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# Chain length dependent termination in radical cross-linking polymerization

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**Abstract**

The work presents an evidence in support of chain length dependent termination during cross-linking polymerization. It is based on the behavior of the ratio of the bimolecular termination coefficient $k_t^b$ to propagation rate coefficient $k_p$ during the after-effect of a photo-induced polymerization. The chain-length dependence was manifested by a decrease of the $k_t^b/k_p$ ratio with the increase in dark reaction time faster than that resulting from the conversion increase. Two monomethacrylate/dimethacrylate and one dimethacrylate/dimethacrylate systems were chosen, which enabled to study the chain-length dependence as a function of cross-link density of the polymer being formed and physical properties of the initial composition. The ratios of the polymerization rate coefficients $k_t^b/k_p$ were calculated for various postpolymerization processes as a function of dark reaction conversion using the mixed termination model (concerning the bimolecular and monomolecular termination occurring parallel). A rapid drop of the $k_t^b/k_t$ ratio during the dark reaction was observed at the beginning of the after-effect and in slightly cross-linked systems suggesting a significant chain length dependence, but when the cross-link density increased with conversion or with cross-linking agent concentration in the feed, the drop of the $k_t^b/k_t$ ratio became much slower indicating that the chain length dependence decreased.

*Keywords:* Kinetics of cross-linking polymerization; Chain length dependent termination; After-effect

## 1. Introduction

The termination process during radical polymerization has received significant attention over the past several decades. From the kinetic point of view, termination is the most complicated reaction occurring in free-radical polymerization [1], thus the detailed mechanism remains the subject of much controversy [2].

The factor, which is responsible for the complicated nature of the termination process, is its strong diffusion dependence. It is accepted that propagation is chemically controlled in an extended conversion range and the propagation rate coefficient, $k_p$, is independent on the physical properties of the polymerization medium (e.g. viscosity) at this conversion range [3]. In such a case diffusion control of the propagation step might be neglected at low and moderate conversion and come into play only at very high degrees of monomer conversion. On the other hand, the reaction of radical–radical termination is diffusion controlled from the very beginning of polymerization and thus may depend on the physical properties of the reaction medium, such as medium viscosity, chain length (its distribution) of macroradicals, their diffusivity and segmental mobility, the polymer concentration (monomer conversion), the type of solvent, etc. [3–5].

The linear chains formed during the polymerization of monovinyl monomers have various lengths, which result in differences in their mobilities. Thus, the bimolecular termination rate coefficient, $k_t^b$, may vary with the chain length of the reacting radical species, so it is chain length dependent. The chain length dependence of $k_t^b$ is normally quantified by the following equation from which macroscopic $k_t^b$ values may be obtained by the averaging procedure [5]:

$$k_t^b = \frac{\sum_i \sum_j k_t^{i,j}[P_i^\bullet][P_j^\bullet]}{\left(\sum_i [P_i^\bullet]\right)^2} \qquad (1)$$

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where $k_t^{i,j}$ corresponds to the individual termination rate coefficients involving two free macroradicals with the chain lengths $i$ and $j$ and $[P^\bullet]$ is radical concentration.

The chain length dependence of the macroscopic $k_t^b$ is usually described by a power-law model:

$$k_t^b = k_t^{b0} i^{-\alpha} \tag{2}$$

where $i$ denotes the average chain length of the radicals (it is proportional to the number average degree of polymerization) and $\alpha$ is the exponent controlling the degree of chain length dependence [1,2,4–9].

The most facile termination reaction occurs between two relatively short chains whereas two longer entangled chains exhibit the slowest termination rate [5,10]. The most probable termination occurs between one short and one long macroradical. Thus, the $k_t^b$ in classical Eq. (3) for the bimolecular termination rate $R_t^b$ denotes an average value:

$$R_t^b = -\frac{d[P^\bullet]}{dt} = 2k_t^b[P^\bullet]^2 \tag{3}$$

The methods for probing the effect of kinetic chain length on the kinetics involve the manipulation of polymerization conditions such as changes in the initiator concentration or an addition of a chain-transfer agent.

The dependence of the termination rate coefficient of linear systems on various factors, including the chain length dependence, has been recently reviewed and discussed [1,5, 9,11].

The experimental methods for measuring the chain length and conversion dependence of $k_t^b$ in linear polymerizations involve laser-based techniques [5,12]; the single-pulse—pulsed-laser polymerization allows for measuring $k_t^b$ over a wide range of monomer conversion [4,9]. Recently, novel methods were introduced which allow for determination of chain length dependent $k_t^b$ from RAFT polymerization (using DSC to monitor the reaction rate) [13–15] and from ATRP process [16].

The chain-length dependence was recently discussed also for the propagation rate coefficient $k_p$ [17–19]. The experimental results indicate that chain length dependence of $k_p$ needs to be considered at low chains lengths [18] although a long-range dependence can also exist [19].

One of the consequences of the diffusional limitations on the bimolecular termination is its conversion dependence. The bimolecular termination rate coefficient of the linear polymerization high at the beginning of the process is controlled by segmental diffusion and is generally chain length independent and almost constant in value. However, it rapidly drops down by several orders of magnitude when becomes translational diffusion controlled and the gel effect begins [5]. When the mobility of radical chain ends becomes strongly limited the only way of movement of radical sites becomes the propagation reaction through unreacted double bonds, so-called reaction diffusion. Reaction diffusion was defined as the diffusive motion of the polymer chain-end radical as a result of propagation [1]. Under such conditions, the termination rate coefficient becomes to be almost independent on the chain length and thus, on conversion degree. Due to its dependence on propagation, the rate coefficient for termination by reaction diffusion, $k_{t,RD}^b$, is proportional to the rate coefficient for propagation and the amount concentration of double bonds $[M]$ with the proportionality constant-reaction diffusion parameter $C_{RD}$. So, the overall termination rate coefficient, $k_t^b$, is given by Refs. [20–24]:

$$k_t^b = k_{t,D}^b + k_{t,RD}^b \tag{4}$$

where $k_{t,D}^b$, is termination rate coefficient for diffusion controlled termination.

