.081 g, 0.54 mmol), CuI (0.015 g, 0.08 mmol), and $Pd(PPh_3)_4$ (0.030 g, 0.026 mmol) were dissolved in 20 mL of dry DMF and 15 mL of dry TEA in a glovebox. The sealed flask was stirred for 3 days at 100 °C. Precipitation were filtered and washed with THF, $CHCl_3$, deionized water, and MeOH. A pale yellow material was purified via soxhlete wash in THF and MeOH for 1 day each. Dried in vacuum at 100 °C and yielded 0.181 g (94%). ^{13}C CP/MAS NMR (cross-polarization magic angle spinning nuclear magnetic resonance) δ: 176, 135, 128, 122, 89. Elemental analysis: calculated: C 81.80%, H 2.62%, S 10.40%, and O 5.19%. Found: C 67.92%, H 3.44%, and S 6.66%.

Synthesis of TX-Ph and TX-TPM Networks. Using a 100 mL two-necked flask TX (5 mmol, 1 equiv) and one of either benzene or TPM (5 mmol, 1 equiv) were dissolved in DCE (20 mL) under nitrogen. Formaldehyde dimethyl acetal (35 or 50 mmol) was added followed by $FeCl_3$ (35 or 50 mmol). The reaction mixture was then heated to 80 °C, after which the solution precipitated. Heating was continued for 18 h, after which the precipitate was removed by filtration and extensively washed with methanol until the filtrate became clear. The product was then Soxhlet extracted with methanol and chloroform for 18 h each after which the polymer was removed by filtration and dried in vacuo at 70 °C.

TX-Ph. Yield 0.9326 g (55%). ^{13}C CP/MAS NMR δ: 176, 134, 127, 34* (*overlaps with spinning sideband). Elemental analysis: calculated: C 83.42%, H 3.74%, S 8.56%, and O 4.28%. Found: C 77.57%, H 4.47%, and S 2.12%.

TX-TPM. Yield 2.1404 g (74%). ^{13}C CP/MAS NMR δ: 176, 134, 127, 51*, 35* (*overlap spinning sideband). Elemental analysis: calculated: C 87.50%, H 4.17%, S 5.56%, and O 2.78%. Found: C 80.06%, H 4.58%, and S 2.25%.

Polymerizations. *Visible Light Induced Free Radical Polymerization.* MMA (1 mL, 9.39 mmol) and TEA (10 μL, 0.07 mmol) (or $Ph_2I^+PF_6^-$ (30 mg, 0.07 mmol)) were dissolved in 2 mL of toluene, and TX polymer (25 mg) was added to the solution. Then the content was transferred to a Pyrex tube and degassed with highly pure nitrogen gas for 20 min. The solution was irradiated using a photoreactor equipped with six lamps emitting light at 400–500 nm. The light intensity was 30 mW cm^{-2} as measured by a Delta Ohm model HD-9021 radiometer. After irradiation, the samples were dissolved in THF, and TX polymers were separated by centrifugation. Then the samples were precipitated into methanol. The obtained polymers were dried under vacuum for 24 h.

Sunlight Induced Free Radical Polymerization. The procedure for sunlight induced free radical polymerization followed that of free radical polymerization under artificial visible light irradiation, except that samples were irradiated under natural sunlight rays. The samples were placed in the campus of Istanbul Technical University in March 2014. The light intensity of sunrays was measured as 15 mW cm^{-2}.

Free Radical Promoted Cationic Polymerization. CHO (1 mL, 9.88 mmol), toluene (2 mL), and $Ph_2I^+PF_6^-$ (30 mg, 0.07 mmol) (or DMA (10 μL, 0.07 mmol)) were charged to a Pyrex tube, and TX polymer (25 mg) was added to the solution. The tube was filled with nitrogen gas prior to irradiation. Then, the solution was irradiated using a photoreactor equipped with six lamps emitting light at 400−500 nm. After irradiation, the samples were dissolved in THF and, after separation of the TX polymers by centrifugation, precipitated into methanol. The polymers were dried under vacuum for 24 h.

