

Synthesis and Characterization of Polymeric Thioxanthone Photoinitiators via Double Click Reactions

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ABSTRACT: Macrophotoinitiators containing thioxanthone (TX) moieties as side chains were synthesized by using “double click chemistry” strategy; combining in-situ 1,3-dipolar azide–alkyne [3 + 2] and thermoreversible Diels–Alder (DA) [4 + 2] cycloaddition reactions. For this purpose, thioxanthone–anthracene (TX–A), *N*-propargyl-7-oxynorbornene (PON), and polystyrene (PS) with side-chain azide moieties (PS–N₃) were reacted in *N,N*-dimethylformamide (DMF) for 36 h at 120 °C. In this process, PON acted as a “click linker” since it contains both protected maleimide and alkyne functional groups suitable for 1,3-dipolar azide–alkyne and Diels–Alder click reactions, respectively. This way, the aromaticity of the central phenyl unit of the anthracene moiety present in TX–A was transformed into TX chromophoric groups. The resulting polymers possess absorption characteristics similar to the parent TX. Their capabilities to act as photoinitiator for the polymerization of mono- and multifunctional monomers, namely methyl methacrylate (MMA) and 1,1,1-tris(hydroxymethyl)propane triacrylate (TPTA) were also examined.

Introduction

Recently macrophotoinitiators, which are considered as macromolecules containing covalently bonded photoinitiating groups, have been the subject to an increased research interest since they may offer various advantages over the low molecular weight photoinitiators such as greater reactivity, low volatility, and low migration due to the well-known polymeric effect. Macrophotoinitiators possessing chromophoric groups either in the main chain or as pendant groups can be prepared in two ways: (i) synthesis and polymerization of monomers with photoreactive groups; (ii) introduction of photoactive groups into polymer chains. In the latter case, macrophotoinitiators were synthesized by using functional initiators and terminators in a particular polymerization or by reacting functional groups of a preformed polymer with other functional groups of low molecular weight compounds possessing also photoreactive groups. Macrophotoinitiators, analogous to the low molecular weight photoinitiators, are divided into two classes, according to their radical generation mechanism, namely cleavage-type (type I) and hydrogen abstraction-type (type II) macrophotoinitiators.¹

Typical type II photoinitiators include benzophenone and derivatives, thioxanthone, benzil, quinones, and organic dyes, while alcohols, ethers, amines, and thiols are used as hydrogen donors. Among these initiators, thioxanthone (TX) derivatives have recently received a revitalized interest because of their absorption characteristics at near-UV range.^{2–11} Moreover, their simple synthetic procedure allows various modifications for wavelength tunability or improved solubility by the incorporation of appropriate substituents on the thioxanthone structure. Free radical generation process is H-abstraction reaction of TX triplets from hydrogen donors such as amines and alcohols. The radical derived from the donor can initiate the polymerization while the radicals stemming from TX are usually not reactive toward vinyl monomers due to bulkiness and/or the delocalization of the unpaired electrons. Various structurally different TX derivatives including dendritic,^{2,3} polymeric,¹¹ and one-

component ones^{4–6,12,13} possessing both light-absorbing chromophoric group and hydrogen-donating sites in the same structure have been synthesized, and their photochemistry has been studied in detail.

The “click”-type reactions, mainly exemplified by Huisgen 1,3-dipolar azide–alkyne,¹⁴ [3 + 2], or Diels–Alder cycloadditions,¹⁵ [4 + 2], have attracted much attention due to their important features including high yields, high tolerance of functional groups, and selectivity.¹⁶ Thiol–ene chemistry¹⁷ has recently been introduced as an alternative click route that can be performed at moderately low temperatures by using photoinitiators. Huisgen 1,3-dipolar cycloaddition occurs between an alkyne and an organic azide to give 1,2,3-triazole ring. The reactions can be performed under mild experimental conditions^{16,18} when catalyzed by copper(I). Click reactions have been extensively used in the synthesis of polymers with different composition and topology, ranging from linear (telechelic,¹⁹ macromonomer,²⁰ and block copolymer)²¹ to nonlinear macromolecular structures (graft,²² star,²³ miktoarm star,²⁴ H-type,²⁵ dendrimer,²⁶ dendronized linear polymer,²⁷ macrocyclic polymer,²⁸ self-curable polymers,²⁹ and network system³⁰). The development and the application of click chemistry in polymer and material science have recently been reviewed extensively.³¹

As part of our continuing interest in the development of photosensitive systems for various synthetic applications, the present paper is devoted to synthesis of macrophotoinitiators containing side-chain TX moieties by taking advantage of two click reactions, namely Diels–Alder and 1,3-dipolar cycloaddition reactions.