For linear systems, reaction diffusion becomes particularly important at high conversion where chains are practically immobile. During the time interval $t_D$ required for center-of-mass diffusion of the polymeric coil to displace over a distance, which is comparable to coil size, the increase in chain length by propagation is significant [3].

In cross-linking polymerization, network formation highly affects the termination process. As the large polymer chains become entangled or cross-linked in the network, center-of-mass diffusion is dramatically suppressed. Thus, reaction diffusion becomes the dominant termination mechanism from the relatively low conversion degrees [25,26] and the effect of chain length should diminish.

The bimolecular termination rate coefficient, $k_t^b$, rapidly decreases just from the beginning of the network formation which results from dramatic drops in the mobility of radicals and double bonds connected to the network. When the reaction diffusion begins to control the termination, $k_t^b$ reaches a region of a much slower change and then begins again to decrease due to the drop in the propagation rate coefficient $k_p$, which becomes also diffusion-limited [27]. Thus, the ratio of the two coefficients at first rapidly decreases with the increase in conversion and then tends to reach a plateau in the range of dominance of reaction diffusion. Reaction diffusion parameter $C_{RD}$ shows similar conversion dependence.

Although many papers were devoted to the chain length dependence of the termination kinetics in linear systems, the cross-linking systems were rather not considered. This might result form the fact that in network-forming systems the majority of radicals is incorporated into the network, so their reactivity should not be affected by the chain length. Additionally, as stated above, the chain length independent termination mechanism, reaction diffusion, begins to dominate at much lower conversions that in the case of linear polymerization.

However, recently some works appeared, in which the chain length dependence of the termination process has been shown to occur also in cross-linking systems and the corresponding models were developed [28–32]. In these works the kinetic chain length was varied by changing the initiation rate and via the addition of a chain transfer agent. Its influence on termination was determined by changes in exponent $\alpha$ in the equation $R_p \propto R_i^{\alpha}$ [29–31], where $R_p$ denotes polymerization rate and $R_i$ denotes the initiation rate. When the polymerization kinetics are not considered as a function of the kinetic chain length, or the kinetic chain length does not affect significantly the kinetics, $\alpha$ takes the classical value 0.5. In the case of chain length dependence $\alpha < 0.5$ and increases with conversion until reaching the classical value. Based on the results of modeling of diethylene glycol dimethacrylate photopolymerization it was suggested that the chain length distribution is most important at low conversions; at moderate conversions, where reaction diffusion begins to control termination, there is a transition region with decreased mobility where $k_t^b$ becomes independent of chain length and at still higher conversions termination becomes fully dominated by reaction diffusion.

The effect of the chain length should be especially important during the after-effect (postpolymerization). The after-effect is observed when a polymerization is initiated by light and after a time the irradiation is interrupted. Then the reaction, which was induced by light continues to proceed in the dark with a diminishing rate and can reach a significant conversion.

However, in the dark, the polymerization conditions drastically change, which immediately affects the termination rate coefficient. Under stationary conditions (during irradiation), at the early and medium polymerization stages, the bimolecular termination is dominated by reactions involving newly formed mobile short-chain radicals able to react with themselves or with macroradicals connected to the network. In non-stationary conditions (in the dark) the formation of short-chain radicals is abruptly stopped. The entire living population is growing longer (including the short-chains not terminated before) and mobilities of macroradicals are dropping rapidly [33]. As a result, $k_t^b$ rapidly decreases with the increase in conversion in the dark [33,34]. Only a small fraction of living chain radicals is able to terminate in bimolecular reaction; it becomes smaller, as the conversion (dark reaction time) increases. Thus, whereas during quasi-stationary conditions a single value of $k_t^b$ corresponds to each monomer conversion, under non-stationary conditions it becomes a function of time because of its chain length dependence [3]. The variations of termination rate coefficient in linear polymerization under non-stationary conditions at different degrees of monomer conversion were investigated [3].

The time dependence of the termination rate coefficient during the after-effect should be observed also for a cross-linking polymerization. This effect will be mitigated by the reaction diffusion which contribution increases with the conversion degree, and will highly depend on the cross-link density. In our earlier works [35,36] we indicated on the possibility of chain length dependence of termination rate coefficient during the after-effect of a dimethacrylate polymerization.

The aim of the present work was to show the chain length dependence of termination at various cross-link densities of the polymer being formed and at various physical properties of initial compositions using the postpolymerization as a probing method.

The model monomers were: dodecyl methacrylate (DDM), ethylene glycol dimethacrylate (EGDM), triethylene glycol dimethacrylate (TEGDM) and 2,2-bis[4-(2-hydroxy-3-methacroyloxypropoxy)phenyl]propane (bis-GMA). The investigated systems were two-component mixtures of these monomers: DDM/EGDM, DDM/bis-GMA and TEGDM/bis-GMA. The cross-link density was manipulated by changing the molar ratio of the two monomers in the system.