Preparation of Photocurable Formulations for Photo-DSC. A typical photopolymerization in photo-DSC is as follows: for 1 mL of TEGDA was added 10 μL (0.07 mmol) of TEA or 30 mg (0.07 mmol) of $Ph_2I^+PF_6^-$. Just before irradiation TX polymer (5 mg) was added into the mixture. Then 6−10 mg of the reaction solution was transferred to a photo-DSC pan and irradiated in an isothermal mode at 25 °C with a nitrogen flow of 20 mL min^{-1}.

■ RESULTS AND DISCUSSION

Microporous TX-based polymeric photoinitiators were prepared by two coupling processes. TX-CMP was synthesized via Sonogashira−Hagihara cross-coupling reaction according to the procedure described by the Cooper group[48] (Scheme 1).

The main structural characterization method of such carbon-rich insoluble polymers, CP/MAS ^{13}C NMR (Figure 1), demonstrated efficient incorporation of two monomers into the polymer via ethynyl linkage. The peaks at 89 and 122 ppm represent the signals of triple bonds and 3° carbons of triethynylbenzene (TEB) within the structure, respectively. The peak at 176 ppm corresponds to the carbonyl carbon of the TX groups. Other peaks are assigned to both TX and TEB moieties.

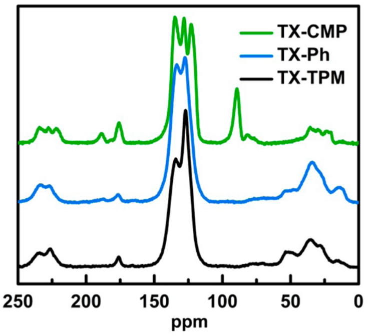


Figure 1. Solid-state ^{13}C NMR spectra of thioxanthone polymers.

The polymers yielded from random copolymerization of TX-Ph and TX-TPM via Friedel−Crafts alkylation process (Scheme 2) were also characterized using CP/MAS ^{13}C NMR spectroscopy.

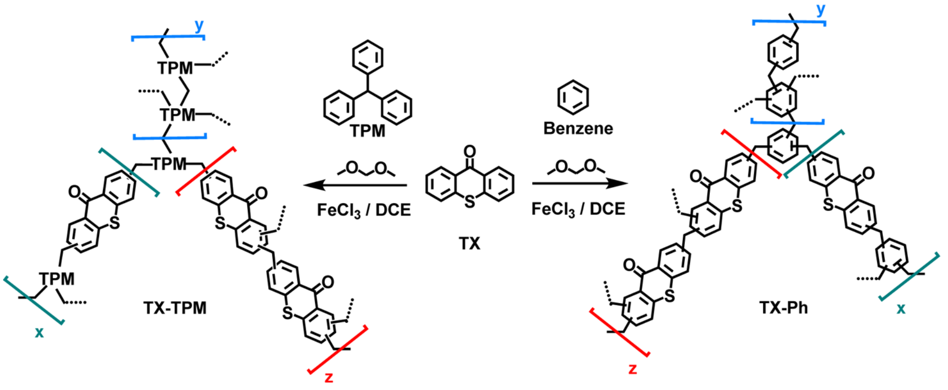
The spectra exhibited a typical carbonyl peak at 176 ppm like their analogue TX-CMP. Since TX-Ph and TX-TPM are random copolymerized materials, comparison of these knitted polymers with their homopolymer analogues without TX clearly indicates the final structures composed of both TX and aromatic comonomers (Figures S3 and S4). In the case of TX-Ph, the slight shift from 134 to 133 ppm and significant increase of the peak intensity at 127 ppm acknowledge the copolymerization of benzene and TX. Similar changes have been observed for the TPM samples as noted by the shift from 135 to 134 ppm and the increase of the peak intensity at around 127 ppm.