Experimental Section

Materials. Styrene (S, 99%, Aldrich) and 4-chloromethylstyrene (CMS, ca. 60/40 meta/para isomer mixture, 97%, Aldrich) were distilled under reduced pressure before use. 2,2'-Azobis(isobutyronitrile) (AIBN, 98%, Aldrich) was recrystallized from ethanol. *N*-Oxyl free radical (TEMPO, 99%, Aldrich) was used as received. *N,N,N',N'',N'''*-Pentamethyldiethylenetriamine (PMDETA, Aldrich) was distilled over NaOH prior to use. Tetrahydrofuran (THF, 99.8%, J.T. Baker) was dried and distilled over benzophenone–Na. Other solvents were purified by conventional procedures. Triethylamine (TEA, 98%, Aldrich) and dichloromethane (99.9%, HPLC grade, Aldrich) were distilled from CaH₂. Dimethylformamide (DMF,

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+99%, Aldrich) and 1,1,1-tris(hydroxymethyl)propane triacrylate (TPTA, 95%, Aldrich) was used as received.

Instrumentation. ^1H NMR measurements were recorded in CDCl_3 with $\text{Si}(\text{CH}_3)_4$ as internal standard, using a Bruker AC250 (250.133 MHz) instrument. FT-IR spectra were recorded on a Perkin-Elmer FTIR Spectrum One-B spectrometer. UV spectra were recorded on a Shimadzu UV-1601 spectrometer. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Diamond DSC. Molecular weights were determined by gel permeation chromatography (GPC) instrument equipped with a Waters styragel column (HR series 2, 3, 5E) with THF as the eluent at a flow rate of 0.3 mL min^{-1} and a Waters 410 differential refractometer detector.

Photo-DSC. Photo-DSC was conducted on a modified Perkin-Elmer Diamond DSC equipped with a homemade aluminum cylinder. UV light (320–500 nm) was applied by a light guide (OmniCure Series 2000) with a light intensity of 18.4 mW cm^{-2} at the level of the surface of the cured samples. The mass of the samples was 8 mg, and the measurements were carried out in an isothermal mode at 30°C under a nitrogen flow of 20 mL min^{-1} . The reaction heat liberated in the polymerization was directly proportional to the number of acrylate reacted in the system. By integrating the area under the exothermic peak, the conversion of the acrylate groups (C) or the extent of the reaction was determined according to eq 1:

$$C = \Delta H_t / \Delta H_0^{\text{theory}} \quad (1)$$

where ΔH_t is the reaction heat evolved at time t and $\Delta H_0^{\text{theory}}$ is the theoretical heat for complete conversion. $\Delta H_0^{\text{theory}} = 19.2 \text{ kcal mol}^{-1}$ for an bond of acrylate.³² The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by eq 2:

$$R_p = dC/dt = (dH/dt) / \Delta H_0^{\text{theory}} \quad (2)$$

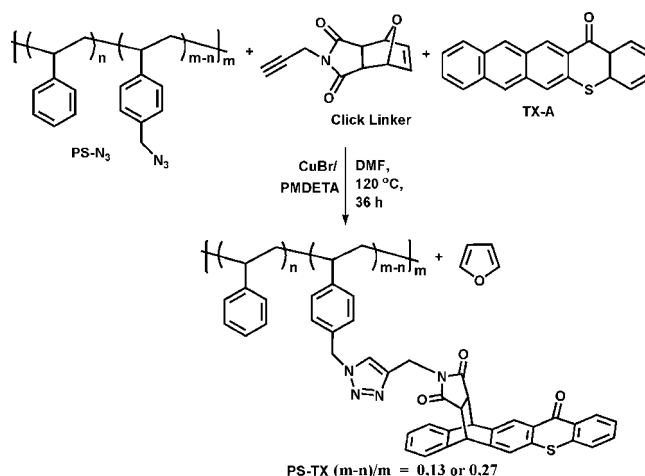
Synthesis of Polystyrene–Azide (PS– N_3). First, poly(styrene-*co*-chloromethylstyrene) (P(S-*co*-CMS)) with two different chloromethylstyrene content (13 and 27 mol %) was synthesized as described previously.³³ A typical procedure for the preparation of PS– N_3 from 13 mol % CMS containing P(S-*co*-CMS) is as follows: P(S-*co*-CMS) (2.0 g, $8.5 \times 10^{-4} \text{ mol}$) was dissolved in *N,N*-dimethylformamide (DMF), and NaN_3 (0.23 g, $3.6 \times 10^{-3} \text{ mol}$) was added. The resulting solution was allowed to stir at 25°C overnight and precipitated in excess methanol/water mixture (1/1 by volume). The same procedure was also applied for P(S-*co*-CMS) with 27 mol % CMS content. ^1H NMR (CDCl_3): δ = 7.40–6.20 (b, 9H), 4.25 (s, 2H) FTIR %T (cm^{-1}): 3060, 2923, 2096, 1681, 1601, 1492, 1452, 757, 698.

Synthesis of *N*-Propargyl-7-oxynorbornene (PON). *N*-Propargyl-7-oxynorbornene (PON) as the click linker was synthesized according to the literature procedure.³⁴ ^1H NMR (CDCl_3): δ = 6.50 (s, 2H), 5.28 (s, 2H), 4.22 (d, 2H), 2.88 (s, 2H), 2.18 (t, 1H). FTIR %T (cm^{-1}): 3256, 2126, 1698, 1154, 1009, 880, 704, 623.

Synthesis of Thioxanthone–Anthracene (5-Thiapentacene-14-one) (TX–A). Thioxanthone–anthracene (TX–A) (5-thiapentacene-14-one) was synthesized according to the literature procedure.¹² ^1H NMR (250 MHz) in CDCl_3 : δ 8.86 (s, 1H), 8.61–8.64 (d, 1H), 8.42–8.45 (t, 1H), 8.35 (s, 1H), 7.96–8.1 (m, 2H), 7.82–7.91 (d, 1H), 7.44–7.72 (m, 5H). FTIR %T (cm^{-1}): 3050, 1672, 1622, 1593, 1339, 1147, 956, 883, 725.

One-Pot Synthesis of Polystyrene–Thioxanthone (PS–TX). A typical procedure for the synthesis of polystyrene–thioxanthone (PS–TX) obtained from the precursor P(S-*co*-CMS) with 13 mol % CMS content. PS– N_3 (0.10 g, 0.043 mmol), click linker (9) (0.019 g, 0.043 mmol), and TX–A (0.029 g, 0.043 mmol) were dissolved in DMF (5 mL) in a Schlenk tube and purged with nitrogen. CuBr (0.018 g, 0.14 mmol) and PMDETA (0.027 mL, 0.14 mmol) were added, and the reaction mixture was degassed by three freeze–pump–thaw cycles and left under nitrogen and stirred at 120°C for 36 h. Polymer solution was then passed through alumina column to remove copper salt, precipitated into methanol, and finally dried in a vacuum oven at 25°C . Yield: 0.22 g (20%).

Scheme 1. Side-Chain Functionalization of PS– N_3 with Anthracene–Thioxanthone (TX–A) in the Presence of *N*-Propargyl-7-oxynorbornene (PON) as Click Linker via Double Click Chemistry



^1H NMR (250 MHz) in CDCl_3 : δ 7.46 (m, 1H); 7.4–6.2 (b, 9H) 5.26 (m, 2H); 5.26 (m, 2H); 4.74 (m, 2H); 3.20 (m, 1H). FTIR %T (cm^{-1}): 3020, 2922, 1709, 1625, 1601, 1493, 1452, 758, 699.

