Macromolecules **1999,** *32,* 2173−2179

Trithianes as Coinitiators in Benzophenone-Induced Photopolymerizations

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Received September 29, 1998; Revised Manuscript Received January 27, 1999

ABSTRACT: A series of 1,3,5-trithiane derivatives, including α- and β-isomers of the methyl and phenyl derivatives, was investigated for use as coinitiators in benzophenone-induced photopolymerizations. To study the mechanism of the photoinduced production of initiating radicals, nanosecond laser flash photolysis was used. The rate constants for quenching the benzophenone triplet state by various trithianes and the associated quantum yields of ketyl-radical formation were determined. Photopolymerizations were carried out with a multifunctional methacrylate model monomer, and the progress of the polymerizations was followed by differential scanning calorimetry. The resulting plots showing the progress of the rates of polymerization and the conversions of double bonds were compared to the photochemical information for the various trithianes. It was found that the polymerization efficiency of the coinitiators did not follow the efficiency of photoinduced formation of the initiating radicals. The reasons for this lack of correlation were discussed in terms of how the hydrogen-donating ability of coinitiators and the reactivity of the radicals formed affected the various stages of the polymerization. Further studies with a cleavage-type photoinitiator in the presence of the trithianes lent supporting evidence for the role that the trithiane radicals play in the polymerization of the benzophenone/trithiane systems investigated in this work.

Introduction

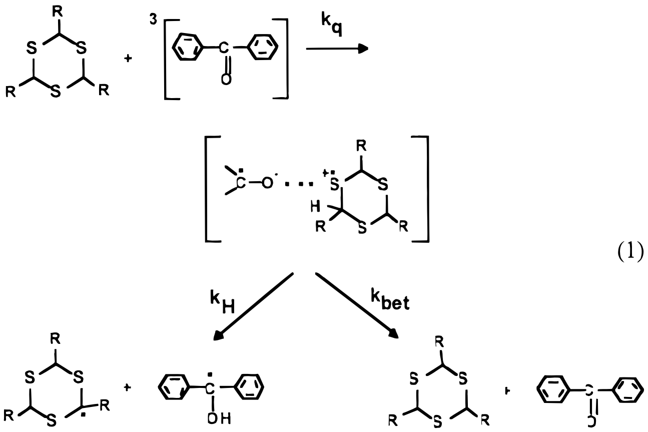
Photopolymerization of multifunctional monomers provides a simple method for the production of highly cross-linked polymers. Such dense polymer networks are resistant to solvent penetration and show enhanced mechanical and thermal stability. These properties, in conjunction with rapid curing of the formulations, have led to applications of these materials for the production of protective coatings (e.g. for optical fibers), dental fillings, and restorative materials, in microlithography, microelectronics, optical data storage, etc.[1,2]

Photoinduced radical polymerizations are usually performed in the presence of photoinitiators of the "cleavage" type (e.g., benzoin derivatives) or H-abstraction type (e.g., aromatic ketones). In the second class of reactions, e.g. with benzophenone (BP), initiation occurs mainly through hydrogen abstraction by ^{3}BP from the monomer and/or a coinitiator molecule, such as an ether, alcohol, or amine.[1,2] The initiating radical is derived from the hydrogen-donating molecule, whereas the ketyl radical that is formed can participate in the termination process.

Our previous studies showed that aliphatic sulfides can also be efficient coinitiators for BP-induced photopolymerizations.[3,4] A number of works has been devoted to the influence of aliphatic sulfides on the polymerization of multi(meth)acrylates both in the presence of photofragmenting initiators[4,5] as well as BP.[3,5] The effect of the sulfide group built into the monomer molecule has also been described.[6−10]

The activity of sulfides in photopolymerizations can range from low to high, depending on their hydrogen-donating ability. Moreover, aliphatic sulfides are also easily oxidized in air, leading to a reduction of oxygen inhibition with an activity comparable to that reached by aliphatic amines.[5] There are also additional advantages of using aliphatic sulfides as coinitiators: they increase the hydrophobicity of the product and improve its thermo-oxidative stability.[5]

Among the sulfides investigated (linear sulfides, sulfides containing other functionalities, cyclic dithioacetals) an exceptionally strong accelerating effect on BP-induced photopolymerization was shown by 2,4,6-trimethyl-1,3,5-trithiane (TMT).[3] A laser flash photolysis study showed that photoreduction of BP by TMT (the cis−cis isomer, R = CH_3 in eq 1) is very efficient and occurs by electron transfer from the sulfur atom to the BP triplet, followed by proton transfer:[11]



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10.1021/ma9815408 CCC: $18.00

Under the same conditions, simple aliphatic sulfides did not reduce BP.[12] In this case, the back electron transfer (k_{bet}) within the radical−ion pair formed was the main process. Thus, the main reason for the high activity of TMT had to be the large quantum yield of ketyl radical formation and an associated formation of initiating TMT radicals. This suggestion was confirmed by photopolymerization studies.[11] Polymerizations were sensitized by BP alone and by BP in the presence of the two simple sulfides, di-*n*-propyl sulfide and 2,2′-thiobisethanol, in addition to TMT. Butane-1,4-diol dimethacrylate (BDM) was used as the model monomer. The formation of initiating radicals can occur by the excited BP abstracting hydrogen from the additives and/or from the monomer itself. Under the conditions used, polymerization occurred only in the presence of TMT. This correlates well with the efficiency of the ketyl radical formation in the photoreduction of BP by TMT and simple sulfides. That means also that the formation of initiating radicals by direct hydrogen abstraction from the monomer used was not efficient.

