Termination of trapped radicals at elevated temperatures during copolymerization of MMA/EGDMA

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Bulk free-radical copolymerization of methyl methacrylate (MMA)/ethylene glycol dimethacrylate (EGDMA) with 0, 25, 50, 75, 100 wt% EGDMA initiated by 2.0 wt% 2,2'-azobis[2-methylpropionitrile] (AIBN) at 70°C was carried out for 96 h (120 h for pure MMA). The final stable radical concentrations obtained were 1.3×10^{-5}, 7.8×10^{-5}, 9.2×10^{-4}, 1.5×10^{-3}, 2.5×10^{-3} mol/l, respectively. Post-effect measurements of bimolecular termination of radicals at terminal conversions ($X = 0.60$–0.95) and at following elevated temperatures, 105, 120, 150 and 180°C were made using an on-line e.s.r. spectrometer. Termination rate constants were estimated using the measured radical decay rates. It was found that the termination rate constants in the post-effect period for the samples having high EGDMA weight fractions and at the lower temperature levels decreased with time. This can be explained by assuming that there exist two radical populations attached to crosslinked gel, active radicals and inactive radicals. An increase in temperature causes a transformation of inactive radicals to active ones. The bimolecular termination rate constants for these active radicals were measured. It was found that the rate constants for active radicals decrease with increasing EGDMA level. The bimolecular termination constant for inactive radicals was taken to be zero. The activation energies for these termination constants decrease with increasing EGDMA weight fraction and are of the order of 10 kcal/mol. The inactive radical concentrations were also estimated. A discussion of the polymerization mechanisms at very high conversions is given based on an analysis of the experimental data. It can be concluded that for linear PMMA at very high conversions during the glassy-state transition, the propagation rate constant, the initiation efficiency and the termination rate constant fall almost simultaneously and dramatically. These conclusions may also be true for crosslinked PMMA.

(Keywords: copolymerization; trapped radicals; methyl methacrylate; ethylene glycol dimethacrylate)

INTRODUCTION

Free radical polymerization with crosslinking is receiving more attention recently due to its potential for development of new polymer products. Although some successes have been achieved in industry, an understanding of the polymerization mechanisms and kinetics which are essential for better control of the gel structure is lacking. One of the major unsolved problems in this area is the inadequate understanding of diffusion controlled reactions. It is well accepted that several kinetic constants decrease with monomer conversion for such polymerizations. The outstanding example is the bimolecular termination rate constant for polymer radicals.

Although the termination reaction has been studied for decades, the molecular processes involved are not well understood at high conversions, particularly when crosslinking occurs. Generally, bimolecular termination consists of three definable steps: two radicals migrate together via translational diffusion; the radical centres re-orient by segmental diffusion; they overcome the chemical activation barrier and react. The activation energy for chemically controlled free radical reactions is often very low. The termination reaction is, therefore, likely to be diffusion controlled for most of the monomer conversion range. At low conversions where macromolecules in a good solvent have a coil conformation, translational diffusion rate of the centre of mass of these isolated coils is not rate limiting and segmental reorientation becomes the rate determining step. As polymer concentration increases, the macromolecular chains become physically entangled and/or chemically crosslinked, the centre-of-mass diffusion rates are then essentially zero. The two possible modes of termination at this stage of conversion are polymeric radicals with oligomeric radicals, and propagation–diffusion[1]. By propagation–diffusion is meant that an active chain end diffuses via propagation. In other words, the propagational growth of polymer chain contributes to the migration of the radical centre.

Elucidation of these reaction mechanisms requires valid and accurate experimental data whose interpretation should not be model dependent. Unfortunately, some conventional experimental techniques employ questionable assumptions. One among these is the use of measured monomer conversion rates to estimate total

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radical concentration changes. This assumes that all radicals have the same reactivity towards monomer double bond addition. These methods are probably not applicable at high conversions where the reacting mass may be heterogeneous on a microscopic scale in terms of the environment of radical centres.