Results and Discussion

As stated in the Introduction, our synthetic approach toward the direct preparation of polymers containing side-chain thioxanthone moieties is based on “double click” chemistry strategy combining in-situ 1,3-dipolar azide–alkyne [3 + 2] and thermoreversible Diels–Alder [4 + 2] cycloaddition reactions. The overall process is represented in Scheme 1.

According to this approach, first poly(styrene-*co*-chloromethylstyrene), P(S-*co*-CMS), copolymers containing two different chloromethylstyrene (CMS) units (13 and 27 mol %) were prepared via nitroxide-mediated radical polymerization (NMP). The compositions of copolymers as determined by using ^1H NMR spectroscopy are in agreement with the expected values and indicate the random copolymer structure. The resulting P(S-*co*-CMS) copolymers were then quantitatively converted into polystyrene–azide (PS– N_3) in the presence of NaN_3 /DMF at room temperature. In the ^1H NMR spectrum of PS– N_3 , while the signal at 4.50 ppm corresponding to $-\text{CH}_2-\text{Cl}$ protons of the precursor P(S-*co*-CMS) disappeared completely, a new signal appeared at 4.25 ppm was attributed to $-\text{CH}_2$ linked to azide groups. The FT-IR spectral analysis also supports this result. The other components of the double click reaction, namely thioxanthone–anthracene (TX–A)¹² and *N*-propargyl-7-oxynorbornene³³ (PON), were synthesized according to the literature procedures.

In the final step of the process, PS– N_3 , TX–A, and PON were reacted in one-pot to yield the desired PS–TX macro-photoinitiator. In this step, two independent click reactions occurred simultaneously. While CuBr/PMDETA catalyzed triazole formation was accomplished between the azide of PS– N_3 and the alkyne functional end group of PON, retro-Diels–Alder reaction proceeded concomitantly between PON and the anthracene moiety of TX–A after deprotection of the maleimide group. Notably, PON acts as a “click linker” in the process, as it contains suitable functional groups for the two click reactions involved. The possible byproduct, i.e., furan, and excess TX–A or PON are completely soluble in the precipitating solvent methanol. Consequently, the side-chain modification was completed with quantitative yields without additional purification steps.

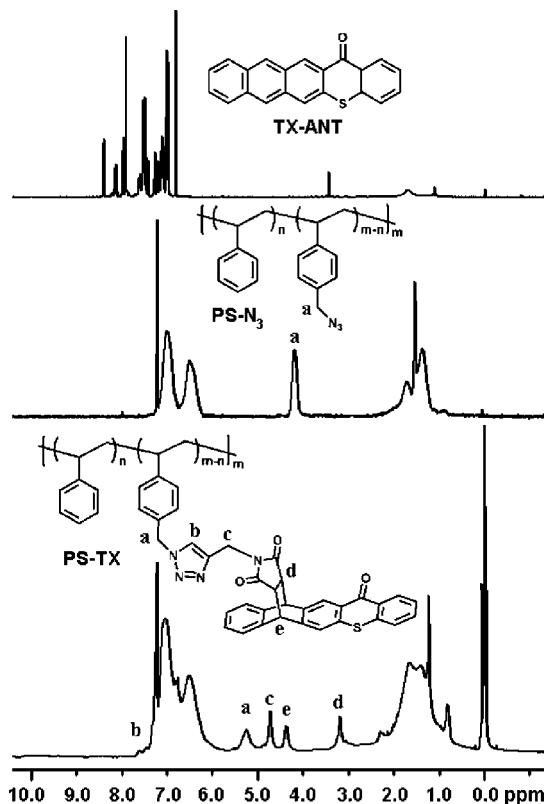


Figure 1. ^1H NMR spectrum of TX-A, PS-N₃ and PS-TX (27%) in CDCl_3 .

