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Photoinduced Cross-Linking Polymerization in the Presence of Aromatic Thiols

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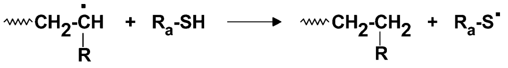
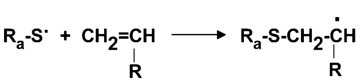
ABSTRACT: The aim of this work was to find the effect of two aromatic thiols (one heteroaromatic and one aromatic), efficient co-initiators in two-component photoinitiating systems, on the termination mechanism of a photoinduced polymerization occurring in stationary and nonstationary conditions. This task has been approached by modeling using two termination models: the *bimolecular termination model* and the *mixed termination model.* For the first time the influence of thiols was considered separately on the monomolecular and bimolecular termination. The effect of the thiols consisting in the increasing contribution of the second-order termination was assumed to reside in higher values of the bimolecular termination rate coefficient (k_t^b) in comparing to polymerization in the absence of thiol. On the other hand, the decreasing contribution of the first-order termination (considered as a significant decrease in the mobility and/or reactivity of radical sites) was assumed to be involved in lower values of the monomolecular termination rate coefficient (k_t^m). It was found that the presence of the thiol increases the contribution of the bimolecular termination and decreases the contribution of the monomolecular termination at the early polymerization stages. Monomolecular termination becomes less important as the contribution of the reaction diffusion in bimolecular termination increases.

Introduction

Thiols are used in many industrially important systems. Their application is often associated with the ability to act as chain-transfer agent. The mechanism of chain transfer, exemplified for a thiol, is shown in reactions 1 and 2. A growing polymer radical abstracts a hydrogen atom from the thiol giving a terminated polymer chain and a new initiating thiyl radical, which adds to the monomer producing a new propagation species.



$$\sim\sim\sim\mathrm{CH_2\text{-}}\underset{\mathrm{R}}{\dot{\mathrm{C}}\mathrm{H}} + \mathrm{R_a\text{-}SH} \longrightarrow \sim\sim\sim\mathrm{CH_2\text{-}}\underset{\mathrm{R}}{\mathrm{CH_2}} + \mathrm{R_a\text{-}S^{\bullet}} \qquad (1)$$



$$\mathrm{R_a\text{-}S^{\bullet}} + \mathrm{CH_2{=}}\underset{\mathrm{R}}{\mathrm{CH}} \longrightarrow \mathrm{R_a\text{-}S\text{-}CH_2\text{-}}\underset{\mathrm{R}}{\dot{\mathrm{C}}\mathrm{H}} \qquad (2)$$

The cross-link density of acrylate-based products can be effectively controlled by the chain-transfer agents with the function to terminate the molecular weight but not to destroy the radical site.[1]

Chain-transfer agents affect not only the molecular weight and molecular weight distribution of the resulting polymer but also the onset and the magnitude of the gel effect. At low conversion the chain-transfer reaction does not have a significant effect on the overall rate of polymerization; at high conversion the chain-transfer reaction affects both the onset of the gel effect and the increase of the polymerization rate in the autoaccelerated region.[2,3] Addition of thiols to the network-forming systems results in a delayed onset of reaction diffusion-controlled termination.[4,7] Thiols exert a much larger influence on the polymerization of methacrylates than of acrylates due to occurrence of inherent chain transfer on the acrylate backbone.[4−7]

Thiols have unusual properties in that although H$^{\bullet}$ may be abstracted very rapidly from S, the resulting thiyl radicals are highly reactive, notably, but not only, in abstracting H$^{\bullet}$. Such hydrogen transfers from and to sulfur compete effectively with other possible hydrogen abstractions and with radical recombination. They may lead to inhibition, or to change of products, as in photoreduction by alcohols.[8] Dodecanethiol has been most widely used as a model thiol in polymerization processes occurring with chain-transfer reactions, and the majority of literature data refers to this compound, e.g. refs 4−13. Sometimes also the influence of simple aromatic thiols, like thiophenol, was investigated.[6] However, considering the effect of thiols, one should take into account that the behavior and reactivity of thiyl radicals deriving from aliphatic and aromatic thiols differ substantially. The most important differences are the following: greater reversibility of arylthiyl (ArS$^{\bullet}$) radical addition to olefins than that of alkylthiyl radicals (RS$^{\bullet}$); low reactivity of ArS$^{\bullet}$ radical in H atom abstraction and very low reactivity toward molecular oxygen (the rate constant $<10^4$ M^{-1} s^{-1} in comparing to 10^7 M^{-1} s^{-1} for RS$^{\bullet}$ radical).[14]

Thiols are used as substrates in thiol−ene photopolymerization.[15−18] It is associated both with the ability of thiols to act as efficient chain-transfer agents as well as with ability to quench triplet states of type II photoinitiators with the formation of thiyl radicals:[19]

$$\mathrm{Ar_2CO} \xrightarrow{h\nu} \mathrm{Ar_2CO^{*}} \xrightarrow{\mathrm{RSH}} \mathrm{RS^{\bullet}} + \mathrm{Ar_2C^{\bullet}OH} \qquad (3)$$

Reaction 3 is enhanced by relatively low S−H bond dissociation energy. Thiyl radicals can be generated also

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via radicals produced by photolyzing a type I initiator reacting with the thiol.[15] The RS$^•$ radicals may then undergo addition to the olefinic double bonds forming carbon-centered radicals, which abstract hydrogen from the thiol continuing the chain process.

Due to the high ability of aromatic thiols to donate hydrogen atoms, some of them were used as co-initiators for hexaarylbis(imidazoles), notably heteroaromatic thiols: 2-mercaptobenzthiazole (MBT); 2-mercaptobenzimidazole; 2-mercaptobenoxazole (MBO).[20−25] MBO and MBT were also used in two- and three-component photoinitiating systems based on coumarin derivatives.[26] These thiols were able to initiate the photopolymerization without any photoinitiator but with low efficiency.[27] It was suggested that their presence in small amounts can accelerate acrylate polymerization induced by photofragmenting initiators mainly due to residual oxygen consumption.[27]

In our previous papers we showed that these heteroaromatic thiols (which do not have an unpleasant smell characteristic for thiols) may work as efficient co-initiators for excited camphorquinone (CQ) and isopropylthioxanthone (ITX). The activity of the (CQ or ITX)/thiol system in initiation of polymerization may be comparable to or even higher than the activity of the (CQ or ITX)/(aromatic amine) system and depends on the structure of the thiol.[28−31] The mechanism of initiation by these photoinitiating systems may involve electron transfer or direct hydrogen atom abstraction, depending on the thiol used.[31] Further work is in progress.