This aim was realized by modeling of the after-effect of a photo-induced polymerization of the above mentioned systems and calculation of the ratios of the termination and propagation rate coefficients $k_t^b/k_p$ (without the steady-state assumption) using termination models described previously [35–39]. The $k_t^b/k_p$ ratio was determined as a function of the double bond conversion during the continuous irradiation and during the after-effect (in the dark). Assuming that in the conversion range investigated the possible changes in propagation rate coefficient are low in comparison to changes in termination rate coefficient, the results of calculations allowed us to follow $k_t^b$ behavior at various degrees of double bond conversion and at various stages of the dark reaction. Moreover, it was expected that $k_t^b$ will drop with the conversion increase. Thus, if we observe a decrease in $k_t^b/k_p$ ratio, it indicates on a decrease of $k_t^b$ value, even if $k_p$ decreases also during the reaction, and the drop of the $k_t^b/k_p$ ratio qualitatively describes the decrease of $k_t^b$.

The question arises how degree of double bond conversion in a cross-linking polymerization is correlated with the average chain length $i$. If we consider the chain length as the kinetic chain length (the average number of double bonds which react with a radical site before any termination reaction), it increases with the double bond conversion. Such an approach is reasonable even in the case when the radical end adds to a pendant double bond, because the polymerizing system loses some of its mobility.

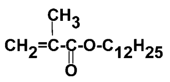
According to the calculation procedure used in this work, the propagation and termination rate coefficients were averaged over increasingly large time of the dark reaction (and corresponding conversion in the dark) [35,36,40], i.e. over first 10, 20, 30, etc. seconds of the dark reaction starting invariably at the moments of discontinuation of illumination. This should reflect changes in rate coefficients, occurring as the time of the dark reaction is protracted. The procedure was repeated for each series of post-polymerization processes (for the given system) occurring after the light was cut off at various double bond conversions.

Most often the termination process is considered to be a bimolecular reaction. However, in cross-linking systems radical trapping (the monomolecular termination, Eq. (5)), becomes important especially at later polymerization stages (although it may occur even at early reaction stages due to microgel formation [37]):

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

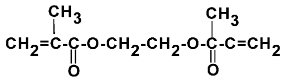
where $R_t^m$ is the monomolecular termination rate, $k_t^m$ is the monomolecular termination rate coefficient and $[P^\bullet]$ is radical concentration.

Thus, at the beginning of the polymerization the bimolecular mechanism prevails; when the conversion increases, the termination mechanism changes to the mixed one, where the bimolecular and the monomolecular reaction are equally important (Eq. (6)).



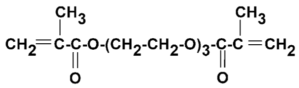
$CH_2{=}C(CH_3){-}C({=}O){-}O{-}C_{12}H_{25}$

DDM



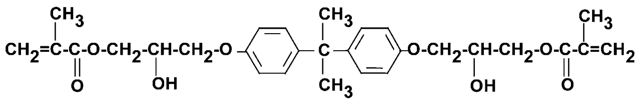
$CH_2{=}C(CH_3){-}C({=}O){-}O{-}CH_2{-}CH_2{-}O{-}C({=}O){-}C(CH_3){=}CH_2$

EGDM



$CH_2{=}C(CH_3){-}C({=}O){-}O{-}(CH_2{-}CH_2{-}O)_3{-}C({=}O){-}C(CH_3){=}CH_2$

TEGDM



Bis-GMA

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

where $R_t^{mix}$ is the mixed termination rate.

At the latest polymerization stages the monomolecular termination dominates [35,41]. During the continuous irradiation the monomolecular termination begins to prevail near the maximum polymerization rate $R_p^{max}$ [35,41]. Under non-stationary conditions, the monomolecular termination mechanism becomes important even if the illumination has been discontinued at lower degrees of double bond conversion (below $R_p^{max}$) but at later stages of the dark reaction, due to the rapid drop of macroradical mobility in the dark [35,36]. The termination behavior can be described by three termination models: monomolecular, bimolecular and mixed [35–39]. It was found that the after-effect is best described by the mixed termination model [35,36,40] and this model has been used in the present work for calculation of the polymerization rate coefficients. Because in linear (or almost linear) systems the radical trapping should not occur until high conversions, the monomolecular termination indicated by modeling in such systems can be associated with a rapid and significant drop in the macroradical mobility. Thus, 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 the experimental method used [40].

## 2. Experimental section

### 2.1. Materials and methods

The monomers: DDM, EGDM and TEGDM were purchased from Aldrich and bis-GMA from Polysciences. DDM, EGDM and TEGDM were purified by column chromatography before use.

Reaction rate profiles and conversions were determined by isothermal differential scanning calorimetry. DSC 605M (UNIPAN-TERMAL, Warsaw) instrument equipped with a lid specially 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 aluminium 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.

Polymerization was initiated with UV light ($\lambda_{max}$ = 366 nm) from a medium pressure Hg lamp (incident light

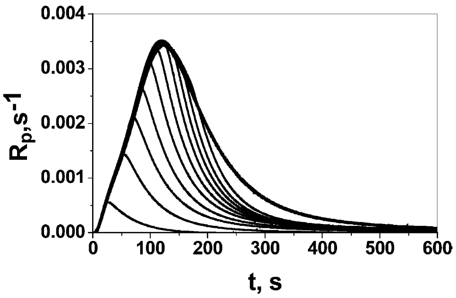


Fig. 1. Rate of polymerization vs time for 10 different dark reactions during the polymerization of the equimolar EGDM/DDM mixture. The upper curve corresponds to the polymerization during the continuous illumination.

intensity 1 mW/cm$^2$) in the presence of 2,2-dimethoxy-2-phenylacetophenone (Ciba) used at a concentration 0.2 wt% for bis-GMA/TEGDM system and 1 wt% for the remaining systems. 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 kinetic data obtained for the after-effect have been shown in Fig. 1. To recalculate the units of the heat flow (mJ/g) to reaction rate units (1/s), the value of the enthalpy of polymerization 56 kJ/mol per one double bond was taken [42]. The degrees of double bond conversion were obtained from areas under time-polymerization rate curves.