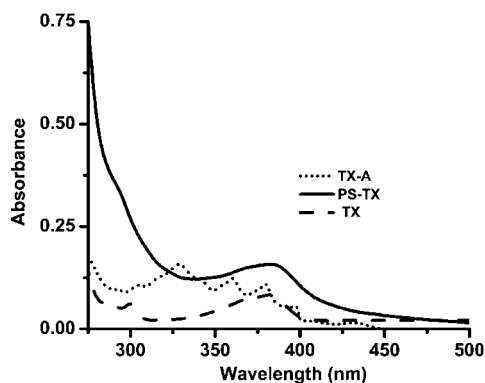


Figure 2. Absorption spectra of PS-TX (27%), TX-A, and TX in CH_2Cl_2 . The concentrations are 1×10^{-5} M in terms of thioxanthone moieties.

Evidence for the occurrence of the double click reactions was obtained from ^1H NMR, UV, and fluorescence spectroscopy. As can be seen from Figure 1, where ^1H NMR spectra of TX-A and PS-N₃ were recorded, the peaks between 7.4 and 8.5 ppm, characteristic for aromatic protons of anthracene, disappeared completely. This indicates the loss of the aromaticity of the central phenyl unit of anthracene by Diels-Alder cycloaddition click reaction. Furthermore, the two new signals corresponding to a bridgehead ($-\text{CH}$) proton of the cycloadduct and $-\text{CH}$ proton on the fused maleimide ring appeared at 4.74 and 3.20 ppm, respectively. The appearance of the peak belonging to $-\text{CH}$ proton of the triazole ring at 7.46 ppm is a typical indication for the successful completion of the other click reaction, 1,3-dipolar cycloaddition. On the basis of a comparison of the integration of the peak intensities at 5.26 and 4.74 ppm, corresponding to the methylene protons linked to triazole ring and adjacent to the cycloadduct, respectively, the obtained ratio of 1:1 clearly indicates the efficiency of the process. The FTIR

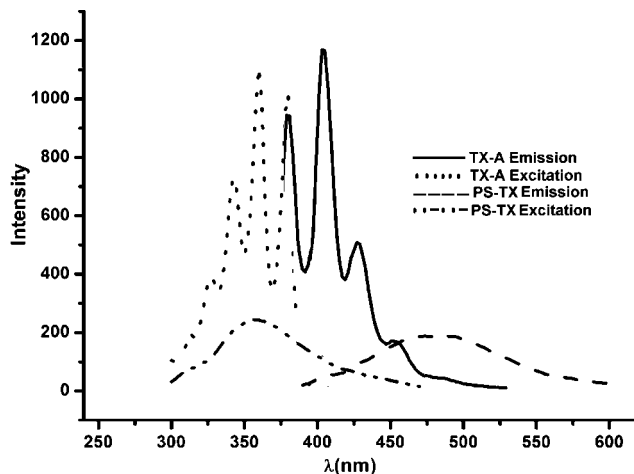


Figure 3. Emission spectra of TX-A and PS-TX (27%) in DMF; $\lambda_{\text{exc}} = 360$ nm. The concentrations are 2×10^{-5} M in terms of thioxanthone moieties.

Scheme 2. Photoinitiated Free Radical Polymerization of Methyl Methacrylate (MMA) by Using PS-TX Macrophotoinitiator

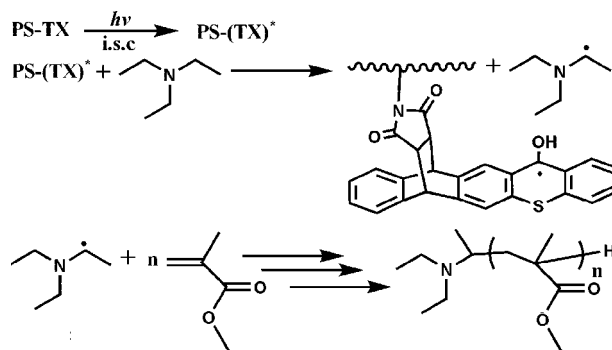


Table 1. Photoinitiated Polymerization^a of Methyl Methacrylate (MMA) with Macrophotoinitiator in CH_2Cl_2

macrophotoinitiator ^b	TEA (mol L ⁻¹)	conversion (%)	$M_n \times 10^{-4}$ (g/mol)	M_w/M_n
PS-TX ^c	15×10^{-4}	13.8	21500	1.59
PS-TX ^d	15×10^{-4}	20.0	20600	1.70
PS-TX ^d	15×10^{-4}	2.00	75000	2.16
	15×10^{-4}	0.30	83200	2.10