The advent of modern e.s.r. techniques has provided a powerful direct method of radical type and concentration measurement. Early studies by Atherton et al.[2] provided measurements of the radical concentration histories for MMA/EGDMA polymerizations using an e.s.r. spectrometer with frozen samples to study radical trapping due to crosslinking. More recently, Kamachi et al.[3] have measured the radical concentrations at the initial stages of polymerization for some homopolymerization systems. Ballard et al.[4] measured the propagation constant over the entire conversion range for the emulsion polymerization of MMA with frozen samples. Shen and others[5,6] investigated the corresponding bulk polymerization of MMA in an e.s.r. cavity.

In our previous papers, we presented the use of an on-line e.s.r. to measure radical concentrations during bulk free radical copolymerization of MMA/EGDMA over the entire conversion range and with various crosslinker levels in the e.s.r. cavity[7]; a model simulation of the e.s.r. spectra for this polymerizing system[8]; and measurements of bimolecular termination rate constants during MMA polymerization using post-effect measurements of the decay in radical concentrations[9]. It was found that very high concentrations of radicals were trapped at high monomer conversions producing so-called reactive gels. Such reactive gels may find commercial applications for the development of new polymer products in industry such as interpenetrating networks, purification agent for trace impurities. In this paper, we report on the investigation of the behaviour of these trapped radicals at elevated temperatures. The approach used is the post-effect measurement of trapped radical concentrations to estimate bimolecular termination rate constants.

Samples with high polymer concentrations were prepared via polymerization to ensure a homogeneous solution of monomer and polymer. The polymerizations were done below the copolymer glass transition temperatures for about 100 h to ensure that the initiator molecules were largely consumed. Samples prepared in this manner were used for post-effect measurements of radical concentration.

samples were polymerized 120 h for pure MMA and 96 h for the copolymer mixtures.

According to the equation $[I] = [I]_0 \exp(-K_d t)$ (neglecting volume contraction), where K_d is the initiator molecule decomposition rate constant which equals 1.87×10^{-3} 1/min for AIBN at 70°C (ref. 10), and $[I]_0$ is the initial AIBN concentration, 0.1032 mol/l, which is equivalent to 2.0 wt%, the residue initiator concentrations, $[I]$, are 2.17×10^{-6} mol/l after 96 h and 1.47×10^{-7} mol/l after 120 h. The effect of the residue AIBN can be neglected in the following post-effect investigation of trapped radicals, because the trapped radical concentrations in this study are much higher than these values.

Prepared samples were then inserted into a TE110 cavity of a Bruker ER100D ESR spectrometer. Post-effect measurements at elevated temperatures of 105, 120, 150, 180°C were made. The temperature was controlled by a gas bath ± 0.5°C. Radical spectra were frequently recorded to follow the reaction process in detail. With the samples at high temperature and low EGDMA level, e.s.r. signal decay rates were so rapid that there was insufficient time to scan the whole e.s.r. spectrum. The e.s.r. pen was then fixed to a central line peak and a chart recorder was used to monitor the decay in e.s.r. spectra.

E.s.r. spectra were integrated twice to obtain absolute radical concentrations which were calibrated by 2,2-diphenyl-1-picrylhydrazyl hydrate (DPPH) (Aldrich Chemicals) dissolved in MMA/EGDMA mixture using the same type of ampoule. In the cases where only the central line heights were available, the peak broadening of e.s.r. spectra was corrected for using $[R^\cdot] \propto H L_{pp}^2$ where H and L_{pp} are height and width of the central line, respectively.

Monomer double bond conversions were measured offline using a laser Raman spectrometer (Conventional Spex, Cat. 14018, Ser. 5420, double-monochromator, 0.85 m, 1800 g/mm). The 1641 cm^{-1} band, due to the C=C stretching mode[11], is characteristic of the unreacted MMA and EGDMA monomers and the pendant carbon–carbon double bonds. The carbonyl group, C=O, at 1729 cm^{-1}, does not change during polymerization and, therefore, was used as an internal standard[11]. The conversions were calculated using $1 - \mu(A_{C=C}/A_{C=O})$, where $A_{C=C}$ and $A_{C=O}$ are the peak areas at 1641 and 1729 cm^{-1}, respectively, and μ is a correction factor which equals $A_{C=O}/A_{C=C}$ from MMA or EGDMA monomers.