### 2.2. Calculations

The experimental data for calculations were obtained from postpolymerization processes, which were registered after stopping the irradiation at various degrees of double bond conversion. This enabled to estimate polymerization rate coefficients as a function of conversion of double bonds. The experimental data were 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) [35–39].

The termination models are given by Eqs. (3), (5) and (6). For calculations they were used in the form describing the polymerization occurring in the absence of initiation, i.e. in the dark [35–39] (Eqs. (7)–(9)):

1. The monomolecular termination model (Model I):

$$-\ln(1-p_\mathrm{d}) = \frac{k_\mathrm{p}}{k_\mathrm{t}^\mathrm{m}}[P^\bullet]_0\left(1-\exp\left(-k_\mathrm{t}^\mathrm{m}t\right)\right) \tag{7}$$

2. The bimolecular termination model (Model II):

$$-\ln(1-p_\mathrm{d}) = \frac{1}{2}\frac{k_\mathrm{p}}{k_\mathrm{t}^\mathrm{b}}\ln\left(1+2[P^\bullet]_0k_\mathrm{t}^\mathrm{b}t\right) \tag{8}$$

3. The mixed termination model (Model III):

$$-\ln(1-p_\mathrm{d}) = \frac{1}{2}\frac{k_\mathrm{p}}{k_\mathrm{t}^\mathrm{b}}\ln\left(1+2[P^\bullet]_0\frac{k_\mathrm{t}^\mathrm{b}}{k_\mathrm{t}^\mathrm{m}}\left(1-\exp\left(-k_\mathrm{t}^\mathrm{m}t\right)\right)\right) \tag{9}$$

where $[P^\bullet]_0$ is the macroradical concentration at the beginning of the dark period, $t$ is time from the start of the dark reaction, and $p_\mathrm{d}$ is the degree of double bond conversion in the dark.

Calculations were performed without steady-state assumption, thus the following parameters were determined: $k_\mathrm{t}^\mathrm{b}/k_\mathrm{p}$ (Model II), $k_\mathrm{t}^\mathrm{m}$ (Model I) and both $k_\mathrm{t}^\mathrm{b}/k_\mathrm{p}$ and $k_\mathrm{t}^\mathrm{m}$ (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 $k_\mathrm{t}^\mathrm{m}$, $k_\mathrm{t}^\mathrm{b}[P^\bullet]_0$ and $k_\mathrm{p}[P^\bullet]_0$ were calculated from the models at various duration of postpolymerization (10–200 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, etc. seconds of the dark reaction. In this way, $[P^\bullet]_0$ was always constant for a given dark reaction [36]. Such a procedure enables the kinetic parameters calculated for increasingly longer times of dark reaction to be compared. Application of multistep statistical analysis enabled to find the model that 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.

The parameters of the Models I–III (Eqs. (7)–(9)) were calculated by the non-linear least-square method.

For each model the residual variance (MSR) and the variance of the model (MSE) were calculated. Exemplary results showing changes in theses variances occurring with the increase in the dark reaction time are given in Table 1.

$$\mathrm{MSE} = \frac{\sum_{i=1}^{N}\left(y_i^\mathrm{exp}-y_\mathrm{mean}\right)^2}{N_\mathrm{par}-1}, \tag{10}$$

$$\mathrm{MSR} = \frac{\sum_{i=1}^{N}\left(y_i^\mathrm{exp}-y_i^\mathrm{calc}\right)^2}{N-N_\mathrm{par}} \tag{11}$$

where $N$ is the number of experimental points, $N_\mathrm{par}$ is the number of model parameters and $N_\mathrm{par}=2$ for Model I and Model II and $N_\mathrm{par}=3$ for Model III.

The changes observed depend on the model considered. The fitting of the Model II decreases with the increase in the time of dark reaction, which is reflected by the increase both in the variance of the model and variance of residuals. Such changes are in agreement with expectations. In the case of the Model I and the Model III the variance of the model also increases, which can be associated with the increasing number of points, but the residual variance after an initial increase passes through a maximum and then decreases. The decrease in the residual variance indicates on the growing importance of the monomolecular termination mechanism as the time of the dark reaction increases. It should be stressed that all the functions obtained for the three models and various dark time periods are statistically significant which is evidenced by the comparison of the both variances in the F-Snedecor test. Similar results were observed for all

Table 1
Residual variances (MSR) and variances of the model (MSE) for various dark reaction times of TEGDM polymerization; the irradiation has been stopped at 0.168 of double bond conversion

| Postpolymerization time (s) | Model I | | Model II | | Model III | |
|---|---|---|---|---|---|---|
| | MSR | MSE | MSR | MSE | MSR | MSE |
| 10 | $1.07\times10^{-9}$ | $4.47\times10^{-3}$ | $1.21\times10^{-9}$ | $4.47\times10^{-3}$ | – | – |
| 70 | $1.09\times10^{-6}$ | $6.89\times10^{-1}$ | $9.05\times10^{-6}$ | $6.81\times10^{-1}$ | $1.45\times10^{-4}$ | $3.11\times10^{-1}$ |
| 100 | $1.72\times10^{-6}$ | 1.17 | $2.97\times10^{-5}$ | 1.15 | $2.73\times10^{-4}$ | $5.11\times10^{-1}$ |
| 170 | $1.51\times10^{-6}$ | 2.19 | $1.25\times10^{-4}$ | 2.09 | $3.01\times10^{-4}$ | $9.17\times10^{-1}$ |
| 200 | $1.49\times10^{-6}$ | 2.44 | $1.58\times10^{-4}$ | 2.31 | $2.51\times10^{-4}$ | 1.02 |

the postpolymerization processes independently of the system studied and the conversion at which the irradiation has been stopped. However, this type of analysis does not allow to find the dominating termination mechanism. This has been done using procedure of comparison of the models in pairs as described in Refs. [36,40].