It is obvious that application of thiols as co-initiators has to affect, in a way, due to their chain-transfer ability, also the polymerization course. The aim of this work was to find the effect of two aromatic thiols (one heteroaromatic and one aromatic), efficient co-initiators in type II photoinitiating systems, on the termination mechanism of a photoinduced polymerization occurring in stationary (during illumination) and nonstationary (after stopping the irradiation, during the aftereffect) conditions. This task has been approached by modeling on the basis of experimental data. To eliminate the effect of the thiols resulting from the acceleration of the initiation process, the polymerization was initiated by a photofragmenting (type I) photoinitiator.

In this work, the termination process was considered as occurring simultaneously by two mechanisms: monomolecular and bimolecular ones. This concept was used for description of the termination during cross-linking polymerization[32−34] and was found to be especially successful in describing the postpolymerization process.[35−37] In this approach the bimolecular termination was assumed to occur via reaction between two radical centers, which meet as a result of usual translational/segmental diffusion or reaction diffusion (a process in which two radical centers move via propagation reaction). The rate of the process is given by

$$R_t^{\ b} = -\frac{d[P^•]}{dt} = 2k_t^{\ b}[P^•]^2 \tag{4}$$

where R_t^b is the rate of bimolecular termination, k_t^b is bimolecular termination rate coefficient, and [P$^•$] is radical concentration.

When physical diffusion becomes limited, reaction diffusion dominates the termination and the overall bimolecular termination rate coefficient k_t^b becomes proportional to the propagation rate coefficient k_p and the concentration of double bonds.

In the polymerization of multifunctional monomers, due to the network formation, the mobility of radicals connected to the network drastically decreases, which, together with shielding effects by the network, makes them inaccessible for further reaction. Thus, one may consider the occurrence of another way of termination—the monomolecular termination—in which radical centers do not decay but are eliminated from further reaction in a first-order process:

$$R_t^{\ m} = -\frac{d[P^•]}{dt} = k_t^{\ m}[P^•] \tag{5}$$

Here R_t^m is the rate of monomolecular termination and k_t^m is monomolecular termination rate coefficient.

In practice, this type of process describes radical trapping. However, in our approach, the monomolecular termination will involve all phenomena leading to such a decrease in the mobility and/or reactivity of radical sites that in the time scale registered by the experimental method used the bimolecular termination is not observed. Due to diffusional limitations on growing macroradicals this way of termination should become increasingly important as the degree of conversion increases.

The rate of the whole (mixed) termination process R_t^{mix} is the sum of the rates of the two processes, bimolecular and monomolecular ones:

$$R_t^{\ mix} = -\frac{d[P^•]}{dt} = 2k_t^{\ b}[P^•]^2 + k_t^{\ m}[P^•] \tag{6}$$

Depending on the reaction stage, either one of the two terms in eq 6 dominates or both of them are equally important.[36,37]

The effect of chain transfer to an additive being an active chain-transfer agent on the polymerization is proposed to enhance the termination,[11,38] mainly due to an increase in mobility of terminating radical sites.[4−6,11] It is generally accepted[38] that the majority of termination events occurs by the reaction between a long and a short macroradical and the chain transfer provides more short, mobile radicals. As a result, k_t^b should be enhanced because diffusion of shorter chains is faster than that of longer chains. At conversions where termination of chains connected to the network is greatly inhibited due to their relative immobility, the active radical site can be transferred to the transfer agent. Thus, the macroradical may be terminated by another molecule which forms a new, short chain that is easily terminated by virtue of being highly mobile.[11]

One may expect that an increase in mobility of reacting species by chain transfer may reduce contribution of the first-order termination increasing in this way the contribution of the second-order termination. However, in the literature, the chain-transfer reaction is considered as influencing the whole termination process during the polymerization, without differentiation on the influence on the reaction between two radicals and on monomolecular deactivation.[4−6,11] In the work presented, we tried to separate these two effects. The effect of thiols consisting in the increasing contribution of the second-order termination was assumed to reside in higher values of the bimolecular termination rate coefficient in comparing to polymerization in the absence of a thiol. On the other hand, the decreasing contribution of the first-order termination would be involved in lower values of the monomolecular termination rate coefficient. We assumed that chain-transfer reaction does not affect the propagation rate coefficient.

Photopolymerization of multifunctional monomers occurs with a marked postcuring effect. After the irradiation has been interrupted, the photoinduced reaction continues to proceed with diminishing rate to a significant conversion. The aftereffect (postpolymerization) is used for determination of propagation and termination rate coefficients, most often from the following equation:[39-44]

$$\frac{[\mathrm{M}]_t}{(R_\mathrm{p})_t} = \frac{2k_\mathrm{t}^{\,\mathrm{b}}}{k_\mathrm{p}}\, t + \frac{[\mathrm{M}]_0}{(R_\mathrm{p})_0} \qquad (7)$$

Here [M] is the double bond concentration, the subscript 0 denotes the polymerization parameters at the beginning of the dark period, and the subscript t denotes the parameters after a time t for the dark reaction.

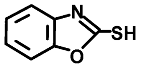
The data obtained during the aftereffect of a photoinduced process in which the illumination of the reacting system was stopped at various degrees of double bond conversion was used for calculations in this work.

After discontinuation of the illumination, the polymerization conditions change rapidly. The mobile short-chain radicals mainly responsible for the bimolecular termination are no longer being generated, and the entire living population of macroradicals is growing longer, which causes a rapid drop in their mobility and affects the termination (the possibility of the bimolecular reaction). As a result, $k_\mathrm{t}^{\mathrm{b}}$ rapidly decreases with the increase in conversion in the dark.[45,46] Thus, whereas during stationary conditions a single value of $k_\mathrm{t}^{\mathrm{b}}$ corresponds to each monomer conversion, under nonstationary conditions $k_\mathrm{t}^{\mathrm{b}}$ becomes a function of time because of its chain-length dependence.[13] In turn, the monomolecular termination rate coefficient, $k_\mathrm{t}^{\mathrm{m}}$, which represents a fraction of radicals immobilized in the polymer network (eliminated from further reaction) per unit of time, should increase with time of dark reaction.[37] The only way of formation of short-chain radicals becomes the chain-transfer reaction. Thus, the addition of thiols should influence also the kinetics of postpolymerization process.

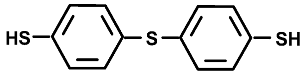
In this work we used a calculation procedure, in which the propagation and termination rate coefficients, determined form three termination models (eqs 4−6), were averaged over increasingly large time of the dark reaction (and corresponding conversion in the dark),[37] i.e., to first 10, 20, 30 s, etc., of the dark reaction starting invariably at the moments of discontinuation of illumination. Changes in rate coefficients should reflect changes in termination mechanism occurring as the time of the dark reaction is protracted. The values obtained for the shortest time interval (10 s) were taken as the rate coefficients during continuous illumination. This procedure was repeated for each series of postpolymerization processes (for given polymerization conditions) occurring after the light was cut off at various double bond conversions. In this way the results of calculations allowed us to determine the influence of the thiol on the termination mechanism at various degrees of double bond conversion and at various stages of the dark reaction.