EXPERIMENTAL

MMA (Fisher Scientific) and EGDMA (Aldrich Chemicals) were purified in the same way: washed with a 10 wt% aqueous KOH solution to remove inhibitor, washed with deionized water, dried successively with anhydrous sodium sulphate and 4Å molecular sieves, and then distilled under reduced pressure to provide a useful middle fraction. AIBN (Eastman Kodak) was recrystallized three times from absolute methanol.

Pyrex ampoules of 4 mm o.d. (2.4 mm i.d.) filled with reactants and deoxygenated using standard freeze-thaw techniques were immersed in an oil bath. The oil temperature was controlled at 70 ± 0.1°C. An initiator level of 2.0 wt% AIBN was used. Five weight fractions of EGDMA used were 0, 25, 50, 75, 100 wt%. The

RESULTS AND DISCUSSION

Conventional kinetic analysis and polymerization with crosslinking

A conventional kinetic analysis for free radical polymerizations which produce linear polymer chains is often based on experimental measurements of conversion and molecular weight. The two fundamental equations used to treat the data are as follows

$$\frac{dX}{dt} = K_p[R^\cdot](1 - X) \tag{1}$$

and

$$\bar{M}_n = \frac{m K_p[M]}{\frac{1}{2}(1 + \Omega)\bar{K}_{tn}[R^\cdot]} \tag{2}$$

where X is the double bond conversion, t is the polymerization time, K_p is the propagation rate constant, $[R^\bullet]$ is the polymer radical concentration, $\bar{M}_n$ is the instantaneous number average molecular weight of polymer chains which contain no radical centres, m is the monomer molecular weight, $[M]$ is the double bond mole concentration, $\bar{K}_{tn}$ is the number average termination rate constant[12], Ω is the fraction of termination by disproportionation. Transfer reactions are neglected.

It is clear that the conversion history and the number average molecular weight alone cannot give one estimates of the propagation and termination rate constants. Therefore, a measurement such as radical concentration is essential. Equation (3) is the polymer radical concentration balance during polymerization

$$\frac{d[R^\bullet]}{dt} = 2fK_d[I]_0 \exp(-K_d t) - \bar{K}_{tn}[R^\bullet]^2 \qquad (3)$$

where f is the initiation efficiency, K_d is the initiator decomposition rate constant, $[I]_0$ is the initial initiator concentration. The factor 2 accounts for the fact that an initiator molecule produces two primary radicals. An examination of the above equations reveals that, in general, measurements of the conversion history, number average molecular weight and radical concentration are sufficient to evaluate the initiation efficiency, propagation rate constant and number average termination rate constant. In addition, the higher order average termination rate constants such as $\bar{K}_{tw}$, $\bar{K}_{tz}$, . . ., can also be evaluated from the higher average molecular weight data[12]; Ω can be estimated from the polydispersity index of molecular weight distribution, $\bar{M}_w/\bar{M}_n$.

It must be pointed out that an extension of this kinetic analysis to a free radical polymerization with crosslinking is not straightforward. Polymer network formation seriously complicates the kinetic analysis, particularly, in the post-gelation period where there exist two macromolecular groups in the reaction system, sol, which is composed of linear and branched polymer chains (sol is soluble in good solvents), and gel, which is crosslinked (insoluble, but swellable in good solvents). Li et al.[13] measured conversions of monomer to sol and crosslinked gel for copolymerization of MMA/EGDMA by gravimetry using Soxhlet extraction. *Figure 1* shows a typical example for the conversion histories for sol and gel and the conversion at the gelation point (X_c). *Figure 2* shows the dependence of the gelation point on the concentration of crosslinker EGDMA.