These results prompted us to study other symmetrically substituted 1,3,5-trithianes as reducing agents for excited BP. Trisubstituted trithianes exist as two stereoisomers[13] whose activity in the photoreduction of BP may differ. The aim of this work was to study the primary photochemical reaction between BP and a series of 1,3,5-trithiane derivatives and to correlate their activity in photoreduction of BP with their efficiency as coinitiators in BP-induced polymerization.

Experimental Section

Benzophenone (BP) was obtained from Aldrich as the best available grade and was used without further purification. The 1,3,5-trithiane derivatives were synthesized from sodium thiosulfate or hydrogen sulfide and the corresponding aldehyde or ketone according to refs 14 and 15. They were purified by repeated crystallization. Tri(ethylene glycol) dimethacrylate (TEGDM) was purchased from Aldrich and 2,2-dimethoxy-2-phenylacetophenone (DMPA) from Ciba-Geigy. Acetonitrile (Fisher, HPLC grade) was used as received.

The nanosecond laser flash photolysis setup has been described generally elsewhere[16] and also as specifically configured in this work.[17] The concentration of benzophenone was 2×10^{-3} M in all experiments. The concentrations of trithianes were in the range 10^{-5}−10^{-3} M for the quenching experiments. However, the concentrations of these quenchers were 0.01 M in the quantum yield determinations and for the experiments that involved recording transient absorption spectra in the time range following complete quenching (>95%) of the BP triplet state. Transient absorption spectra and quantum yield measurements were performed using a flow-cell system. All solutions were deoxygenated by bubbling high-purity argon through them.

The polymerization kinetics was monitored under isothermal conditions at 40 ± 0.01 °C in a high-purity argon atmosphere (<0.0005% of O_2) by a differential scanning calorimeter (DSC 605 M, Unipan-Termal, Warsaw), equipped with a lid specially designed for photochemical measurements. The procedure was the same as that given in ref 7. Polymerization was initiated by a BP (0.06 M)−trithiane (0.02 or 0.04 M) system with radiation (366 nm) from a Hg medium-pressure lamp. From the heat flux measured by the DSC, the rate of polymerization (R_p) as a function of irradiation time was determined. By integration of this curve, the double-bond conversion (p) was also determined as a function of irradiation time. For computations, the heat of polymerization was taken to be 56 kJ/mol per double bond.

Results and Discussion

The trithianes investigated were 1,3,5-trithiane (TT), R = H; α-2,4,6-trimethyl-1,3,5-trithiane (α-TMT), R = CH_3; *β*-2,4,6-trimethyl-1,3,5-trithiane (*β*-TMT), R = CH_3; α-2,4,6-triphenyl-1,3,5-trithiane (α-TPT), R = C_6H_5; *β*-2,4,6-triphenyl-1,3,5-trithiane (*β*-TPT), R = C_6H_5; and 2,4,6-trimethyl-2,4,6-triphenyl-1,3,5-trithiane (TMTPT).

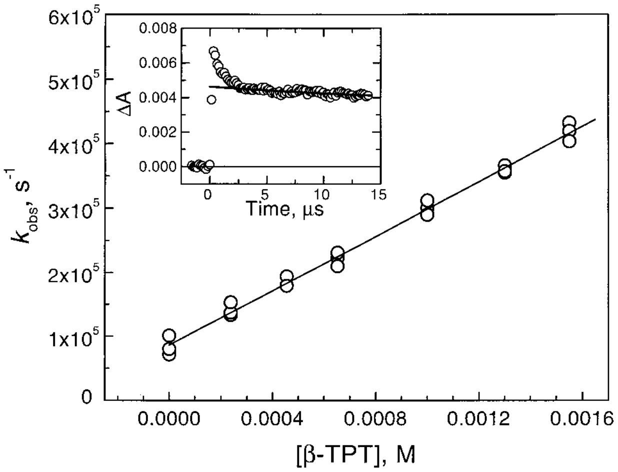
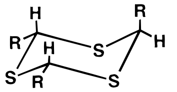
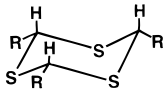


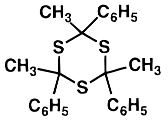
Figure 1. Stern−Volmer plot for the quenching of BP triplet state by *β*-TPT in acetonitrile. Insert: kinetic trace at 540 nm in the presence of 0.01 M *β*-TPT ([BP] = 2 × 10^{-3} M).



α−form (cis-trans)



β−form (cis-cis)



TMTPT

TMTPT exists only in the cis−trans form.