N_2 gas sorption properties and pore size distribution of the photoinitiators were also investigated. Typical N_2 adsorption/desorption isotherms of the TX polymers are presented in Figure 2. The BET surface areas and pore sizes of the TX photoinitiators are tabulated in Table 1.

Conventional TX photoinitiators usually have absorption in the near-UV range. The microporous TX photoinitiators exhibit a broad and strong absorbance peak in the visible region enabling initiating activity even in the sunlight (vide infra) (Figure 3).

To demonstrate the photocatalytic activity of the synthesized TX polymers, free radical polymerization of MMA was examined under visible light irradiation. For this purpose, triethylamine (TEA) and diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$) were used as co-initiators. Table 2 summarizes the results of the photopolymerization of MMA under visible light irradiation. Control experiments indicated that both initiating components (TX and co-initiator) were indispensable, and irradiations in the absence of each component gave no polymer. In addition, no polymer was resulted in the dark condition signifying a light-driven process. All new macrophotoinitiators could initiate the polymerization of MMA. However, TX-TPM was more efficient than the

Scheme 2. Synthesis of TX-TPM and TX-Ph by Friedel−Crafts Alkylation Process (Knitting Method)



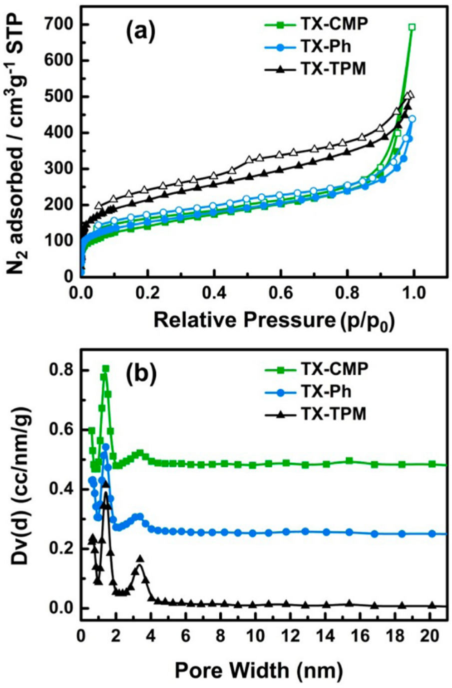


Figure 2. (a) N_2 sorption isotherms of BET surface area measurement and (b) pore size distribution of the TX polymers.

Table 1. BET Surface Area Measurement and Pore Size Distributions of Thioxanthone Polymers

TX type	surface area (m^2 g^{-1})	pore size (nm)
TX-CMP	497	1.4
TX-Ph	537	1.4
TX-TPM	749	1.4

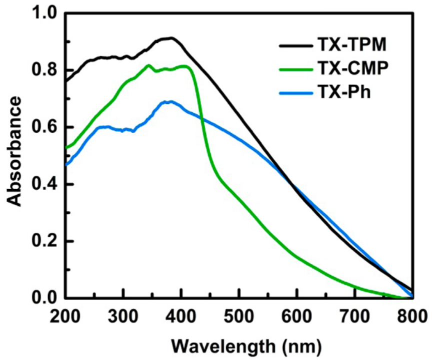


Figure 3. Solid-state UV−vis spectra of thioxanthone polymers.

others were, as it provided higher monomer conversion. Furthermore, as co-initiator, TEA behaved more efficient than the iodonium salt.