Polymerization up to the gelation point proceeds, in general, in three stages: formation of 'primary' (linear) macromolecules with pendant/internal double bonds; branching via these double bonds; and intermolecular crosslinking leading to gelation. The primary chains are formed almost instantaneously. As the concentration of these chains increases, the pendant double bonds, which are not wasted in the formation of intramolecular loops, become available for inclusion in other growing primary chains. Therefore branched polymers are formed. These polymer chains may contain many radical centres. Such intermolecular reactions as propagation with pendant double bonds and termination by recombination between these polymer chains generate 'infinitely large' molecules (in micro-scale), and therefore cause gel formation. The gel once formed grows very rapidly consuming sol
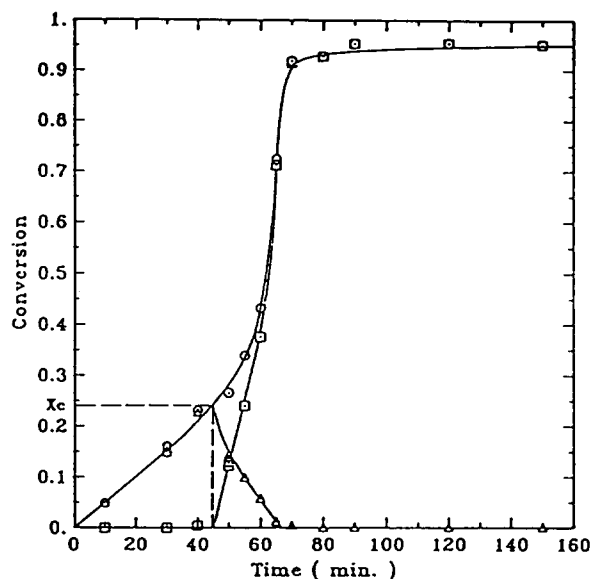

Figure 1 Conversion time histories for conversion of monomer to sol and gel ($\triangle$, sol; $\square$, gel; $\bigcirc$, total) for polymerization of MMA/EGDMA at 70°C, 0.3 wt% EGDMA and 0.3 wt% AIBN showing onset of gelation (Xc). Data from reference 13
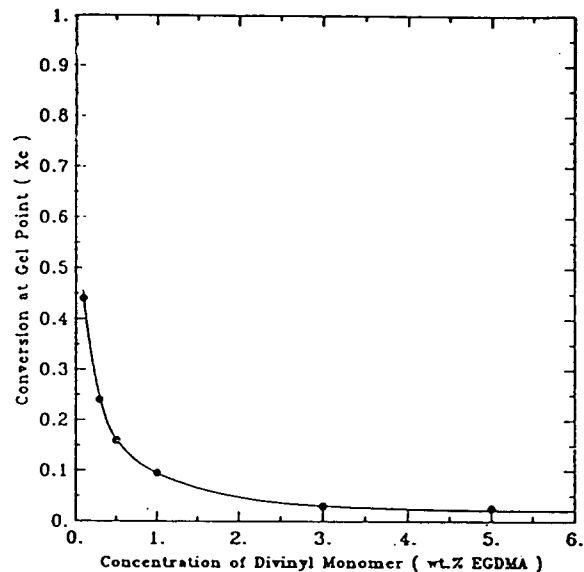

Figure 2 Conversion at gelation point (Xc) and its dependence on level of EGDMA for polymerization of MMA/EGDMA at 70°C, 0.3 wt% AIBN. Data from reference 13

polymers and monomer molecules. The microstructure development within crosslinked polymer is predominantly achieved during this stage via intramolecular reactions.