Benzophenone Photoreduction Study. Quenching of the BP triplet state by trithianes in acetonitrile was investigated by means of nanosecond laser flash photolysis. The quenching rate constants, k_q, were measured by monitoring the decays of the triplet−triplet absorption of BP at 520 nm. The concentration of BP was held fixed (2 mM), while the concentrations of trithianes varied over a range that reduced the lifetime of the triplet. The k_q values were determined by a linear least-squares fit of k_{obs} vs the quencher concentration plots by employing the formula

$$k_{obs} = (\tau_T)^{-1} + k_q[Q] \qquad (2)$$

where τ_T is the BP triplet-state lifetime in the absence of quencher, Q. An example of this method is illustrated in Figure 1, which shows the quenching of the BP triplet by *β*-TPT. The resulting rate constants k_q for all trithianes used are listed in Table 1.

In the case of the flash photolysis of benzophenone in the presence of TMT, it was shown recently[11] that the transient absorption spectra had spectral features reminiscent of the BP triplet and the ketyl radical, depending on the time delay. A typical spectrum of this type obtained 2.5 *μ*s after the flash is presented in Figure 2a, which shows the characteristic band of the ketyl radical at 545 nm with a shoulder around 520 nm.

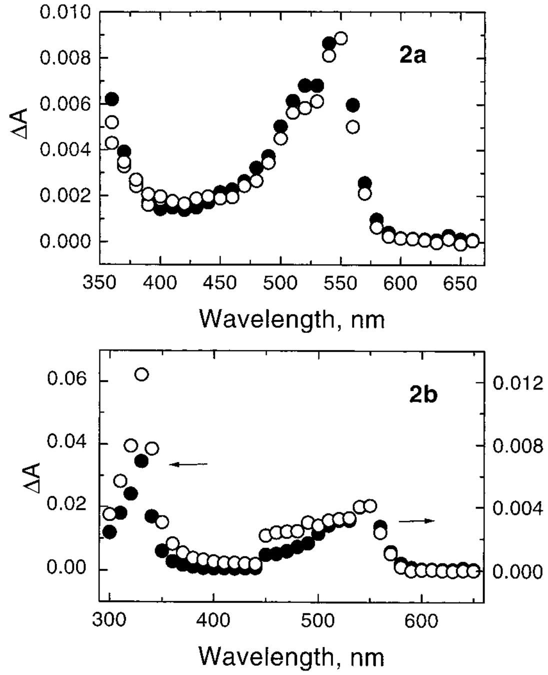


Figure 2. Transient absorption spectrum following quenching of the BP triplet state by *β*-TMT (0.01 M) (Figure 2a) and by *β*-TPT (0.01 M) (Figure 2b) in acetonitrile taken 2.5 *μ*s after the flash and the reference spectrum of BPH$^{\bullet}$ radical in acetonitrile (shown as ● ● ●).

Table 1. Rate Constants for Quenching of the BP Triplet (k_q) and Quantum Yields of Ketyl Radical Formation ($\Phi_{BPH^{\bullet}}$) during Photoreduction of BP by Trithianes in Acetonitrile

compound	k_q (M^{-1} s^{-1})	$\Phi_{BPH^{\bullet}}$
TT	$(2.5 \pm 0.1) \times 10^8$	0.28
β-TMT	$(4.2 \pm 0.4) \times 10^8$	0.62
α-TMT	$(3.4 \pm 0.2) \times 10^8$	0.53
β -TPT	$(2.1 \pm 0.1) \times 10^8$	0.81
α -TPT	$(1.6 \pm 0.1) \times 10^8$	0.32
TPTMT	$\leq 5 \times 10^6$	

A reference spectrum of the ketyl radical is also shown in Figure 2a; it is taken from ref 11 and normalized to the maximum of the BPH$^{\bullet}$ absorption.

The presence of an equivalent amount of α-alkyl thioalkyl radical (see reaction 1) was not observed for TMT and TT in the spectral range studied. However, the use of phenyl substituents in the trithiane ring (TPT) led to the formation of α-phenyl thioalkyl radicals that can absorb in the spectral region investigated. This is shown in Figure 2b for the *β*-TPT isomer, where the displayed spectral range has been truncated from the original data to illustrate how the quantum yields were determined from the spectrum. When the difference between the observed spectrum (open circles) and the ketyl radical was taken over the range 310−620 nm, there was a sharp maximum of $\Delta A \approx 0.03$ in the range of 310−320 nm. The strong absorption around 310−320 nm is reminiscent of the benzyl radical[18] and lends some support to the suggestion that the excess absorption between 300 and 500 nm is that of an α-phenyl thioalkyl radical.