Experimental Section

The thiols investigated were a heteroaromatic thiol, 2-mercaptobenzoxazole (MBO, Aldrich), and an aromatic thiol, 4,4′-thiobis(benzenethiol) (MAS, Aldrich).

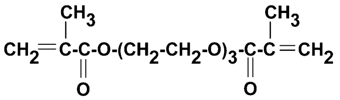


MBO



MAS

The monomer was triethylene glycol dimethacrylate (TEGDM) from Aldrich. It was purified by column chromatography before use. Ethyl (4-(dimethylamino)phenyl)benzoate



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

TEGDM

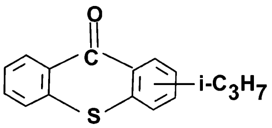
(EDAB) was purchased from Aldrich.

Reaction rate (R_p) profiles and conversions (p) were determined by isothermal differential scanning calorimetry. A DSC 605M (UNIPAN-TERMAL, Warsaw, Poland) instrument equipped with a lid especially designed for photochemical measurements was applied. Throughout the experiments the DSC unit was operated isothermally at 40 ± 0.01 °C. The 10-mg samples were polymerized in open aluminum pans with the diameter of 6.6 mm. The DSC chamber was purged with argon of high purity (<0.0005% of O_2) for 10 min prior to irradiation to remove oxygen from the chamber and that dissolved in the sample.

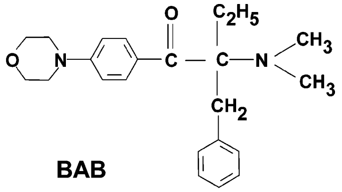
For measurements of the aftereffect the polymerization was initiated with UV light (wavelength: 366 nm) from a medium-pressure Hg lamp in the presence of 2-benzyl-2-(dimethylamino)-1-(4-morpholinophenyl)butan-1-one (BAB, Ciba, $\lambda_{\max}$ = 320 nm) used at a concentration of 0.001 M (about 0.034 wt %). The low initiator concentration was dictated by the necessity of working at low polymerization rates, which enabled stopping the initiation at low degrees of conversion (as low as 1%).

The initiating light intensity was 1.3 mW/cm^2 at the sample pan position. After a chosen reaction time, the irradiation of the sample was interrupted by closing the shutter and the polymerization in the dark was monitored. Examples of kinetics data obtained for the aftereffect have been shown in Figure 1.

When the thiols were used as co-initiators, the polymerization was initiated by ITX (Aldrich, $\lambda_{\max}$ = 385 nm) and by the light of a halogen lamp (Phillips 500 W GY 9,5, total light intensity 415 mW/cm^2).



ITX



BAB

Calculations

The TEGDM polymerization was analyzed using three termination models, which assume that the termination occurs only by radical trapping (*monomolecular termination model*, model I), only in a bimolecular process (*bimolecular termination model*, model II), or simultaneously by these two mechanisms (*mixed termination model*, model III).[32-35,44] They are described by eqs 4−6, respectively. The experimental data for calculations were obtained from postpolymerization processes, which were registered after stopping the irradiation at various degrees of double bond conversion

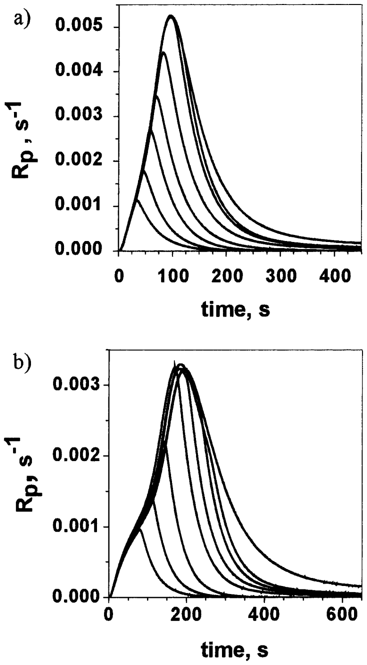


Figure 1. Rate of polymerization vs time for seven different dark reactions during the TEGDM polymerization: (a) in the absence of any thiol, with the light cut off at 0.020, 0.040, 0.074, 0.109, 0.165, 0.232, and 0.367 of double bond conversion; (b) in the presence of 0.06 M MAS, with the light cut off at 0.042, 0.084, 0.142, 0.248, 0.309, 0.380, and 0.471 of double bond conversion. The upper curves correspond to the polymerization under continuous illumination.

(called *starting conversion*). This enabled to estimate polymerization rate coefficients as a function of conversion of double bonds.

The termination models were used in forms given by eqs 8−10. They describe the polymerization occurring in the absence of initiation, i.e., in the dark.[32−35,44]

Monomolecular termination model (model I):

$$-\ln(1-p_{\rm d}) = \frac{k_{\rm p}}{k_{\rm t}^{\rm m}}[{\rm P}^\bullet]_0(1-\exp(-k_{\rm t}^{\rm m}t)) \qquad (8)$$

Bimolecular termination model (model II):

$$-\ln(1-p_{\rm d}) = \frac{1}{2}\frac{k_{\rm p}}{k_{\rm t}^{\rm b}}\ln(1+2[{\rm P}^\bullet]_0k_{\rm t}^{\rm b}t) \qquad (9)$$

Mixed termination model (model III):

$$-\ln(1-p_{\rm d}) = \frac{1}{2}\frac{k_{\rm p}}{k_{\rm t}^{\rm b}}\ln\left(1+2[{\rm P}^\bullet]_0\frac{k_{\rm t}^{\rm b}}{k_{\rm t}^{\rm m}}(1-\exp(-k_{\rm t}^{\rm m}t))\right) \qquad (10)$$

Here k_p is the propagation rate coefficient, $[P^\bullet]_0$ is the macroradical concentration at the beginning of the dark period, t is time from the start of the dark reaction, and p_d is the degree of double bond conversion in the dark.

It should be noted that eq 9 corresponds to fully integrated form of eq 7.

Calculations were performed without steady-state assumption; thus, the following parameters were determined: k_t^b/k_p (model II); k_t^m (model I); both k_t^b/k_p and k_t^m (model III). To find their dependence on the time of the dark reaction, the postpolymerization curves were divided into segments corresponding to time intervals of 10 s. The parameters k_t^m, $k_t^b[P^\bullet]_0$, and $k_p[P^\bullet]_0$ were calculated from models I−III at various duration of postpolymerization (10−300 s at 10-s increments) starting invariably at the moments of discontinuation of illumination. Thus, the propagation and termination rate coefficients were averaged over increasingly large dark conversion corresponding to first 10, first 20, first 30 s, etc., of the dark reaction. In this way, $[P^\bullet]_0$ was always constant for a given dark reaction.[37] Such a procedure enables the kinetic parameters calculated for increasingly longer times of dark reaction to be compared. Application of statistical analysis enabled us to find the model that best fits to the experimental data indicating the dominating type of termination mechanism (monomolecular, bimolecular, or mixed) during the considered time of dark reaction. This procedure was repeated for each postpolymerization process.