Various models have been proposed for the kinetics of network formation. The pioneering work of Flory[14] and Stockmayer[15-17] in the early 1940s achieved great progress. This model is often called the classical theory, and it enjoys the simplicity of a mean-field theory. The cascade theory developed by Gordon[18], and the Macosko–Miller[19,20] model using conditional probability theory are in the same category. The percolation theory by Broadbent and Hammersley[21,22] belongs in another category, which is based on a non-mean-field theory. At present, differences of opinion exist on the applicability of these theories to various polymerization systems, except based on intuition, it is expected that the percolation theory, due to the inherent properties of

lattice models, is more accurate near the gelation point and in the post-gelation period when the polymerization system becomes rigid. Recently, based on the pseudo-kinetic rate constant method (a mean-field theory), Tobita and Hamielec[23-26] proposed a kinetic model which is capable of accounting for all of the important reactions and provides greater insight into the phenomena of network formation.

The application of kinetic models requires a knowledge of kinetic parameters. The major ones are the initiation efficiency, the propagation rate constant with monomeric double bonds, the reactivity ratio, the propagation rate constant with pendant double bonds, cyclization rate constants, and the bimolecular radical termination rate constants for sol/sol, gel/gel and sol/gel reactions. All of these parameters strongly depend on monomer conversion and the polymer chain micro-structure. A full estimation of these rate constants appears very difficult.

It is clear that the propagation rate constant estimated from the measurements of total double bond conversion and total radical concentration according to equation (1) is an average rate constant for all the reactions which consume double bonds. These reactions include the cyclization and propagation with monomeric double bonds and pendant double bonds. It is also clear that the number average termination rate constant defined in terms of the number of monomeric units on crosslinked polymers does not have a clear physical interpretation as it does for polymerizations producing linear polymer chains. A more realistic definition of the termination constant should include the distribution of mobility of radical centres chemically bound to the crosslinked gel.

Although these average kinetic parameters do not provide great insight into gel structure development, they do provide a guide for understanding overall kinetic rates. The following analysis is based on the use of average kinetic parameters.

Polymerization mechanisms at very high conversions

Figure 3 shows an example of a radical concentration history for bulk copolymerization of MMA/EGDMA. It can be seen that after a dramatic rise the radical concentration levels off at about where the polymerization rate approaches zero (c. 90% double bond conversion) and remains almost constant for 96 h. Therefore, it can be concluded that the propagation rate constant must approach zero as the conversion rate, dX/dt approaches zero, according to equation (1), and that the initiation efficiency and the number average termination rate constant must change simultaneously at the limiting conversion, according to equation (3).

A point worth mentioning is that, in conventional kinetic modelling (see references 27-31 for a review of these models), the initiation efficiency is assumed to remain unchanged throughout the whole course of polymerization while there is a dramatic fall in the termination rate constant at the limiting conversion. More recently, based on the fact that the limiting conversion of a bulk polymerization is often lower than that of its corresponding emulsion polymerization, Russell *et al.*[32] suggested that the initiation efficiency falls earlier than the termination rate constant which is assumed to be proportional to the propagation rate constant in light of the propagation diffusion concept[33]. We examined these two extreme cases as shown in *Figure*
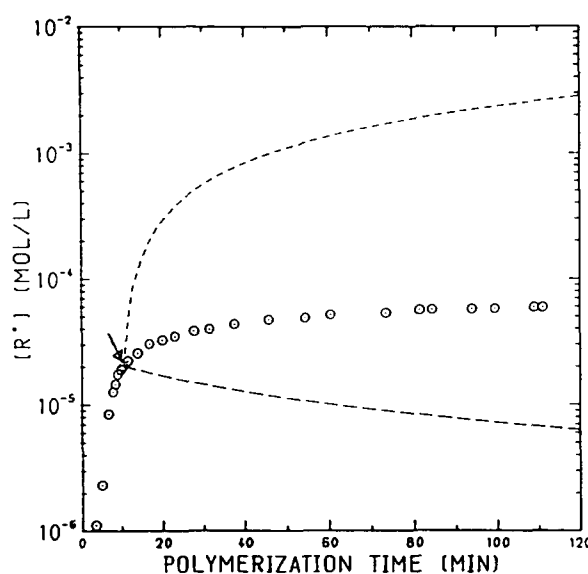