^a $[\text{MMA}] = 9.28$ mol L⁻¹; irradiation time = 2 h. ^b $[\text{PS-TX}] = 3.2 \times 10^{-4}$ mol L⁻¹. ^c Obtained from the precursor PS-co-PCMS with 13 mol % CMS content. ^d Obtained from the precursor PS-co-PCMS with 27 mol % CMS content.

spectra also confirm quantitative reaction, as the azide stretching band at around 2094 cm^{-1} disappears completely and a new carbonyl band at 1709 cm^{-1} appears.

Photophysical characteristics of the obtained PS-TX were investigated by UV and fluorescence spectroscopy (Figures 2 and 3). As can be seen from Figure 2, TX-A displays characteristic five-finger absorbance in 300–400 nm range. On the contrary, the PS-TX macrophotoinitiator shows a different absorption signature with a maximum at 380 nm, which is similar to the absorption spectrum of pure thioxanthone, indicating that the absorption regime of the precursor has changed as a result of the modification. Indeed, DA reaction between anthracene and deprotected maleimide moieties causes the loss of the aromaticity of central phenyl unit of anthracene. In other words, the TX-A group is transformed into thioxanthone group by the so-called double click reaction.

Fluorescence spectra of PS-TX may also provide further evidence for the efficiency of the modification process and

Table 2. Effect of Solvent on the Photoinitiated Polymerization^a of Methyl Methacrylate (MMA) with PS-TX^b at Room Temperature

solvent	conversion (%)
DMF	21.5
THF	1.00
CH ₂ Cl ₂	13.8
— ^c	19.3

^a [MMA] = 9.28 mol L⁻¹; [PS-TX] = 3.2 × 10⁻⁴ mol L⁻¹; [TEA] = 15 × 10⁻⁴ mol L⁻¹, irradiation time = 2 h. ^b Obtained from the precursor PS-co-PCMS with 13 mol % CMS. ^c Polymerization was performed in bulk.

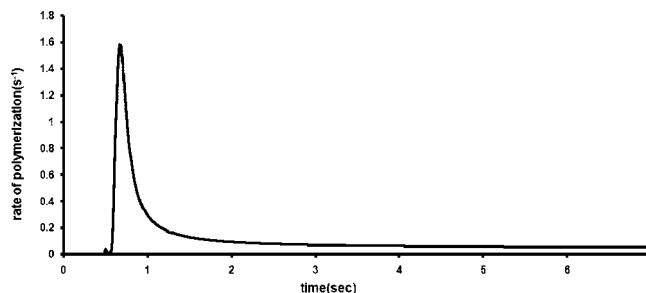
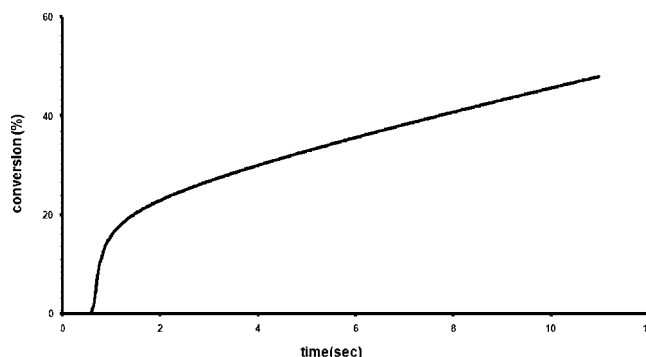
information on the nature of the excited states involved. As can be seen from Figure 3, excitation and emission fluorescence spectra in DMF of TX-A and PS-TX obtained by double click reaction are quite different. TX-A exhibits characteristic emission bands of the excited (singlet) of anthracene moiety. In contrast, PS-TX has no significant emission of this kind, and the spectrum shows a nearly mirror-image-like relation between absorption and emission again similar to bare TX. Expectedly, the intensities are lower in the case of side-chain thioxanthone bound polymer.