For sake of comparison a model reaction, employing low molecular weight TX was performed for both TEA and iodonium salt co-initiators under the same experimental conditions (run 4, Table 2). Apparently, the polymeric photoinitiators exhibit enhanced initiation efficiency probably due to the better absorption characteristics arising from the 2D/3D structures.[52−54]

From the point of view of energetic issues, many attempts in the field of photopolymerization have been focused on designing such initiating systems that need low energetic requirements. This can be achieved, for instance, by suitable initiating systems working under visible light or more favorably under natural sunlight irradiation. To investigate the versatility of the so-prepared TX macrophotoinitiators, photopolymerization of MMA was studied using the same procedure but under sunlight illumination. Polymerizations were conducted by irradiation directly under sunlight without use of any light filter. Table 3 shows the results of these experiments.

Table 2. Visible Light Induced Polymerization of MMA Using Microporous Thioxanthone Polymers in the Presence of Amine or Iodonium Salt Co-initiators at Room Temperature[a]

		co-initiator					
		TEA			$Ph_2I^+PF_6^-$		
run	TX type	conv[b] (%)	M_n[c] (g mol^{-1})	M_w/M_n[c]	conv (%)	M_n (g mol^{-1})	M_w/M_n
1	TX-TPM	26	151000	1.85	22	163550	2.35
2	TX-CMP	15	202000	1.70	10	95200	1.80
3	TX-Ph	21	141500	2.10	16	154360	2.15
4	TX	13	40540	1.45	10	51660	1.75

[a] Irradiation time = 4 h, [MMA] = 3.13 M, [TEA] = 0.023 M, [$Ph_2I^+PF_6^-$] = 0.023 M, toluene = 2 mL, TX-polymer = 25 mg. [b] Measured gravimetrically. [c] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) determined by GPC.

Table 3. Sunlight Induced Polymerization of MMA Using Thioxanthone Macrophotoinitiators in the Presence of Amine and Iodonium Salt Co-initiators at Ambient Temperature[a]

		co-initiator					
		TEA			$Ph_2I^+PF_6^-$		
run	TX type	conv[b] (%)	M_n[c] (g mol^{-1})	M_w/M_n[c]	conv (%)	M_n (g mol^{-1})	M_w/M_n
1	TX-TPM	31	114700	2.62	23	86400	1.95
2	TX-CMP	19	126700	2.25	14	114700	1.75
3	TX-Ph	25	112850	2.45	18	109650	2.05

[a] Irradiation time = 4 h, [MMA] = 3.13 M, [TEA] = 0.023 M, [$Ph_2I^+PF_6^-$] = 0.023 M, toluene = 2 mL, TX-polymer = 25 mg. [b] Measured gravimetrically. [c] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) determined by GPC.

A bifunctional monomer, triethylene glycol diacrylate (TEGDA), was used to study the kinetics of the free radical polymerization initiated by TX polymers by means of photo-DSC. Bifunctionality results in formation of polymeric films, which have achieved immense industrial applications. Photo-DSC is capable of measuring any liberating heat during the photopolymerization process. This is directly proportional to the number of acrylate double bonds reacted in the photocuring process. Consequently, the rate of polymerization (the number of monomers being consumed over total number of monomers per time), R_P (1/s), can be determined according to eq 1:

$$R_P = (Q_t) \times 1000/[n \times (E_{db})] \qquad (1)$$

where Q_t (J mol^{-1} s^{-1}) is the amount of released heat at time t, n the number of acrylate double bonds, and E_{db} (kJ mol^{-1}) is