The whole calculation procedure has been described in details elsewhere [36,40]. The coefficients calculated are average values for a given polymerizing system consisting of a mixture of two monomers at their given molar ratio and present average values for monomeric and pendant double bonds.

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 polymerization.

## 3. Results and discussion

The consideration of the chain length influence on the termination process was based on the analysis of the conversion dependence of the rate coefficients $k_t^b/k_p$ calculated from postpolymerization data.

The statistical analysis performed for increasingly large dark conversions indicated that, in each case considered, in the conversion range investigated (always not exceeding the conversion corresponding to $R_p^{max}$), at the beginning of the after-effect the termination occurred mainly via a bimolecular reaction. However, at longer times of the after-effect, the monomolecular termination (considered as significant reduction of radical center mobility) became increasingly important and the termination mechanism changed to the mixed one.

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, only two termination mechanisms could be considered: the bimolecular and the mixed ones.

The rate of polymerization in the dark drops down rapidly, which must result from a rapid drop in active radical concentration. The radicals are eliminated from propagation in a termination process, which may be a first- or second-order reaction. The bimolecular termination model (Model II) takes into account only one termination rate coefficient and a rapid drop in the polymerization rate (strictly speaking: faster increase in the reverse polymerization rate than the decrease of double bond concentration [36]) at a constant $k_p$ must be interpreted by this model as caused by an increase in $k_t^b$ coefficient (and $k_t^b/k_p$ ratio, Fig. 2, for explanation see below). However, it is expected that during the after-effect $k_t^b$ should decrease.

To explain the decreasing polymerization rate at quickly decreasing bimolecular termination rate coefficient the monomolecular termination mechanism has to be taken into account, and its rate coefficient $k_t^m$ has to increase with time of the dark reaction. Introduction of two termination rate coefficients into the termination model (Model III) gives the correct result: a decreasing $k_t^b$ ($k_t^b/k_p$ ratio) and an increasing $k_t^m$ coefficient during the after-effect [35,36,40] (Fig. 3, for explanation see below). Thus, in the present work we discuss mainly the results obtained by the mixed termination model (Model III).

Fig. 2 shows an example of the results obtained from the Model II. It has been given to explain the way of

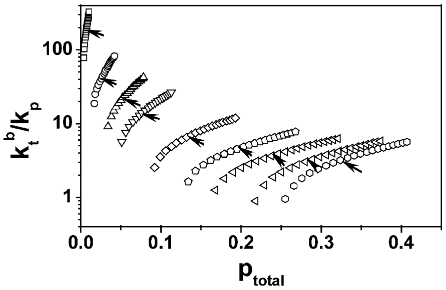


Fig. 2. Rate coefficients in relation to the total degree of double bond conversion calculated from Model II for TEGDM polymerization. See text for explanation. The arrows indicate changes in termination mechanism from the bimolecular to the mixed one. The results are given for all time intervals, regardless of which model is indicated by statistical analysis to fit to the corresponding segment of the curve.

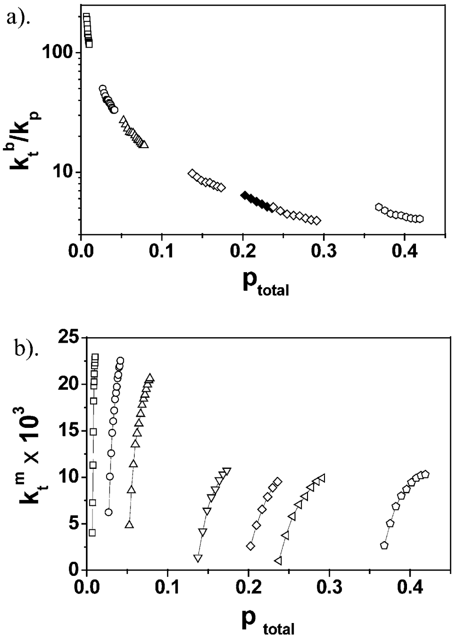


Fig. 3. Rate coefficients in relation to the total degree of double bond conversion calculated form Model III for TEGDM polymerization. The parameters are given only for time intervals where mixed termination dominates (corresponding to total conversions shown by points next to arrow in Fig. 2).

presentation of the results and shows the dependence of the $k_t^b/k_p$ ratio on total conversion $p_{\text{total}}$ for several TEGDM postpolymerization processes. The total conversion is the sum of starting conversion (reached during illumination) and of the conversion during the considered period of time of the dark reaction (final conversion of this period of time).

The results are plotted in series corresponding to after-effects beginning at various degrees of conversion. Each point in series corresponds to one time interval of the dark reaction (and conversion increment during dark reaction). The first points in series correspond to the starting conversions at which the initiation has been discontinued and show the result for the first 10 s of the dark reaction. The other points in series correspond to the conversions of double bonds during 20, 30, etc. seconds of the dark reaction (always starting at the moments of discontinuation of illumination). Arrows indicate the change in the termination mechanism from the bimolecular to the mixed one. The values of the first points, which may be assumed to describe the polymerization during continuous irradiation, decrease with the increase in starting conversion tending to reach a plateau. This could indicate that bimolecular termination in stationary conditions becomes to be controlled by reaction diffusion [27,43,44].