Polymeric systems bearing side-chain TX groups can act as bimolecular photoinitiators when used in conjunction with hydrogen donors analogous to the low molecular weight TXs. PS-TX was used as a photoinitiator for the polymerization of methyl methacrylate (MMA) in the presence of triethylamine (TEA) as hydrogen donor. The overall process is shown in Scheme 2.

Because of steric bulkiness and delocalization, the polymeric ketyl radical is insufficiently reactive to initiate the polymerization of vinyl monomers. Although not entirely elucidated, presumably these radicals undergo bimolecular termination. The results are compiled in Table 1. For comparison, photopolymerizations in the absence of either PS-TX itself or TEA are also included. As can be seen, PS-TX is not an efficient photoinitiator in the absence of a co-initiator. The presence of an amine such as TEA is important for effective photoreduction and photopolymerization. In this connection, it should be pointed out that this result also specifies the change of the photophysical properties of TX-A. Previously, it was shown¹² that TX-A generates initiating species without requirement of an additional hydrogen donor. It is also interesting to note the effect of TX content in the macrophotoinitiator. A higher conversion was attained when the TX content was higher, indicating that the rate of initiation is proportional to the absorbed light and consequently to the amount of the TX functional side groups.

Among the several solvents tested in our experiments (Table 2), dimethylformamide (DMF) seemed to be the most suitable solvent for the photopolymerization initiated by PS-TX. Obviously, the situation is complex and two effects are combined. First, PS-TX dissolves in DMF better than the other solvents. Second, although radical polymerizations are not sensitive to the polarity of the solvent,³⁴ triplet-state lifetime of photoinitiators involving electron transfer such as TX derivatives may depend on some polarity effects.³⁵

We have also tested the polymerizability of styrene (S) monomer with PS-TX. In complete contrast to TX-A, polymerization of S with this macrophotoinitiator in the presence of TEA did not proceed. Although aromatic carbonyl/amine combinations represent an effective photoinitiator system for the polymerization of (meth)acrylates, they appear to be less reactive toward styrene monomers due to the high quenching rate of the monomer and the low reactivity of α -amino radicals with S.³⁶ This behavior is in accordance with the spectral findings indicating that PS-TX exhibits photochemical characteristics of typical aromatic carbonyl compounds.

**Figure 4.** Photo-DSC profile for polymerization of TPTA in the presence of TEA and PS-TX (27%) macrophotoinitiator, cured at 30 °C by UV light with an intensity of 180 mW/cm².**Figure 5.** Conversion vs time for polymerization of TPTA in the presence of TEA and PS-TX (27%) macrophotoinitiator, cured at 30 °C by UV light with an intensity of 180 mW/cm².

The efficiency of the PS-TX in the photocuring of formulations containing multifunctional monomers was also studied. In Figure 4, photo-DSC exotherm referring to the polymerization of 1,1,1-tris(hydroxymethyl)propane triacrylate (TPTA) containing PS-TX and TEA under polychromatic light is shown. Figure 5 displays a plot of the conversion vs irradiation time derived from Figure 4. The shape of this “conversion–time” kinetics curve indicates two stages: a rapid first stage followed by a slow stage. At the second stage, gelation and vitrification of the polymerizing trifunctional acrylate most likely render the diffusion of the components more difficult.

In conclusion, we have successfully combined 1,3-dipolar azide–alkyne [3 + 2] and thermoreversible Diels–Alder (DA) [4 + 2] click reactions for the synthesis of polymers bearing side-chain TX photoactive groups. One of the consequences of the method is that such modification causes a dramatic change in the photochemistry of the precursor TX-A. The obtained polymeric photoinitiators were shown to efficiently initiate the free radical polymerization of mono- and multifunctional monomers via type II mechanism. Generally, the in-situ double click chemistry strategy described here is simple and quantitative and may permit a wide range of derivatives of polymers with various functional groups to be prepared in high yields. Currently, this concept is being transferred to other functional groups, and results will be presented in the near future.

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