The quantum yields of ketyl radical formation were determined for concentrations of trithianes large enough to quench 95% of the BP triplets. To measure the quantum yields, the relative actinometry method[19] was used. An acetonitrile solution of BP with no quencher was used as an actinometer. The experiments were performed in matched optical cells having identical absorption at 337 nm due to the presence of benzophenone. The quantum yields were determined using the following equation:

$$\Phi = \Delta A_p \epsilon_T / (\Delta A_T \epsilon_p) \qquad (3)$$

where ΔA_p is the ketyl radical's absorption change at 545 nm extrapolated to the end of the BP triplet decay and ΔA_T is the absorption change in the actinometer immediately after the flash due to the BP triplet (at 520 nm) under conditions of no quenching. $\epsilon_p = 3400$ M^{-1} cm^{-1} and $\epsilon_T = 6500$ M^{-1} cm^{-1} are the corresponding molar absorption coefficients of the ketyl radical and the BP triplet state, respectively.[20] Using this procedure, the quantum yields of ketyl radical formation for the reduction of BP by various trithianes were determined, and they are summarized in Table 1.

The quenching rate constants, which reflect the ability of trithianes to form radical-ion pairs with BP, are on the same order and are very close in value. The only exception is the hexasubstituted trithiane. The low value of k_q for TMTPT suggests that the attack of the carbonyl group of the excited BP on the lone electron pairs of the sulfur atoms in the trithiane ring is not likely to occur, probably due to steric hindrance (three bulky substituent groups on each side of the ring). That means also that methyl hydrogens in this compound are not sufficiently labile to be directly abstracted by excited BP. The steric factors can also influence k_q values of the remaining trithianes, since *β*-isomers always show higher quenching rate constants than α-isomers (see Table 1).

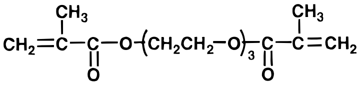
As can be seen in Table 1, the quantum yields of ketyl radical formation are rather high and decrease in the following order:

$$\beta\text{-TPT } (0.81) > \beta\text{-TMT } (0.62) > \alpha\text{-TMT } (0.53) > \alpha\text{-TPT } (0.32) > \text{TT } (0.28)$$

The quantum yields of ketyl radical formation are the highest for the *β*-isomers that have three bulky substituent groups on one side of the trithiane ring. Because the first step of the reaction is the attack of the BP triplet on the lone electron pairs of the sulfur atoms, we may conclude that this attack is determined by steric hindrance. This is of special importance in the case of phenyl substituents, where the change in configuration from the cis−cis to the cis−trans isomer drastically reduces radical formation.

The next step in the photoreduction is proton transfer within the radical-ion pair (k_H in eq 1). It is determined by the acidity of the hydrogens of the trithiane ring. The acidity is higher for phenyl-containing derivatives; therefore, radical formation is more effective for *β*-TPT than for *β*-TMT. Another factor that plays a role in determining acidity is the overlap of the sulfur orbitals and the C−H bond that is being broken. Such overlap is better for axial hydrogens. This gives an additional factor favoring radical formation in *β*-isomers, because they have all their hydrogen atoms axial to the trithiane ring. However, radical formation is also affected by the stability of the radical being formed. In the case of the unsubstituted trithiane, whose radical is not stabilized by substituents, its quantum yield is the lowest.

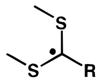
Photopolymerization Study. Photopolymerization studies were undertaken to compare the efficiency of radical formation by the trithiane−BP system with the ability of trithianes to accelerate the polymerization. As a model monomer, tri(ethylene glycol) dimethacrylate (TEGDM) was chosen. This monomer was chosen be-



$$CH_2{=}\overset{CH_3}{C}{-}\underset{O}{\overset{\|}{C}}{-}O{-}(CH_2CH_2{-}O)_3{-}\underset{O}{\overset{\|}{C}}{-}\overset{CH_3}{C}{=}CH_2$$

cause the BP-induced polymerization of TEGDM occurs much faster and efficiently than the polymerization of BDM, which we used previously.[11] This enables a more precise study of differences in the activities of the various trithianes. The polymerization was carried out in an inert atmosphere, to avoid the complicating influence of atmospheric oxygen. The unsubstituted trithiane was not checked as the coinitiator due to its very poor solubility.

In Figure 3 the results are given for the photopolymerization of TEGDM initiated by 0.06 M BP in the absence of any trithiane and also in the presence of 0.02 M trithianes. The system free of coinitiator is able to polymerize, and this is likely connected with a high concentration of monomer-derived $-CH_2O-$ groups in the polymerizing system. These groups can act as the reducing agent for excited BP, but the mechanism of radical formation does not involve electron transfer. The initiating radical has the following structure: $-C^{\bullet}HO-$. This scenario of how the photopolymerization takes place in the absence of coinitiators is supported by noting that, under the same conditions, polymerization does not occur with a monomer (BDM) that does not contain oxyethylene units.[11] In the presence of trithianes, generation of initiating radicals is enhanced by the formation of radicals of the type:



with an efficiency given by the quantum yields $\Phi_{BPH^{\bullet}}$ in Table 1. However, since the quenching rate constants by the trithianes are very similar, we can assume that the concentrations of $-C^{\bullet}HO-$ radicals are about the same in each of the polymerizing systems.