However, as discussed above, this model gives incorrect picture of processes occurring in the dark, since calculated values of $k_t^b/k_p$ ratios increase in the dark, thus, the mixed termination model should be used.

The statistical analysis showed that bimolecular reaction was the main (but not exclusive) termination mechanism until about 50–100 s of the dark reaction. Thus, discussion of the results obtained from the Model III will concern the later stages of the dark reaction where mixed mechanism of termination dominates. After 50–100 s of the reaction, depending on the system investigated, we were able calculate both $k_t^m$ and $k_t^b/k_p$ ratio.

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.

Fig. 3 presents the results of calculation for TEGDM polymerization by the use of the Model III. Only the results for time intervals where mixed termination dominates are given; the parameters correspond to total conversions shown by points next to arrows in Fig. 2.

As could be expected, the $k_t^b/k_p$ ratios decrease as the dark reaction proceeds (Fig. 3(a)). A decrease in the $k_t^b/k_p$ values with the increase in conversion and further tendency to plateau when reaction diffusion begins to dominate the bimolecular termination is usually observed for both linear and cross-linking systems in stationary conditions.

However, the drop of the $k_t^b/k_p$ values during the after-effect is somewhat faster than that resulting from the increase in double-bond conversion. This effect, although very slight but visible (mainly at conversions $>0.2$), must result from an additional decrease in the overall mobility of macroradicals caused by their chain length dependence (their longer period of growing before termination due to lack of formation of short-chain radicals). We can explain it as follows: the termination is dominated by the reaction between two short or one short and one long macroradical (in our case attached to the network). When the light is extinguished, the short-chain radicals existing in the polymerizing system are growing longer before termination and their diffusivity decreases. Thus, after a time of the dark reaction and at a degree of dark conversion reached, the meeting of these radicals with other macroradicals is more difficult that at the beginning of the after-effect. As the result, the bimolecular termination rate coefficient decreases. However, if the light has been cut off somewhat later, at somewhat higher starting conversion degree, the short-chain radicals present at the moment of discontinuation of illumination will need a shorter time to grow to produce the same total conversion degree as that discussed in the previous case. Thus, their diffusivity will be higher and, in consequence, $k_t^b$ value, although will decrease in the dark, will be higher than that in the previous case at the same conversion degree.

If the termination rate coefficients were constant and independent of time of dark reaction (in the absence of chain length dependence during the after-effect), their averaging over increasingly long periods of time (and corresponding conversion increments) would give always the same value for the same conversion degree reached in different postpolymerization processes.

On the other hand, if the monomolecular termination is considered as a significant slowing down of diffusion of macroradicals, its rate coefficient must increase with the chain length, which is really observed (Fig. 3(b)). Thus, the radicals are continuously eliminated from further reaction by the first-order mechanism and growing $k_t^m$ compensates for the drop of $k_t^b$.

A good example of the chain length dependence of the termination during the after-effect of the cross-linking polymerization is the polymerization of DDM+EGDM mixtures at various molar ratios of the monomers (Fig. 4). This system contains two low viscosity monomers, the mono- and divinyl ones. As could be expected, the chain length dependence of the $k_t^b/k_p$ ratio is only slight for the polymerization of neat EGDM, when the cross-link density is the highest (it is visible mainly for the three last series, Fig. 4(a)), and intensifies with the increasing monoester content in the monomer mixture (Fig. 4(b)–(d)). The dependence discussed is substantial at the beginning of the polymerization and abates with the increase in conversion when the $k_t^b/k_p$ ratios tend to reach plateau associated with increasing contribution of the reaction diffusion in the bimolecular termination.

However, even at this reaction stage the values of the points in series decrease faster than it could result from the total conversion increase indicating that the termination is still slightly chain length dependent and reaction diffusion is not exclusive termination mechanism. At loosely cross-linked systems (Fig. 4(d)) the chain length dependence of the $k_t^b/k_p$ ratio seems to be considerable at the whole conversion range studied suggesting that in this case reaction diffusion does not control the termination.

The second investigated system, DDM/bis-GMA, contains a very viscous monomer: bis-GMA, and its high viscosity additionally affects the termination, in addition to cross-linking density. The results of calculations are shown in Fig. 5.

In the case of neat bis-GMA (Fig. 5(a)) the values of points in series decrease only slightly, especially from conversions about 0.08, indicating that in the highly viscous system the conditions for the dominance of the reaction diffusion (and a significant decrease in dependence of the $k_t^b/k_p$ ratio on conversion) appear soon after stopping the illumination. Under non-stationary conditions, even a slight growth of the short-chain radicals existing at the moment of discontinuation of irradiation leads to their quick immobilization in the viscous medium and the bimolecular termination becomes almost completely reaction diffusion controlled and chain length independent.