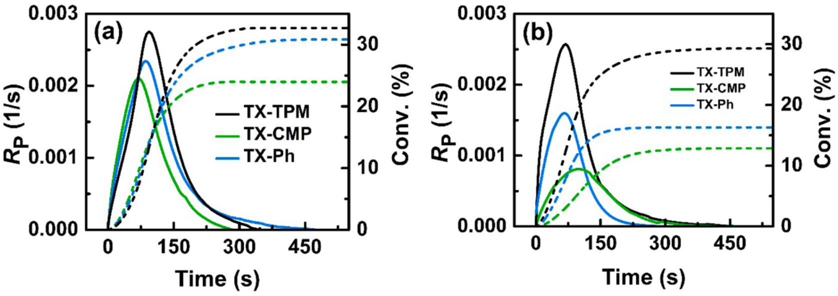
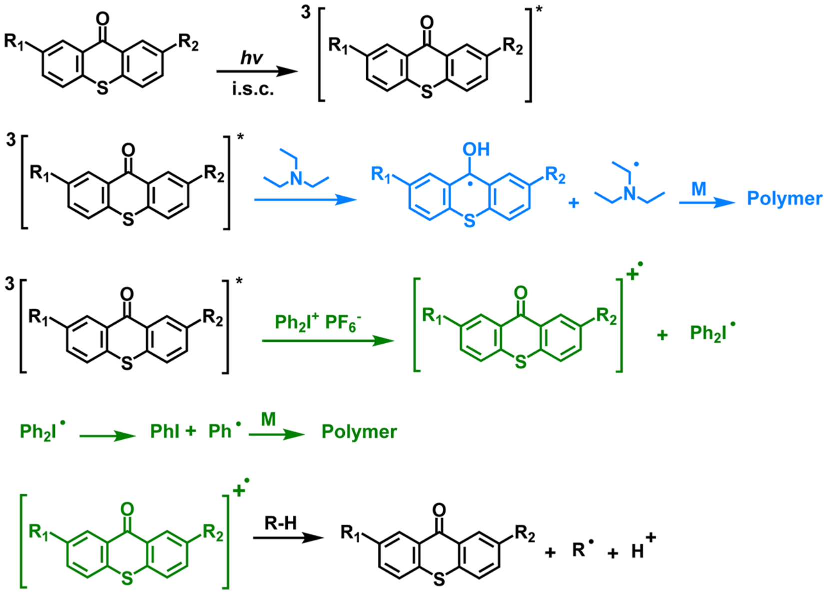


Figure 4. Kinetics of the photopolymerization of TEGDA with TX macrophotoinitiators using (a) TEA and (b) iodonium salt as co-initiator measured by photoDSC. Solid lines: rate of polymerization (R_P (1/s)); dashed lines: conversion (%).

Scheme 3. Proposed Initiation Mechanism of Free Radical Polymerization Using Thioxanthone Macrophotoinitiators in the Presence of Amine or Iodonium Salt Co-initiators under Visible Light or Sunlight Irradiation



the energy of acrylate double bond (~86 kJ mol^{-1}). By integrating the area under R_P–t graph, the conversion of the acrylate monomer is obtained. Figure 4 depicts the kinetics of the photopolymerization of TEGDA using TX polymers in the presence of TEA or iodonium salt co-initiators, measured by photo-DSC.

Kinetic results revealed photocatalytic activity of TX-TPM to be the highest among all TX polymers. This was in agreement with the UV–vis measurements and gas sorption results, which had indicated higher photocatalytic activity of this knitted polymer (higher absorbance and larger specific surface area).

Depending on the type of co-initiator, we propose two distinct initiation mechanisms, namely hydrogen abstraction and electron transfer reactions. In the case of TEA, photoexcited TX species abstracts hydrogen to form initiating radicals on the co-initiator. With iodonium salt, however, a different situation is encountered. The photoexcited TX moiety forms an exciplex with the ground state iodonium salts which is reduced to $Ph_2I^\bullet$. The subsequent decomposition of this unstable species ultimately forms initiating phenyl radicals. Scheme 3 illustrates the general mechanism of photopolymerization using TX compounds in the presence of amine or iodonium salt co-initiators. The failure of the polymerization in the absence of co-initiator indicates that intramolecular hydrogen abstraction or electron transfer reactions are not probable.

An important advantage of heterogeneous photoinitiators is their easily separable properties from the polymerization mixture, which can be used further to initiate polymerization. To clarify the reusability of these heterogeneous TX macrophotoinitiators, polymerization of MMA was repeated three times under the same conditions, which followed separation and refining the TXs and reloading them for the next polymerizations. Figure 5 shows the conversion of the polymerization of MMA in three cycles in which remained almost constant for all of TXs.