The presence of any of the four trithianes (α-TMT, β-TMT, α-TPT, or β-TPT) with hydrogens on the ring accelerates some aspect of the polymerization as compared to BP-induced polymerization in the absence of these trithianes. This is illustrated in Figure 3a by comparing the rates of polymerization without trithianes present to those with α-TMT, β-TMT, and β-TPT present. α-TPT accelerates the polymerization only at the very beginning of the reaction, but in later stages of polymerization, it suppresses the autoacceleration, lowering the maximum polymerization rate R_p^{max} and shifting it to longer times (see Figure 3a). A similar shift of R_p^{max}, observed in the presence of β-TPT, suggests that this isomer also suppresses the autoacceleration to a certain degree. However, its accelerating influence prevails.

Consideration of the order of the quantum yields in Table 1 suggests that the most active coinitiator should be β-TPT. However, the results presented in Figure 3 show that the ability of trithianes to increase the maximum polymerization rate R_p^{max} decreases in the following order:

$$\beta\text{-TMT} > \alpha\text{-TMT} > \beta\text{-TPT} > \text{no trithiane} \geq \alpha\text{-TPT}$$

Thus, the R_p^{max} values are higher for the β-isomers than for the α-isomers, and in addition, they are higher for the methyl-containing trithianes compared to the phenyl derivatives. These results do not correlate with the activity of the trithianes in BP photoreduction as measured by the quantum yields in Table 1. Polymerization occurs with the highest rate in the presence of β-TMT, not β-TPT, which has the highest quantum yield of ketyl radical formation among the trithianes in Table 1.

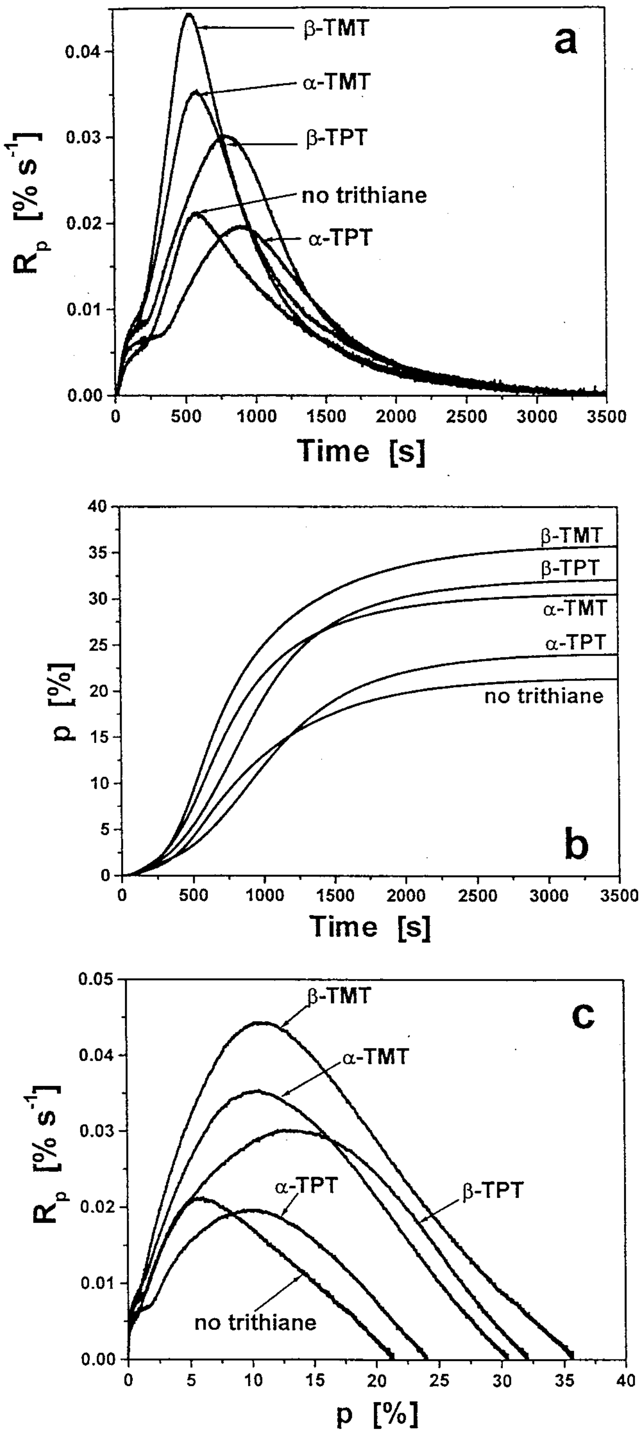


Figure 3. The kinetic curves of TEGDM polymerization initiated by 0.06 M BP in the presence of 0.02 M trithianes. Incident light intensity $I_0 = 1.1$ mW cm^{-2}. (a) Polymerization rate as a function of irradiation time, (b) double-bond conversion as a function of irradiation time, and (c) polymerization rate as a function of double-bond conversion.