An addition of 60 mol% of the low viscosity difunctional monomer increases the mobility of the system and the chain length dependence of the $k_t^b/k_p$ ratio also increases. However, at the end of the after-effects one can observe again that the $k_t^b/k_p$ ratio becomes chain length independent (Fig. 5(b)). When the system contains only 2% of bis-GMA (Fig. 5(c)) much looser network is formed, which considerably increases the chain length dependence of the

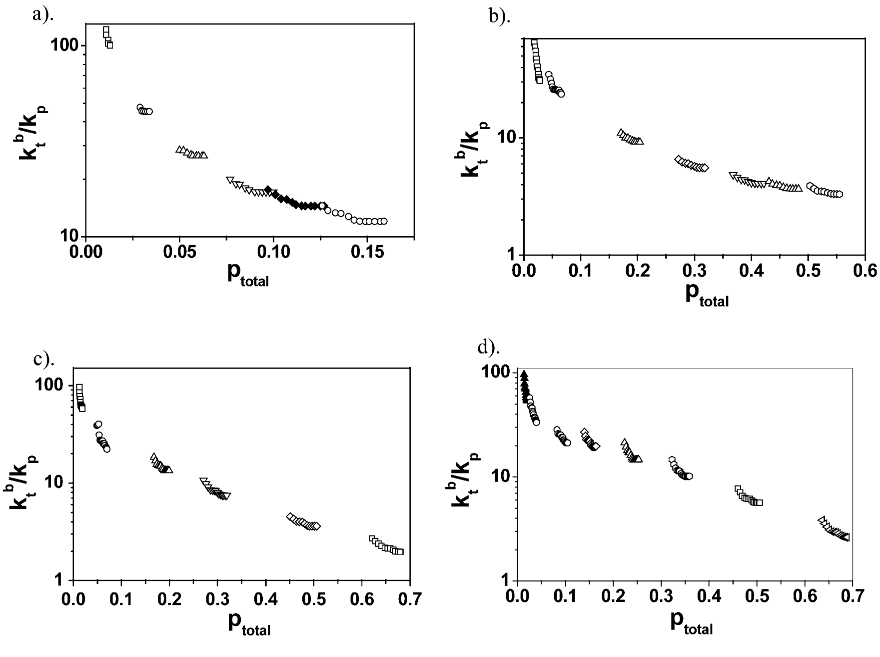


Fig. 4. Rate coefficients in relation to the total degree of double bond conversion calculated from Model III for polymerization of DDM/EGDM system. The parameters are given only for time intervals where mixed termination dominates. DDM content (mol%): (a) 0, (b) 60, (c) 80, (d) 90.

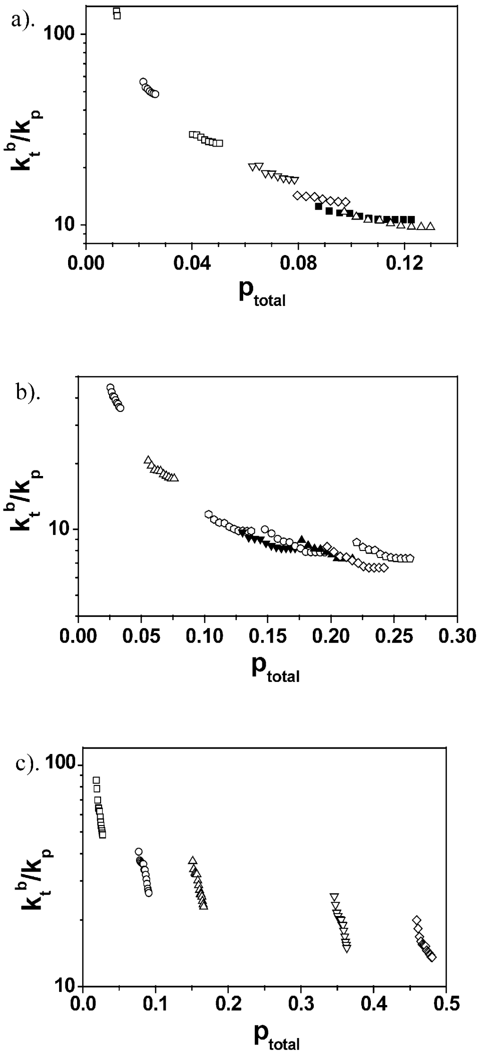


Fig. 5. Rate coefficients in relation to the total degree of double bond conversion calculated from Model III for polymerization of DDM/bis-GMA system. The parameters are given only for time intervals where mixed termination dominates. DDM content (mol%): (a) 0, (b) 60, (c) 98.

$k_t^b/k_p$ ratio and is the reason of the fast drop of this parameter in the dark.

The last investigated system: bis-GMA/TEGDM is the mixture of the two tetrafunctional monomers. Fig. 6 presents the results obtained for this system (the results of calculation for the neat monomers are given in Figs. 3 and 5(a)). Series of the $k_t^b/k_p$ ratios showing changes which occur in this parameter during the after-effect clearly indicate that even in highly cross-linked and viscous systems the termination can be chain length dependent, especially at the beginning of the polymerization (as can be seen for the two first series in Fig. 6(a)). At the later reaction stages, in the case discussed, the chain length dependence is observed rather at earlier stages of the after-effect; at the end of the after-effects the reaction diffusion becomes the exclusive mechanism of the bimolecular termination (three last series in Fig. 6(b)).

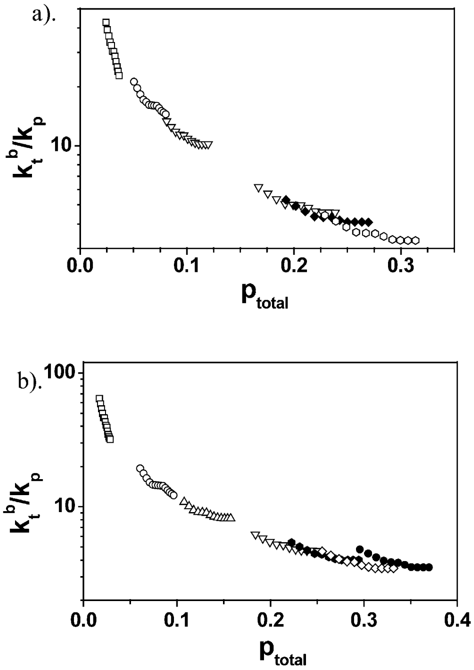


Fig. 6. Rate coefficients in relation to the total degree of double bond conversion for polymerization of TEGDM/bis-GMA system calculated from Model III. The parameters are given only for time intervals where mixed termination dominates. TEGDM content (mol%): (a) 70, (b) 90.