Figure 3 Experimental measurements of radical concentration history (O) for bulk copolymerization of MMA/EGDMA at 70°C with 0.3 wt% AIBN and 25 wt% EGDMA, and predictions of radical concentration behaviour at terminal conversion using equation (3) when neglecting initiation ($\bar{K}_{tn} \approx 10^3$ l/mol s; ref. 32) (———) or when neglecting termination ($f = 0.5$; ref. 27) (— — — —). The point indicated by an arrow is taken as the onset of a glassy state transition

3 and found that neither of these models agrees with the experimental measurements. The former predicts a dramatic rise in radical concentration at the limiting conversion and the latter does the opposite while the experimental data level off.

In order to separate the initiation efficiency and the termination rate constant, one may resort to the use of molecular weight measurements. The number average termination rate constant can be extracted from the number average molecular weight using equation (2), provided that one polymer chain contains at most one radical centre. This condition can be met in MMA homopolymerization initiated by AIBN, which produces only linear polymer chains. The experimental data from the literature[34] show that, at very high monomer conversion, there is no order of magnitude change in the molecular weight averages. This suggests that the termination rate constant must also fall at the limiting conversion, simultaneously with the propagation rate constant. Our direct post-effect measurement of the radical concentration decays[6,9] verifies that the termination constant falls dramatically. Therefore, it can be concluded that the propagation rate constant, the initiation efficiency and the termination rate constant all fall dramatically and almost simultaneously at very high conversions.

As far as the discrepancies between the apparent values of the propagation rate constants in bulk polymerizations and the corresponding emulsion ones[32] are concerned, it is proposed that there exist two radical populations in the reacting mass in terms of the radical environments, active radicals and inactive radicals. The former are in an environment with greater free volume and this allows monomer molecules to diffuse more readily to the radical centres, and the latter radical centres are trapped in domains which consist mainly of polymeric segments. This heterogeneity in the polymerization medium seriously complicates the kinetic analysis at high conversions. One complication among many others is

the definition of the propagation rate constant. The propagation rate might be expressed as

$$R_p = K_{pina}[R^\bullet]_{ina}[M] + K_{pact}[R^\bullet]_{act}[M] \qquad (4)$$

where the subscripts ina and act represent the inactive radicals and the active ones, respectively. With $K_{pina} = 0$, equation (4) becomes

$$R_p = K_{pact}\theta[R^\bullet][M] \qquad (5)$$

where $[R^\bullet]$ is the total radical concentration, θ is the active radical fraction, $[R^\bullet]_{act}/[R^\bullet]$. The commonly defined propagation rate constant K_p in terms of the total radical concentration actually equals $K_{pact}\theta$. In bulk polymerizations, the active radical concentrations are low (primary and oligomeric radicals) due to the dramatic fall in the initiation efficiency at the limiting conversion. The θ value is therefore close to zero. On the contrary, in emulsion polymerizations, initiator radicals are generated in the water phase, and oligomeric radicals then diffuse into the monomer–polymer particles. Therefore, an appreciable concentration of radicals with short chains always exist in the polymer particles to give a significant value for θ. This leads to higher terminal conversions and explains the discrepancies between bulk and emulsion polymerizations[32].