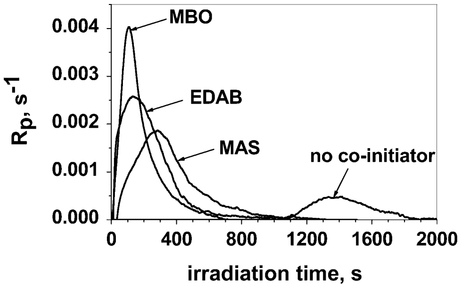


Figure 2. Polymerization rate R_p as a function of irradiation time for TEGDM photopolymerization initiated by ITX (0.06 M) in the presence of MBO (0.06 M), EDAB (0.06 M), and MAS (0.03 M) and in the absence of any co-initiator.

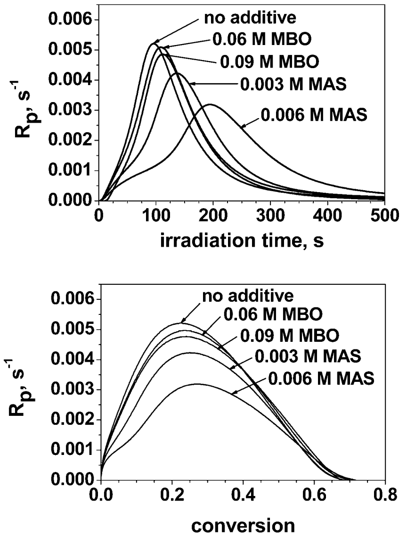


Figure 3. Effect of aromatic thiols on the TEGDM photopolymerization initiated by the photofragmenting initiator (0.001 M) in the presence and in the absence of various amounts of MBO and MAS.

The parameters of the models I−III (eqs 8−10) were calculated by the nonlinear least-squares method. The sampling rate was five experimental points/s; thus, the number of experimental points increased with time of the dark reaction. The residual variance calculated for the models determined over various periods of dark reaction was very low, in the range 10^{-5}−10^{-9}, depending on the number of experimental points and the model used. For instance, for the starting conversion 0.029 (the example shown in Results and Discussion in Figure 4) the residual variance changed in model II from 2.56×10^{-9} (for the first 10 s) to 1.26×10^{-6} (the first 100 s) and in model III from 1.33×10^{-9} (for the first 10 s) to 5.62×10^{-5} (the first 100 s).

The significance of each model was tested using the following test function:

$$F_{\mathrm{calc}} = s_{\mathrm{reg}}{}^2/s_{\mathrm{res}}{}^2 \qquad (11)$$

Here $s_{\mathrm{reg}}{}^2$ is a variance of the regression function and $s_{\mathrm{res}}{}^2$ is the residual variance.

The calculated value of F_{calc} was compared with a critical value F_{crit} from F-Snedecor tables for (N - 2) and 1 degrees of freedom (N denotes the number of experimental points) and at a confidence level $\alpha = 0.05$. In each case the calculated values of the test function, depending on the model used and the number of experimental points, were in the range $10^{3-}10^5$. In the example presented above, the test function was equal to 3×10^5 and 1.4×10^4 for 10 and 100 s of the dark reaction, respectively (model II), and to 2.9×10^4 and 1.4×10^3, respectively, in the case of model III. Such high values of the test function indicate that independently of the number of experimental points taken for calculations all the models considered were statistically significant.

To find the model that fits best to the experimental data and indicates the type of the termination mechanism, a method described by Draper and Smith was used.[47] According to this method a comparison of three models (I–III) has been drawn. Because model III may be considered as the "full" model, then the two other models arise from the reduction of the mixed one. This means, that models I and II are nested in model III. The values of the test function of model III were high (in the range 10^4–10^6) indicating the significance of the model.

In the next step the significance of the parameters of the model III was tested using t-Student distribution function.[47] When the test indicated that the termination rate coefficient associated with one of the models was insignificant, it was assumed that the experimental data were best described by the other model. When both termination rate coefficients in model III were statistically significant, the models were compared in pairs (III with I and III with II). The comparison was based on variance analysis and assumed verification of the models and their parameters on the basis of the following statistics:

$$F'_{\mathrm{calc}} = \frac{s_{\mathrm{mix}}{}^2 - s_{\mathrm{simple}}{}^2}{s_{\mathrm{mix}}{}^2} \qquad (12)$$

Here $s_{\mathrm{mix}}{}^2$ and $s_{\mathrm{simple}}{}^2$ are residual variances of the mixed termination model and the simple (monomolecular or bimolecular termination) model, respectively.

The calculated value of F'_{calc} was compared with a critical value F_{crit} from F-Snedecor tables for 1 and (N − 3) degrees of freedom and at a confidence level $\alpha = 0.05$. If $F'_{\mathrm{calc}} < F_{\mathrm{crit}}$, the compared models are statistically identical. It means that the influence of the term corresponding to one of the simple models (I or II) is unimportant. If models I and III are statistically identical, the bimolecular termination is unimportant; if models II and III are statistically identical, the contribution of the first-order reaction to the overall termination process can be omitted. On the other hand, if model I or II and model III are not statistically identical in pairs, both the first-order and the second-order reaction are important. Thus, the termination mechanism is represented by model III.

Because of complexity of processes described by rate coefficients included in models I–III, these parameters are not true reaction rate constants but coefficients characteristic for a mathematical model proposed. Their dependence on conversion of double bonds gives rather qualitative picture of processes, which lead to elimination of radicals from further reactions at various stages of the reaction.

Results and Discussion

Aromatic Thiols as Co-initiators. Figure 2 depicts reaction rate profiles of TEGDM polymerization reflecting the activity of the investigated thiols (MBO and MAS) as co-initiators for ITX. For comparison, the rate profile obtained in the presence of an aromatic amine, EDAB, is also shown. EDAB, due to its high efficiency, is widely used as co-initiator in type II initiating systems, in this number with ITX.[19]

The role of a co-initiator is the production of initiating species in the reaction with excited initiator molecule (e.g. reaction 3). In the case of thiols the initiating species are thiyl radicals. In the absence of any co-initiator, the hydrogen donor molecule is a monomer itself; in the TEGDM molecule the source of abstractable hydrogens is the three oxyethylene units. Very low polymerization rate in the absence of any co-initiator must result from the fact that ethers react efficiently only with n,π* electronic transition states of carbonyl group, whereas the lowest excited triplet state of ITX has essentially π,π* character.[19]

An addition of the investigated co-initiators increases significantly the polymerization rate due to efficient photoreduction of ITX*. The highest increase in the maximum polymerization rate $R_{\mathrm{p}}{}^{\mathrm{max}}$ was observed in the presence of the heteroatomatic thiol, MBO, which efficiency surpassed the efficiency of the aromatic amine, EDAB. Somewhat lesser increase in the polymerization rate was observed in the presence of MAS (to keep the same concentration of SH groups, the concentration of this compound was twice reduced in comparing to MBO and EDAB). However, the final result depends not only on the efficiency of initiating radical formation but also on the reactivity of initiating radicals and the influence of processes resulting from the presence of strong hydrogen-donating molecules. In this work we tried to find out how far these latter processes may affect the efficiency of the thiols as co-initiators.