In order to gain insight into the possible effect of photopolymerization on the TXs structures, FTIR analysis was performed. Figure 6 shows typical FTIR spectra of one of the TX photoinitiators (TPM-TX) before and after photopolymerization of MMA as well as that of PMMA. The FTIR results showed no significant changes in the structure of TX macrophotoinitiator without any detectable traces of PMMA in the structure.

To expand the applicability of TX macrophotoinitiators even further, cationic polymerization of cyclohexene oxide (CHO) was also examined using all of three TXs under visible light irradiation. Irradiation of a mixture of CHO, TX, and iodonium salt under visible light failed to form any polymer. However, by addition of an H-donor compound, for instance *N,N*-dimethylaniline (DMA) or tetrahydrofuran (THF), the system

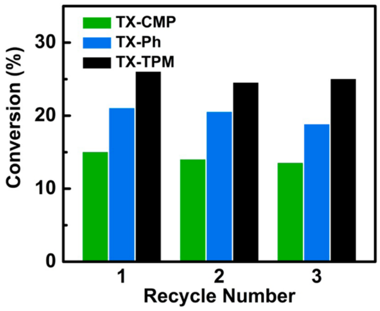


Figure 5. Reusability of TX polymers in free radical polymerization of MMA under visible light irradiation by applying the same conditions (irradiation time = 4 h, [MMA] = 3.13 M, [TEA] = 0.023 M, toluene = 2 mL).

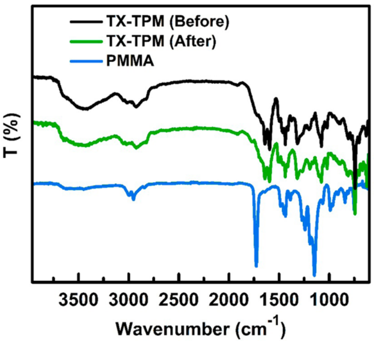


Figure 6. FTIR spectra of TX-TPM (before and after photopolymerization) and PMMA.

could successfully polymerize CHO. TX ketyl radical undergoes electron transfer reactions with iodonium salt to yield protonic acids capable of initiating cationic polymerization. DMA was deliberately chosen as the amine co-initiator in the cationic system so as to prevent possible termination reactions. Because of the higher basicity, aliphatic amines are known to terminate cationic polymerization.[55] The radicals formed from the co-initiator DMA as described for the free radical polymerization are readily oxidized to corresponding carbocation. Similarly, THF generates oxidizable radicals by hydrogen abstraction. The polymerization mechanism involving all possibilities is presented in Scheme 4. The polymerization results are collected in Table 4.

Reusability was also examined in the cationic pathway. As illustrated in Scheme 4, oxidation of ketyl radicals results in regeneration of the TX functionality facilitating the reusability of the TX macrophotoinitors. Figure 7 shows the conversion of CHO polymerized by TX macrophotoinitiators in the presence of DMA co-initiator after three times recycling, which verifies no decay in the photocatalytic activity.

■ CONCLUSION

In summary, new classes of TX macrophotoinitiators were synthesized via different cross-coupling reactions resulting in high porosity (500−750 m^2 g^{-1}) and excellent optical characteristics. The obtained conjugated microporous TX networks readily initiate free radical and cationic polymerizations of vinyl monomers and cyclic ethers, respectively. In the polymerization processes, hydrogen abstraction and electron transfer reactions of the photoexcited TX play a major role for the generation of the reactive species. In the free radical mode, excited TX abstracts hydrogen from the amine

Scheme 4. Free Radical Promoted Cationic Polymerization of CHO by Using TX Polymers and Iodonium Salt in the Presence of a Hydrogen Donor Compound (DMA or THF) under Visible Light Irradiation