Trapped radical termination at elevated temperatures

The trapped or inactive radicals are likely stable due to very small diffusion rates in the polymerization medium. Copolymerizations of MMA/EGDMA were done with 0, 25, 50, 75 and 100 wt% EGDMA initiated by 2.0 wt% AIBN at 70°C for 96 h (120 h for pure MMA). As shown in *Figure 4*, the trapped radical concentrations were found $1.3 \times 10^{-5}, 7.8 \times 10^{-5}, 9.2 \times 10^{-4}$, 1.5×10^{-3} and 2.5×10^{-3} mol/l, respectively. The terminal double bond conversions were measured using a laser Raman spectrometer. (The conversion measured with the laser Raman spectrometer is a total double bond conversion, which, coupled with monomer conversion data measured by gravimetric methods, permits one to estimate the pendant double bond content during the polymerization of MMA/EGDMA.) The
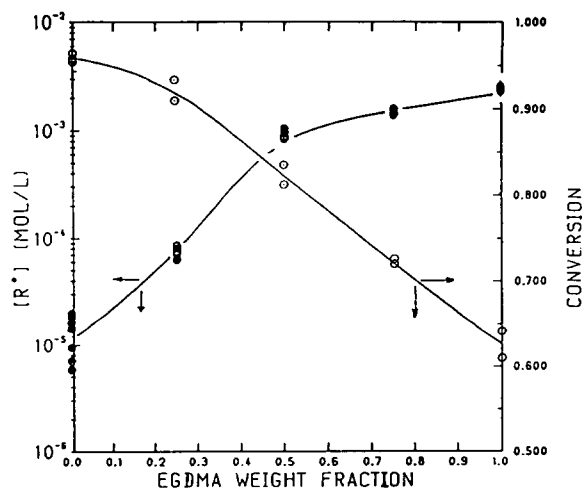

Figure 4 Terminal conversion measured by a laser Raman spectrometer and trapped radical concentration measured by an e.s.r. *versus* EGDMA weight fraction for bulk free radical copolymerization of MMA/EGDMA at 70°C with 2.0 wt% AIBN and reaction time: 120 h for pure MMA, 96 h for the copolymerization

trapped radical concentration increases with the EGDMA amount, and the terminal conversion does the opposite. The former is because the radicals bound on the gel structure find it difficult to mutually terminate, and the latter indicates that the polymer chains with higher levels of crosslinking have higher glassy state transition temperatures. The radical trapping due to the glassy state transition and/or crosslinking is an important phenomenon. The reasons for this are two-fold. Firstly, these radicals may have some influence on polymer product quality, such as molecular weight stability. Secondly, they may also find some applications in the development of new polymer products, such as interpenetrating polymer network and in purification by removal of trace impurities. Therefore, studies on the nature of trapped radicals are desirable. In this work, we investigated the bimolecular termination behaviour of these radicals at elevated temperatures. *Figures 5, 6, 7, 8* and *9* show the decays in radical concentration during the post-effect period at five EGDMA levels and at four temperatures: 180, 150, 120 and 105°C. It can be seen that the decay rate is a strong function of both temperature and EGDMA level. The decay rate of radicals increases with temperature and decreases with increasing level of EGDMA. Because the amount of residue AIBN is negligible, equation (3) reduces to

$$\frac{d[R^\bullet]}{dt} = -\bar{K}_{tn}[R^\bullet]^2 \qquad (6)$$

Equation (6) may be arranged into a more convenient form as follows.

$$\bar{K}_{tn} = \frac{d(1/[R^\bullet])}{dt} \qquad (7)$$

Therefore, the number average termination rate constant can be directly estimated by plotting the reciprocal of radical concentration $(1/[R^\bullet])$ as a function of time (t). *Figures 10* and *11* show some examples. It can be seen that the plots for low EGDMA levels and high temperatures are straight lines while the others show a decrease in $\bar{K}_{tn}$ with time. Calculation of the slopes for these curves provides the termination rate constant histories in the post-effect period. *Figure 12* shows $\bar{K}_{tn}$ variations for 150°C at five EGDMA levels. As can be seen, the termination rate constants do not change with time for samples with low EGDMA weight fractions (0 and 25 wt%), but decrease significantly for samples with high EGDMA fractions (50, 75 and 100 wt%, notice the log scale) in the post-effect periods.