More information on initiation of photopolymerization by type II initiators in the presence of a series of heteroaromatic thiols is given elsewhere.[31]

Effect of Aromatic Thiols on the Polymerization Rate and Conversion. The polymerization was initiated by the type I photoinitiator, BAB, in the concentration of 0.001 M. The thiol concentration was the following: MAS, 0.003 and 0.006 M (about 0.07 and 0.14 wt %, respectively); MBO, 0.06 and 0.09 M (about 0.8 and 1.25 wt %, respectively). As can be seen in Figure 3, both investigated thiols reduce the maximum polymerization rate $R_{\mathrm{p}}{}^{\mathrm{max}}$ and retard the autoacceleration. The final degree of conversion, p^{f}, remains almost unaffected, which is consisted with the literature data.[6]

Possible additional heat effects, which could affect the polymerization exotherms (and the calculated polymerization rates) would be negligible. The rough estimation of the heat evolved during 100% addition[48] (this case will never occur in our systems) of the 0.09 M thiol to the monomer to the whole reaction heat assuming only 70% of double bond conversion gives only 2.32%, which is within the experimental error observed in this work (about 3%). The contribution of the heat from another possible reaction, hydrogen abstraction, would amount to no more than 2%. Thus, we assumed that the exotherms practically reflect polymerization rates.

The effect of MBO on the polymerization rate and conversion is very low. Whereas an addition of 0.003 M MAS causes a marked decrease in the polymerization rate, in the case of MBO any visible decrease in the polymerization rate is achieved when the thiol concentration is about 20 times higher. On the other hand, the influence of MAS is so strong that it causes an appearance of a shoulder on the kinetic curves at the low conversion range, which is associated with a strong suppression and delay of the autoacceleration. This points to a strong acceleration of termination which, in relation to the gel effect, is controlled by diffusion of the shortest radical chains present in reasonable number.[11]

According to theory,[38] the chain-transfer agent does not influence the polymerization rate when the reinitiation rate coefficient (k_{re}) is close to the propagation rate coefficient. If $k_{re} < k_p$, the polymerization is retarded and reduction of the polymerization rate depends on the chain-transfer constant. If the chain-transfer constants were the same for MBO and MAS, then the polymerization rate would be a measure of the reaction rate of the derived thiyl radicals with the monomer. The results obtained may suggest that reinitiation by MBO-derived radicals is fast at the thiol concentration similar to those used for MAS, whereas by MAS-derived radicals is retarded. However, the chain-transfer constants to MBO and MAS are probably different. The chain-transfer constant of poly(methyl methacrylate) propagating radical to 2-mercaptobenzthiazole (MBT) has been determined to be 1.56,[20] whereas to benzenethiol it is 4.7 and to *p*-toluenethiol it is 7.4.[49] If chain-transfer constant to MBO is similar to that to MBT and that of MAS similar to that to benzenethiol derivative, MAS should influence the polymerization much stronger. Both the possible slow reinitiation and higher chain-transfer constants will increase the possibility of the reaction between $RS^{\bullet}$ radical and another radical center and, as a result, the bimolecular termination.

Although the main side reaction during the polymerization in the presence of thiols is the chain transfer, also hydrogen abstraction by initiating radicals may be important. However, both MBO- and MAS-deriving radicals must reinitiate the polymerization efficiently, since they are the main initiating radicals in the above-described process induced by the two-component systems. The fact that MAS may serve as co-initiator for ITX* despite its retarding effect proves that formation of $RS^{\bullet}$ radicals in the reaction between MAS and ITX* is more efficient than in the reaction between the monomer and ITX*. This may be associated with higher quenching rate constants of ITX* by aromatic thiols than by the monomer.

Effect of Aromatic Thiols on the Termination Mechanism. The consideration of the effect of thiols on the termination mechanism was based on the analysis of the conversion dependence of the rate coefficients k_t^b/k_p and k_t^m calculated from postpolymerization data according to the termination models.

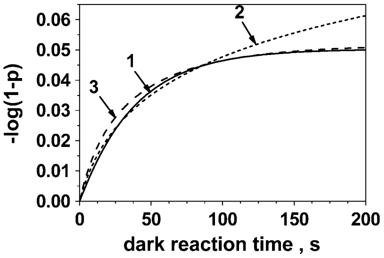


Figure 4. Kinetics of the aftereffect of TEGDM polymerization in the presence of 0.003 M MAS. The light has been cut off at 2.9% of double bond conversion. Key: 1, experimental data; 2, bimolecular termination model prediction (model parameters: $k_p[P^{\bullet}]_0 = 1.7845 \times 10^{-3}\ s^{-1}$; $k_t^b[P^{\bullet}]_0 = 8.3698 \times 10^{-2}\ s^{-1}$); 3, mixed termination model prediction (model parameters: $k_p[P^{\bullet}]_0 = 2.1520 \times 10^{-3}\ s^{-1}$; $k_t^b[P^{\bullet}]_0 = 6.7549 \times 10^{-2}\ s^{-1}$; $k_t^m = 1.6586 \times 10^{-2}\ s^{-1}$). The parameters were determined over 100 s of the dark reaction.

The statistical analysis showed that all the models used describe the postpolymerization satisfactorily. This analysis performed for increasingly large dark conversions indicated also that, in each case considered, at the beginning of postpolymerization the experimental data were best described by model II. This fact means that the termination occurred mainly via a bimolecular reaction. However, at longer times of the aftereffect, the statistical analysis showed the mixed termination model (model III) to yield the best fit to the experimental data, indicating the occurrence and the increasing importance of the monomolecular termination (considered as significant reduction of radical center mobility). An example of the correlation between the experimental data and the model calculations is shown in Figure 4.

Because the rate coefficients were averaged over increasingly long time intervals of the dark reaction and during the shortest times of the dark reaction the bimolecular termination dominated, statistical analysis could never indicate the first-order process to be the main termination mechanism, despite its importance at higher conversions and later dark reaction stages. Thus, in this paper we present only the results obtained by the use of models II and III. Our approach provides insight into changes in the termination mechanism (changes in termination rate coefficients) under the influence of the chain-transfer reaction at various stages of the polymerization and at various stages of the aftereffect.