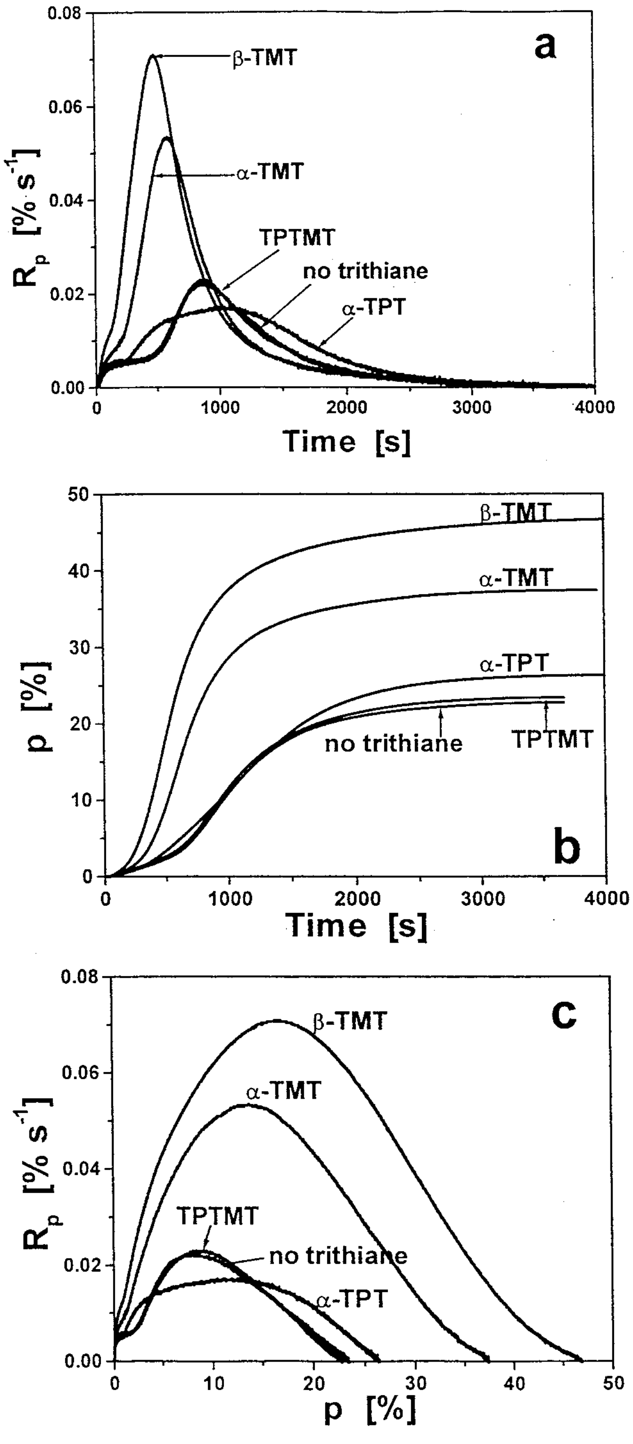
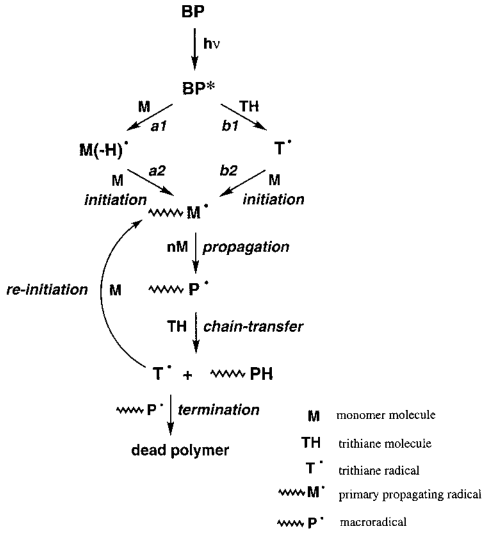


Figure 4. The kinetic curves of TEGDM polymerization initiated by 0.06 M BP in the presence of 0.04 M trithianes. I_0 = 0.9 mW cm^{-2}. (a) Polymerization rate as a function of irradiation time, (b) double-bond conversion as a function of irradiation time, and (c) polymerization rate as a function of double-bond conversion.

Scheme 1



An increase in the concentration of the trithianes from 0.02 to 0.04 M increases their influence on the course of the polymerizations (Figure 4). This is seen both in the acceleration of the polymerization in the presence of TMT as well as in the reduction of the maximum polymerization rate by α-TPT (Figure 4a). In addition, a comparison of the initial polymerization stages of the α-TPT curves (Figure 4c) shows that the increase in concentration of α-TPT leads to an earlier appearance of autoacceleration (namely, a shift in its onset from ≈2.5% with no trithianes to ≈1% of double-bond conversion for α-TPT). β-TPT at this higher concentration (0.04 M) could not be used due to its limited solubility. As expected on the basis of the lack of BP photoreduction by TMTPT, even relatively high concentrations of TMTPT do not influence the polymerization. This is consistent with the lack of ketyl radical formation in the attempted quenching of BP triplets by TMTPT (see Table 1). It also shows that the chain transfer (Scheme 1, see below) involving H-abstraction from the methyl groups of TMTPT is not efficient.

The lack of a direct correlation between the activities of the trithianes in BP photoreduction and the acceleration of the polymerization can be traced to two factors, the initiation rate and the chain-transfer reaction (see Scheme 1).