## 4. Conclusion

The results of modeling of the after-effect of a cross-linking polymerization show a drop of the $k_t^b/k_p$ ratio with the increase in dark reaction time faster than that resulting from the conversion increase. Such a behavior can be associated with the chain length dependence of the termination process. The dependence of the $k_t^b/k_p$ ratio on dark reaction time decreases with the increase in cross-link density and starting conversion. For very viscous systems, the viscosity plays a significant role in addition to the cross-link density.

Because the after-effect can be considered as a method for probing the effect of chain-length, the results presented can make an evidence for chain length dependent termination in cross-linking polymerization.

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## References

[1] de Kock J, Van Herk A, German A. J Macromol Sci, Part C: Polym Rev 2001;41:199.
[2] Shipp DA, Solomon DH, Smith TA, Moad G. Macromolecules 2003; 36:2032.

[3] Buback M, Barner-Kowollik C, Egorov M, Kaminsky V. Macromol Theory Simul 2001;10:209.

[4] Buback M, Egorov M, Feldermann A. Macromolecules 2004;37: 1768.

[5] Barner-Kowollik C, Vana P, Davis TP. The kinetics of free radical polymerization. In: Matyjaszewski K, Davis TP, editors. Handbook of radical polymerization. New York: Wiley; 2002. p. 187–262.

[6] Shipp DA, Solomon DH, Smith TA, Moad G. Macromolecules 2003; 36:2032.

[7] Smith GB, Russel GT, Heuts JPA. Macromol Theory Simul 2003;12: 299.

[8] Olaj OF, Zoder M, Vana P. Macromolecules 2001;34:441.

[9] de Kock JBL, Klumperman B, van Herk AM, German AL. Macromolecules 1997;30:6743.

[10] Litvinenko GI, Kaminsky VA. Prog React Kinet 1994;19:139.

[11] Beuermann S, Buback M. Prog Polym Sci 2002;7:191.

[12] Buback M. Macromol Symp 2001;174:213.

[13] Vana P, Davis TP, Barner-Kowollik C. Macromol Rapid Commun 2002;23:952.

[14] Feldermann A, Stencel MH, Davis TP, Vana P, Barner-Kowollik C. Macromolecules 2004;37:2404.

[15] Theis A, Feldermann A, Charton N, Stencel MH, Davis TP, Barner-Kowollik C. Macromolecules 2005;38:2595.

[16] Shipp DA, Yu X. J Polym Sci, Part A: Polym Chem 2004;42:5548.

[17] Olaj OF, Kornherr A, Zifferer G. Macromol Theory Simul 2001;10: 881.

[18] Smith GB, Russel GT, Yin M, Heuts JPA. Eur Polym J 2005;41:225.

[19] Olaj OF, Zoder M, Vana P, Kornherr A, Schnöll-Bitai I, Zifferer G. Macromolecules 2005;38:1944.

[20] Schulz VZ. Phys Chem 1956;8:2906.

[21] Soh SK, Sundberg DS. J Polym Sci, Polym Chem Ed 1982;20: 1299–313.

[22] Soh SK, Sundberg DS. J Polym Sci, Polym Chem Ed 1982;20: 1315–29.

[23] Buback M, Huckenstein B, Russel GT. Macromol Chem Phys 1994; 195:539–54.

[24] Buback M. Macromol Symp 1996;111:229–42.

[25] Anseth KS, Wang CM, Bowman CN. Macromolecules 1994;27: 650–5.

[26] Anseth KS, Kline LM, Walker TA, Anderson KJ, Bowman CN. Macromolecules 1995;28:2491–9.

[27] Young S, Bowman CN. Macromolecules 1999;32:6073.

[28] Zhu S. Macromolecules 1996;29:456.

[29] Lovestead KA, Berchtold KA, Bowman CN. Macromol Theory Simul 2002;11:729.

[30] Berchtold KA, Lovestead KA, Bowman CN. Macromolecules 2002; 35:7968.

[31] Berchtold KA, Lovell LG, Nie J, Hacioğlu B, Bowman CN. Polymer 2001;42:4925.

[32] Lovell LG, Bowman CN. Polymer 2003;44:39.

[33] O'Shaughnessy B, Yu J. Macromolecules 1998;31:5240.

[34] O'Shaughnessy B, Yu J. Phys Rev Lett 1998;80:2957.

[35] Andrzejewska E, Bogacki MB, Andrzejewski M. Macromol Theory Simul 2001;10:842.

[36] Andrzejewska E, Bogacki MB, Andrzejewski M, Janaszczyk M. Phys Chem Chem Phys 2003;5:2635.

[37] Andrzejewska E. Prog Polym Sci 2001;26:605.

[38] Andrzejewska E, Bogacki MB. Macromol Chem Phys 1997;198: 1649.

[39] Andrzejewska E. Macromol Symp 2001;171:243.

[40] Andrzejewska E, Zych-Tomkowiak D, Bogacki MB, Andrzejewski M. Macromolecules 2004;37:6346.

[41] Wen M, Mc Cormick AV. Macromolecules 2000;33:9247.

[42] Odian G. Principles of polymerisation. 2nd ed. New York: Wiley; 1981.

[43] Mateo JL, Serrano J, Bosch P. Macromolecules 1997;30:1285.

[44] Mateo JL, Calvo M, Serrano J, Bosch P. Macromolecules 1999;32:52.