The statistical analysis showed that in the absence of thiols bimolecular reaction was the main (but not exlusive) termination mechanism until about 80−100 s of the dark reaction. In reality, the dominance of the mixed termination begins at shorter times than indicated by statistical analysis. The procedure of calculations used in this work, which averages the termination rate coefficients over increasingly long times of dark reaction, always include a period of time where bimolecular termination dominates. Thus, at a degree of conversion in the dark where according to the procedure used the mixed termination becomes the main mechanism of termination, in reality the contribution of the monomolecular reaction is already significant.

The appearance of the dominance of the mixed process in the presence of thiols was shifted to longer times by about 10−20 s, which suggests that the presence of the chain-transfer agent increases the mobility of the reacting species.

Effect of Thiols on the Bimolecular Termination. The comparison of the k_t^b/k_p ratios calculated from

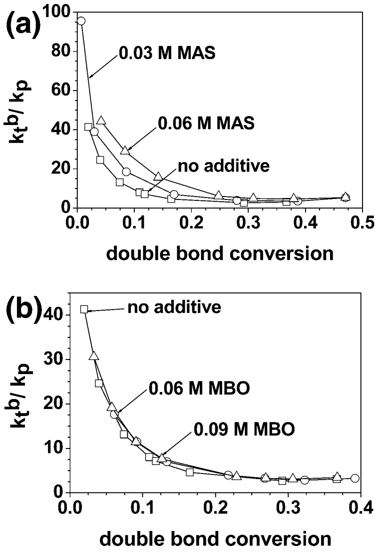


Figure 5. Conversion dependence of k_t^b/k_p ratios calculated from model II, averaged over the first 80 s of the dark reaction, in the absence and presence of MAS (a) and MBO (b). Initiator concentration: 0.001 M. The points on curves correspond to double bond conversions at which the irradiation has been interrupted.

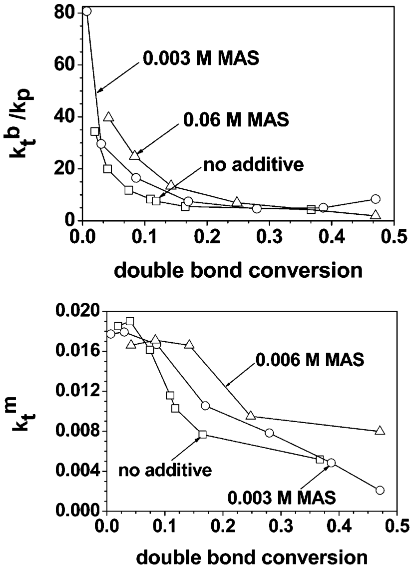


Figure 6. Conversion dependence of k_t^b/k_p ratios and k_t^m values calculated from model III, averaged over 120 s of the dark reaction in the presence and absence of MAS. The points on curves correspond to double bond conversions at which the irradiation has been interrupted.

model II for the polymerization of TEGDM carried out in the presence and absence of thiols is shown in Figure 5.

The plots represent the conversion dependence of the rate coefficients averaged over the 80 s of the dark reaction (and the corresponding conversion increment), where still the bimolecular termination dominated. Qualitatively the same result was obtained for shorter periods of the dark reaction.Although during the time of the dark reaction the conversion increased, for the simplicity the rate coefficients were related to conversions at the moment of stopping the irradiation. The relationship of the k_t^b/k_p ratios with the whole conversion (during irradiation and in the dark) gives qualitatively the same result.

The dependence of k_t^b/k_p ratios on conversion shows, as described in ref 44, a rapid drop from the beginning of the reaction and then a tendency to plateau, when the reaction diffusion begins to dominate the bimolecular termination.

As can be seen in Figure 5a, the addition of MAS to TEGDM increases the values of k_t^b/k_p ratios, the more, the higher is the concentration of the additive. The difference between k_t^b/k_p ratios in the absence and presence of the thiol decreases as the conversion increases and becomes very small (but still exists) at the plateau level, from conversions close to those at which maximum polymerization rate appears (compare Figure 3). This means that when the reaction diffusion begins to dominate the bimolecular termination, the effect of chain transfer decreases and becomes less important at higher conversion degrees. Thus, the effect of the thiols may result mainly from the shift of the reaction diffusion dominated termination to higher conversions (delayed drop of k_t^b/k_p ratios). An analogous conclusion was obtained in ref 4 on the basis of the observation of the behavior of reaction diffusion parameter. It was suggested that the change in the plateau level, although small, indicates that changes in the kinetic chain length initiated at early polymerization stages still influence the reaction kinetics, even when it is controlled by the reaction diffusion.

The effect of MBO on TEGDM polymerization, despite 10 times higher thiol concentration, is much less pronounced (Figure 5b). At such a high thiol concentration the frequency of termination events is expected to be strongly enhanced, which would lead to a considerable increase in k_t^b and a decrease of the polymerization rate. However, this effect may be reduced by the high reactivity of the thiyl radical (in this case MBO-derived) due to the rapid reinitiation or lower chain-transfer constant to MBO. In the case of less reactive thiyl radicals and/or their higher concentration (in the presence of MAS) the probability of the meeting of another radical and the reaction between them increases, which accelerates the bimolecular termination.

Effect of Thiols on the Mixed Termination. A discussion of the influence of thiols on the mixed termination mechanism must take into account both changes in the k_t^b/k_p ratio as well as changes in k_t^m values. This information can be obtained using model III. The model assumes a significant contribution of the two termination mechanisms and can be used for conditions were monomolecular termination is important, i.e., at later stages of the dark reaction.[36,37]

The contribution of the monomolecular termination becomes increasingly important as the dark reaction proceeds. Statistical analysis showed that the mixed mechanism begins to dominate in the termination when calculations were performed (and the rate coefficients averaged) over about 90 (MBO) ÷ 120 s (MAS) of the dark reaction. Beginning from these durations of the aftereffect, we were able to calculate both k_t^m as well as k_t^b/k_p ratios using model III.

The results of calculations are shown in Figures 6 and 7. The k_t^b/k_p ratios show the same conversion dependence as described above, i.e., a shift of the plateau region to higher conversions. Again the influence of MAS on the k_t^b/k_p ratio was significant and that of MBO practically negligible.