The initiation rate itself is not totally determined by only the efficiency of radical formation given by $\Phi_{BPH^\bullet}$ (path b1, Scheme 1); it also depends on the reactivity of the T• radicals formed (path b2, Scheme 1) and on the contributions from path a in the initiation process. From considerations above, it appears that contributions of path a to the initiation process is about the same in each polymerizing system. That leaves the reactivity of the trithiane radicals as the suspect component of the initiation process for spoiling the correlation under consideration. The determining property of the reactivity of the trithiane radicals appears to be their stability. All the trithianes used in this work form more or less stabilized radicals. The stability is influenced by the two sulfur atoms and the substituent, all being adjacent to the C-centered radical center. The higher the resonance stabilization of the unpaired electron, the lower the reactivity of the radical in the initiation of the polymerization. The TPT-derived radicals are highly stabilized by phenyl (electron-withdrawing) substituents that make them less reactive than the TMT-derived radicals with electron-donating alkyl substituents. This results in the lower initiation rates for the radicals with phenyl substituents. For initiating radicals coming from two trithiane stereoisomers, the radicals have the same structure at the radical site; thus, the main difference between the rates of initiation must come from the efficiency of formation of these initiating radicals (given by $\Phi_{BPH^\bullet}$). Despite the low reactivity of trithiane-derived radicals, the contribution of path b to the initiation of the polymerization is still significant due to much more efficient quenching of the BP triplet by trithianes than by ethers ($k_q \sim 10^6$ M^{-1} s^{-1}).[21]

The second factor spoiling the correlation is the chain-transfer reaction in which active coinitiators that possess labile hydrogen atoms can be involved. The overall effect of this reaction is to increase the mobility of the radical population. This overall increase in the mobility of the radicals enhances bimolecular termination, which leads to lower reaction rates and lower conversions. For multifunctional monomers, chain transfer also reduces the cross-link density (see below). Moreover, chain transfer transforms a part of the highly reactive propagating radicals into less reactive initiating radicals $T^{\bullet}$ having the same structure as radicals formed in the photochemical process (path b1). This additionally lowers the polymerization rate due to slow reinitiation.

From this scenario it can be seen that the influence of trithianes on BP-induced polymerizations is a combination of two opposing processes: acceleration of the initiation by their relatively efficient formation as initiating radicals and interference with efficient polymerization through their participation in the chain-transfer reaction.

The effect of the chain-transfer reaction can be isolated from that of initiation by addition of trithianes to a polymerizing system initiated by a "cleavage-type" photoinitiator. The results for TEGDM polymerization initiated by DMPA in the presence of various trithianes are given in Figure 5. Because of the very high efficiency of this photoinitiator, the molar ratio of DMPA:trithiane had to be as high as 1:10 to observe any slowing-down effect from the chain-transfer reaction involving the trithianes. From Figure 5 it can be seen that β-TMT lowers the polymeriztion rate only slightly. The largest effect is observed for α-TPT. This trend in slowing down the polymerization correlates very well with the activity found for these same trithianes as coinitiators. That means that the polymerization rate is determined mainly by the efficiency of the chain-transfer reaction.

The question why α-isomers lower the polymerization rate more than β-isomers arises. For instance, the reactivity of the radicals formed from both TPT isomers should be the same because of the conjugation of the unpaired spin with the phenyl group and the resulting planarity of the radical. The most likely explanation seems to be that there is a larger production of trithiane radicals in the chain-transfer reaction from the α-isomer (two axial, one equatorial hydrogen) compared to the β-isomer (three axial hydrogens). This effect is likely a consequence of the presence of the equatorial hydrogen atoms in the α-isomer being more readily abstractable by the growing macroradical than are the axial hydrogen atoms. For comparison, equatorial hydrogen atoms of trithianes are exchanged faster with deuterium atoms than are axial hydrogen atoms in the presence of strong bases.[22]

The time–conversion and conversion–polymerization rate curves (Figures 3b,c and 4b,c) show that all the trithianes, even α-TPT, increase the final conversion of double bonds (p^f) compared to BP-induced polymerizations in the absence of any trithianes. In general, as the rate of polymerization increases, the final double-bond conversion also increases, and the maximum rate of polymerization is shifted to higher conversions. This is a direct consequence of the coupling of volume relaxation with the polymerization kinetics.[23] At faster rates of polymerization, the macroscopic rate of volume shrinkage is much slower than the rate at which double bonds are consumed. If the system relaxes much slower than the rate of polymerization (which is often the case for photopolymerization of multifunctional monomers), an excess free volume is present in the system. This excess free volume results in greater mobility of the reacting species, which leads to a higher final double-bond conversion and a shift in the peak maximum of the rate to higher conversions.