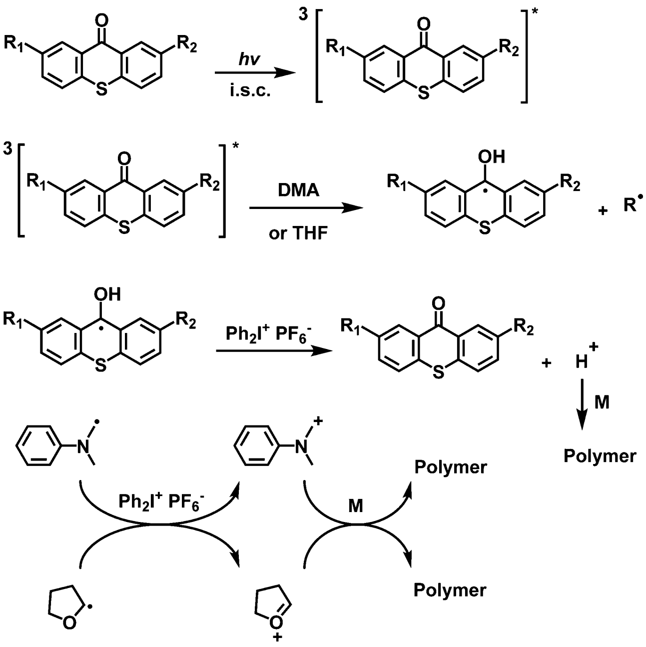


Table 4. Visible Light Induced Free Radical Promoted Cationic Polymerization of CHO Using Microporous Thioxanthone Polymers and Iodonium Salt in the Presence of DMA or THF as H-Donors at Room Temperature[a]

		H-donor					
		DMA			THF		
run	TX type	conv[b] (%)	M_n[c] (g mol^{-1})	M_w/M_n[c]	conv (%)	M_n (g mol^{-1})	M_w/M_n
1	TX-TPM	37	4960	3.25	31	5120	2.80
2	TX-CMP	18	2140	2.70	15	2610	2.15
3	TX-Ph	29	3250	2.90	28	3100	3.10

[a] Irradiation time = 4 h, [CHO] = 3.30 M, [$Ph_2I^+PF_6^-$] = 0.023 M, [DMA] = 0.023 M, [THF] = 0.023 M, toluene = 2 mL, TX-polymer = 25 mg. [b] Measured gravimetrically. [c] Number-average molecular weight (M_n) and molecular weight distribution (M_w/M_n) determined by GPC.

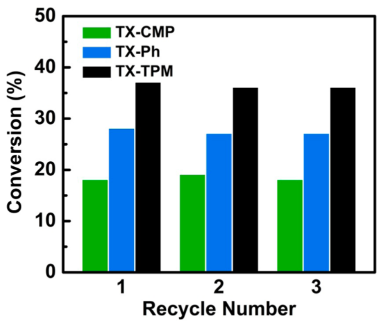


Figure 7. Reusability of TX-polymers in free radical promoted cationic polymerization of CHO under visible light irradiation applying the same conditions (irradiation time = 4 h, [CHO] = 3.30 M, [$Ph_2I^+PF_6^-$] = 0.023 M, [DMA] = 0.023 M, toluene = 2 mL).

co-initiator or directly reduces iodonium salt to initiate the polymerization. In the corresponding cationic polymerization, the oxidation of the photochemically formed electron donor radicals is responsible for the successful initiation. Facile separation of these heterogeneous photoinitiators from the polymer mixture, retaining photocatalytic activity after several uses in both free radical and cationic polymerizations, microporosity, capability of being carried out under visible light or even sunlight irradiation, applicability to different polymerization modes, eliminating any possible problem associated with the low molecular weight compounds make them high potential photoinitiators for widespread applications.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR and CP/MAS ^{13}C NMR spectra of thioxanthone photoinitiators. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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