An important information was obtained from the conversion dependence of k_t^m. According to expectations, the contribution of the monomolecular termination should increase with the conversion degree. In reality

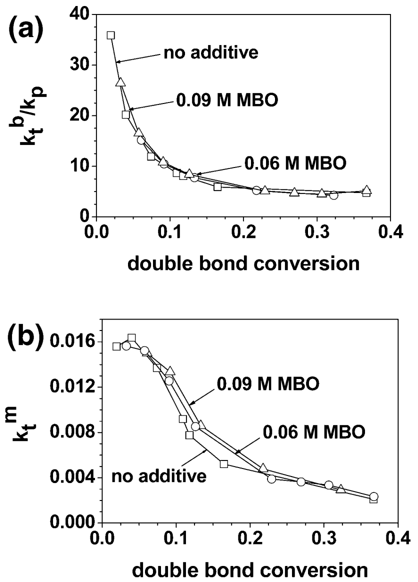


Figure 7. Conversion dependence of k_t^b/k_p ratios and k_t^m values calculated form model III, averaged over 100 s of dark reaction in the in the presence and absence of MBO. The points on curves correspond to double bond conversions at which the irradiation has been interrupted.

(Figures 6 and 7) we observe only a very short stage at the beginning of the reaction where k_t^m slightly increases. After that a rapid drop of k_t^m occurs, which is followed by a stage with much slower changes.

In our approach the monomolecular termination is considered as a significant slowing down of diffusion of macroradicals, which precludes the reaction between two radical centers in the time scale registered by DSC or such a reduction of the reaction rate between two radical centers that it is not registered by DSC (in the case of strongly delayed reinitiation). As can be seen in Figures 6 and 7, the beginning of the rapid drop of k_t^m corresponds to conversions at which the decrease of k_t^b/k_p ratios comes to the end and a plateau begins to form. This may suggest that the influence of monomolecular termination considered as slowing down of macroradical diffusion decreases as the contribution of the reaction diffusion control in bimolecular termination increases. It is reasonable when taking into account that the termination is a chain length dependent process but only to conversion at which the rapid drop of k_t^b is halted. Thus, because physical diffusion is no longer a limiting factor, the influence of monomolecular termination and hence k_t^m decreases.

It was expected that the addition of thiols will enhance the bimolecular termination at the cost of the monomolecular one. Thus, k_t^m should decrease with increasing concentration of the chain-transfer agent. It was really observed but again only at low conversion degrees (Figures 6 and 7). In the region of the rapid drop of k_t^m, an apparent inversion of the influence of the thiol is observed: at the same conversions k_t^m is higher in the presence of the thiol. In reality the beginning of the drop of k_t^m values is shifted to higher conversions, which must be associated with a delayed dominance of reaction diffusion in bimolecular termination.[4] It is worthy to note that at conversion degrees at which the rapid drop of k_t^m begins, the values of k_t^b/k_p ratios of the all compositions are very similar (Figures 6 and 7).

In the presence of MAS the beginning of the rapid drop of the k_t^m value shifts to markedly higher conversions than in the presence of MBO, for which this effect is small but clearly visible.

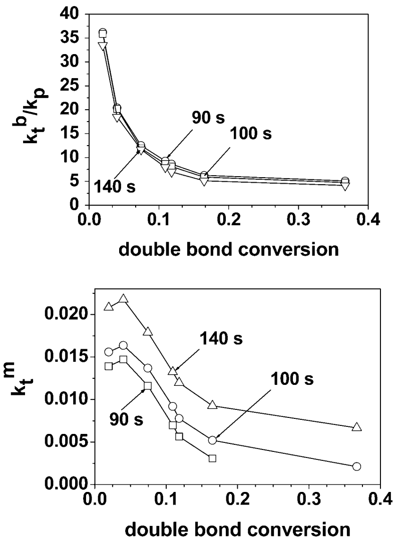


Figure 8. Dependence of k_t^b/k_p ratios and k_t^m values on conversion, averaged over 90, 100, and 140 s of the dark reaction. The points on curves correspond to double bond conversions at which the irradiation has been interrupted.

The decrease in k_t^m values becomes less rapid starting from conversions somewhat lower than those at which maximum polymerization rates occur. At this polymerization stage, the thiol-containing compositions show somewhat higher k_t^m values than in the absence of the thiol. This result is rather unexpected. One of the effects of thiols on the polymerization may be delayed reinitiation, and one can speculate that the mixed termination model “feels” the slow reinitiation as a monomolecular termination. The slow reinitiation would relate mainly to MAS since the plots showing the k_t^m behavior at the stage of its slower change in the presence of various amounts of MBO practically overlap. The explanation of the described effect needs further work.

In the above considerations the effect of thiols at various conversion degrees was discussed with respect to conversions reached during the continuous illumination, which in this work were indicated by conversions at which the illumination has been stopped. However, as stated previously, during the dark reaction the termination mechanism changes from the bimolecular to the mixed one. Thus, the reaction parameters should change continuously as the dark reaction proceeds: k_t^b decreasing and k_t^m increasing. This situation is visualized in Figure 8.

The values of k_t^b/k_p ratios slightly decrease with the increase in time (and conversion) of the dark reaction, which indicates that the contribution of the bimolecular termination and k_t^b decrease. On the other hand, k_t^m rapidly increases, independently on the conversion of stopping the irradiation. This may prove that the termination by reaction diffusion lags behind with rapidly changing conditions in the dark, i.e., with drop in radical concentration and increase in the kinetic chain length.

Conclusions

In the work presented, the influence of thiols on the termination mechanism was for the first time considered separately for the bimolecular and the monomolecular (considered as a significant decrease in the mobility and/or reactivity of radical sites) processes. The results of mathematical modeling using experimental data obtained in nonstationary conditions showed that thiols accelerate the bimolecular termination and reduce the monomolecular one at early polymerization stages but also may apparently enhance the monomolecular termination at higher conversions.

The changes in rate coefficients observed in the presence of various amounts of the heteroaromatic thiol, MBO, indicate that this thiol only slightly influences both mono- and bimolecular termination, which points to the high reactivity of the derived thiyl radical and/or to relatively low chain-transfer constant to MBO. On the other hand, the effect of the aromatic thiol, MAS, on the mono- and bimolecular termination is significant. Thus, lower activity of MAS as co-initiator for type II initiating system in comparing to MBO may result at least in part from retardation of the polymerization by this thiol.

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References and Notes

(1) Woods, J. G. In *Radiation Curing Science and Technology*; Pappas, S. P., Ed.; Plenum Press: New York, 1992; Chapter 9, p 333.

(2) Cardenas J. N.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 1883.

(3) Cardenas J. N.; O'Driscoll, K. F. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 2097.

(4) Berthold, K. A.; Hacioğlu, B.; Lovell, L.; Nie, J.; Bowman, C. N. *Macromolecules* **2001**, *34*, 5103.

(5) Berthold, K. A.; Lovestead, T. M.; Bowman, C. N. *Macromolecules* **2002**, *35*, 7968.

(6) Lovell, L.; Bowman, C. N. *Polymer* **2003**, *44*, 39.

(7) Berchtold, K. A.; Lovell. L. G.; Nie, J.; Hacio_lu, B.; Bowman, C. N. *Polymer* **2001**, *42*, 4925.