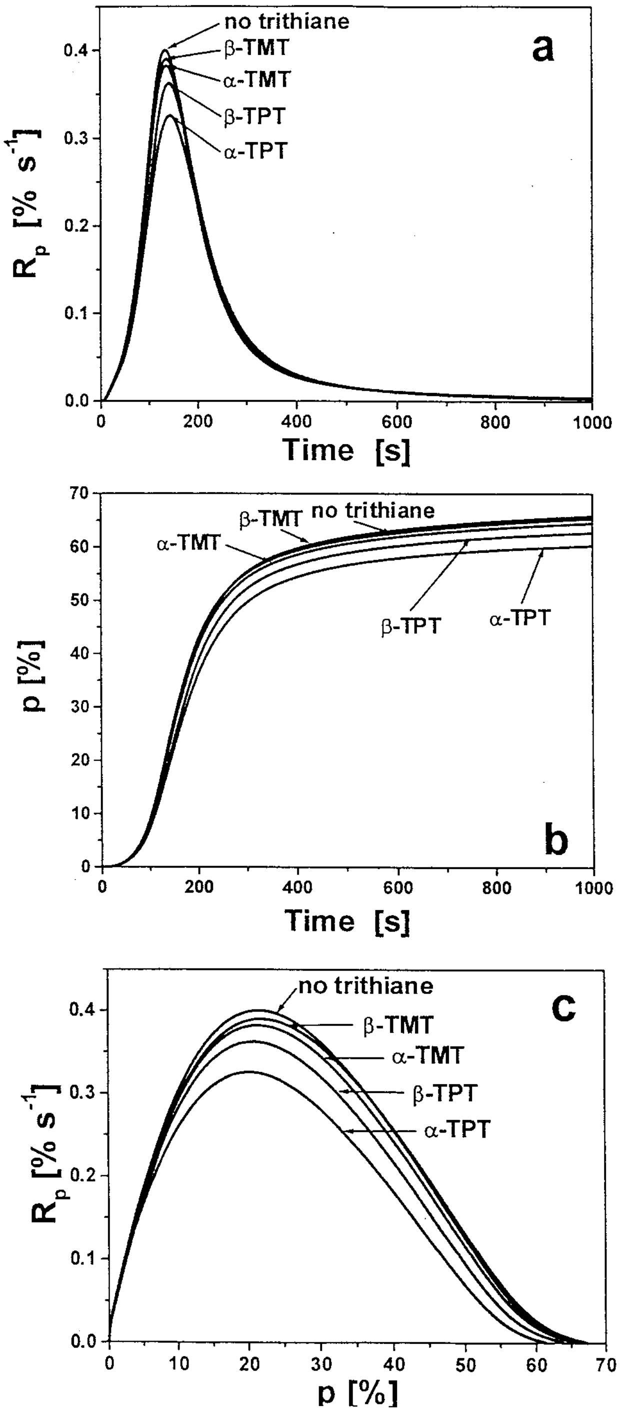


Figure 5. The kinetic curves of TEGDM polymerization initiated by 0.002 M DMPA in the presence of 0.02 M trithianes. $I_0 = 1.1$ mW cm^{-2}. (a) Polymerization rate as a function of irradiation time, (b) double-bond conversion as a function of irradiation time, and (c) polymerization rate as a function of double-bond conversion.

This picture is complicated by the occurrence of the chain-transfer reaction. As indicated earlier, trithianes intensify the chain-transfer process, which is more efficient in the presence of phenyl derivatives than other trithianes. Thus, the reduction of the cross-link density by TPT is greater. Decreasing cross-linking increases the free volume of the system at a given conversion and increases the mobility of the polymerizing system. The autoacceleration becomes less pronounced, resulting in lower R_p^{max}, which appears at somewhat higher conversion. As a consequence, the onset of autodeceleration (caused by dense network formation and vitrification effects that limit diffusion of reacting species) is shifted also to higher conversions. This enables the system to reach a higher p^f level. This may explain why in two cases, β-TPT vs α-TMT (Figure 3) and α-TPT vs no trithiane (Figures 3 and 4), somewhat higher conversions are reached at lower maximum polymerization rates.

Conclusions

The 1,3,5-trithiane derivatives are active coinitiators in benzophenone-induced photopolymerizations. Among the compounds investigated, the most efficient coinitiator is the trimethyl derivative: β-TMT isomer (cis−cis), whose reactivity significantly exceeds that of the α-isomer (cis−trans). Generally, the activity of trithianes in accelerating the BP-induced polymerization is a resultant of the efficiency of initiating radical formation (photochemical process, path b1 in Scheme 1), the reactivity of initiating radicals (path b2 in Scheme 1), and the influence of processes resulting from the chain transfer to coinitiators (Scheme 1). The photochemical process depends on electron transfer from the sulfur atoms to the benzophenone triplet and proton transfer within the radical-ion pair. This step of initiating radical formation is governed by steric factors and the acidity of the trithiane-ring protons. The subsequent polymerization steps depend on the resonance stabilization energy of the various trithiane radicals (determining their reactivity) and on the hydrogen-donating ability of the various trithiane derivatives (in the chain transfer to coinitiator).

Acknowledgment. The work described herein was supported by the Committee of Scientific Research Poland (E.A. and M.A. DS-32/282/98) and the Office of Basic Energy Sciences of the U.S. Department of Energy. This paper is Document No. NDRL 4099 from the Notre Dame Radiation Laboratory.

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MA9815408