(8) Stone, P. G.; Cohen, S. *J. Am. Chem. Soc.* **1980**, *102*, 5686.

(9) Matsumoto, A.; Mitomi, D.; Aota H.; Ikeda, J. *Macromol. Rapid Commun.* **1999**, *20*, 365.

(10) Matsumoto, A.; Mitomi, D.; Aota H.; Ikeda, J. *Polymer* **2000**, *41*, 1321.

(11) O'Neil, G. A.; Torkelson, J. M. *Macromolecules* **1999**, *32*, 411.

(12) De La Fuente, J. L.; Madruga, E. L. *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 170.

(13) Buback, M.; Barner-Kowollik, C.; Egorov, M.; Kaminsky, V. *Macromol. Theory Simul.* **2001**, *10*, 209.

(14) Ito, O. In *The chemistry of free radicals. S-centered radicals*; Alfassi, Z. B., Ed.; John Wiley & Sons: New York, 1999; Chapter 6, p 193.

(15) Jacobine, A. F. In *Radiation Curing in Polymer Science and Technology*; Fouassier J. P., Rabek, J. F., Eds.; Elsevier Applied Science: London, 1993; Vol. 3, Chapter 7, p 219.

(16) Morgan, C. R.; Magnotta, F.; Ketley, A. D. *J. Polym. Sci., Polym. Chem. Ed.* **1977**, *15*, 627.

(17) Davidson S. *Exploring the Science, Technology and Applications of U.V.; E.B. Curing*; SITA Technology Limited: London, 1999.

(18) Hoyle, C. E.; Cole, M.; Bachemin, M.; Kuang, W.; Kalyanaraman, V.; Jonsson, S. *Photoinitiated Polymerization*; Belfield, K. D., Crivello, J. V. Eds.; ACS Symposium Series 847; American Chemical Society: Washington, DC, 2003; Chapter 5, p 52.

(19) Rabek, J. F. *Mechanisms of Photophysical Processes and Photochemical Reactions in Polymers. Theory and Applications*; Wiley: Chichester, New York, Brisbane, Toronto, Singapore, 1987; Chapter 5, p 169.

(20) Eaton, D. F.; Horgan, A. G.; Horgan, J. P. *J. Photochem. Photobiol., A: Chem.* **1991**, *58*, 373.

(21) Krongauz, V. V. In *Processes in Photoreactive Polymers*; Krongauz, V. V., Trifumac, A. D., Eds.; Chapman & Hall: New York, 1995; Chapter 5, p 185.

(22) Kaji, M.; Hidaka, T. Papers and Posters presented at the RadTech Europe'99, Vincentz: Berlin, Nov 8−10, 1999; 393.

(23) Urano, T.; Ishikawa, M.; Sato, Y.; Itoh, H. Papers and Posters presented at the RadTech Europe'99, Vincentz: Berlin, Nov 8−10, 1999; 745.

(24) Urano, T. Conference Proceedings, RadTech Europe 2001, Basel, Oct 8−10, 2001; 195.

(25) Caspar, V. C.; Khudyakov, I. V.; Torro, N. J.; Weed, G. C. *Macromolecules* **1995**, *28*, 636.

(26) Allonas, X.; Fouassier, J. P.; Kaji, M.; Miyasaka, M.; Hidaka, T. *Polymer* **2001**, *42*, 7627.

(27) Krongauz, V. V.; Chawla, Ch. P. *Polymer* **2003**, *44*, 2871.

(28) Andrzejewska, E.; Zych-Tomkowiak, D.; Andrzejewski, M. *Polimery* **2000**, *45*, 639.

(29) Andrzejewska, E.; Andrzejewski, M.; Socha, E.; Zych-Tomkowiak, D. *Dent. Mater.* **2003**, *19*, 501.

(30) Zych-Tomkowiak, D.; Andrzejewska, E. *The VIIth International Symposium "Chemistry Forum 20001", Conference Proceedings*; Warsaw University of Technology, K2: Warszawa, 2001; 70.

(31) Andrzejewska, E.; Zych-Tomkowiak, D.; Andrzejewski, M. *RadTech Europe 2003, Conference Proceedings*, Vincentz: Berlin, Nov 3−5, 2003; 565.

(32) Andrzejewska, E.; Bogacki M. B. *Macromol. Chem. Phys.* **1997**, *198*, 1649.

(33) Andrzejewska, E.; Bogacki M. B.; Andrzejewski, M.; Tyminska, B. *Polimery (Warsaw)* **2000**, *45*, 502.

(34) Andrzejewska, E. *Macromol. Symp.* **2001**, *171*, 243.

(35) Bogacki M. B.; Andrzejewska, E.; Andrzejewski, M. *Polimery (Warsaw)* **2001**, *46*, 721.

(36) Andrzejewska, E.; Bogacki M. B.; Andrzejewski, M. *Macromol. Theory Simul.* **2001**, *10*, 842.

(37) Andrzejewska, E.; Bogacki, M. B.; Andrzejewski, M.; Janaszczyk, M. *Phys. Chem. Chem. Phys.* **2003**, *5*, 2635.

(38) Barner-Kowollik, C.; Vana P.; Davis T. P. In *Handbook of Radical Polymerization*; Matyjaszewski, K., Davis, T. P., Eds.; Wiley-Interscience: New York, 2002; p 201.

(39) Tryson, G. R.; Shulz, A. R. *J. Polym. Sci., Polym. Phys. Ed.* **1979**, *B17*, 2059.

(40) Decker, C. *Prog. Polym. Sci.* **1996**, *21*, 593.

(41) Rabek, J. F. In *Radiation Curing in Polymer Science and Technology*; Fouassier, J. P., Rabek, J. F., Eds.; Elsevier Applied Science: London, 1993; Vol. I, Chapter 7, p 329.

(42) Timpe, H.-J.; Strehmel, B. *Macromol. Chem.* **1991**, *192*, 771.

(43) Anseth, K. S.; Wang, C. M.; Bowman, C. N. *Macromolecules* **1994**, *27*, 650.

(44) Andrzejewska, E. *Prog. Polym. Sci.* **2001**, *26*, 605.

(45) O'Shaughnessy B.; Yu, J. *Macromolecules* **1998**, *31*, 5240.

(46) O'Shaughnessy B.; Yu, J. *Phys. Rev. Lett.* **1998**, *80*, 2957.

(47) Draper N. R.; Smith, H. *Applied Regression Analysis*, 2nd ed.; Wiley: New York, 1981.

(48) Andrzejewska, E.; Andrzejewski, M.; Malinowska, M. *Research works of Institute of Organic Technology and Plastics of Wrocław University of Technology, No. 52, Series: Conferences, No. 25*; Wrocław University of Technology: Wrocław, 2003, p 524.

(49) *Polymer Handbook*, 3rd ed., Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989.

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