The free radical termination mechanisms in crosslinked system at high conversions appear very complex and remain unsolved to date. Two possible modes of termination are by propagation diffusion and termination by oligomeric radicals (including primary radicals). Based on the former concept, Russell *et al.*[1] derived the following equation

$$\bar{K}_{tn} = \frac{8\pi a^2 r}{3} K_p[M] \qquad (8)$$

where a is the root-mean-square end-to-end distance per square root of the number of monomer units in the polymer chain (0.69 nm for PMMA[35]), r is the reaction radius within which two radicals overcome the chemical activation barrier and mutually terminate. It was found that the changes in $[M]$ were small in the post-effect
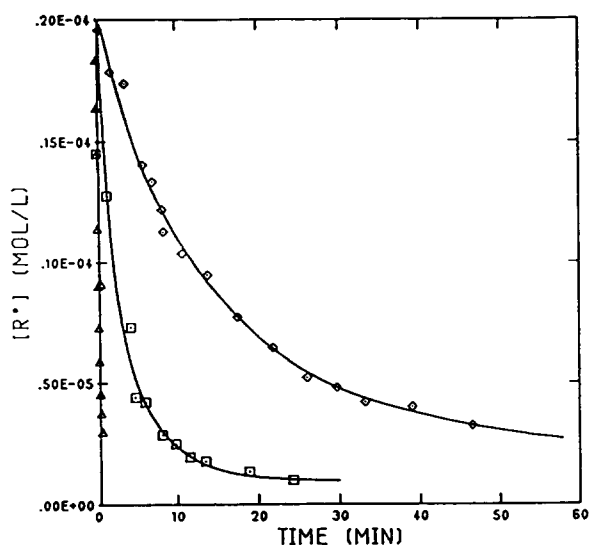
Figure 5 Trapped radical concentration (mol/l) decay *versus* time (min) in post-effect period for pure MMA polymerized previously for 120 h at 70°C with 2.0 wt% AIBN. Elevated temperatures are △, 150°C; □, 120°C; ◇, 105°C
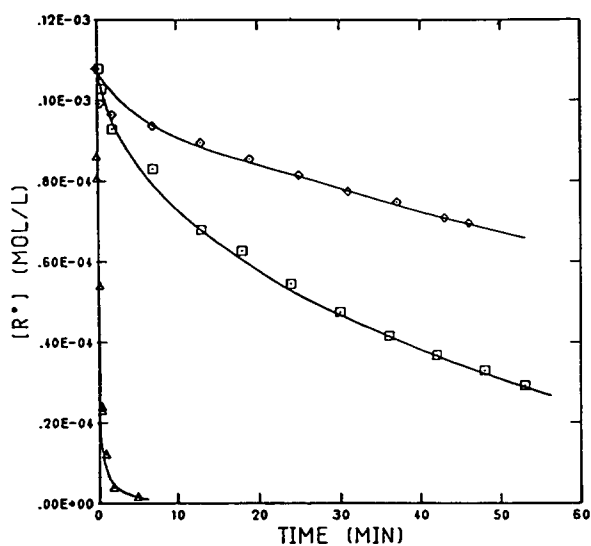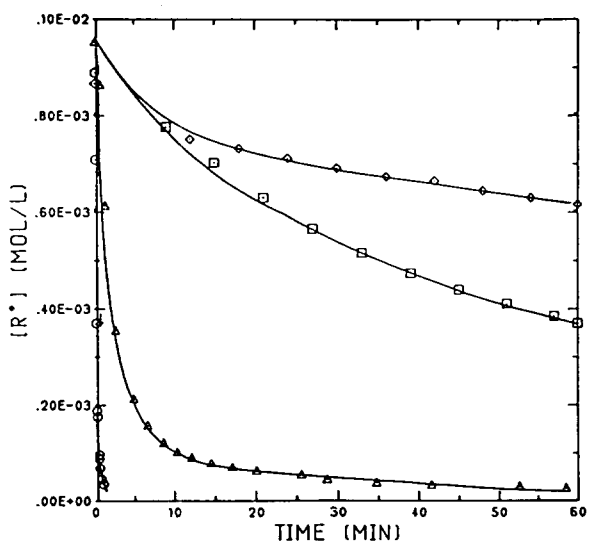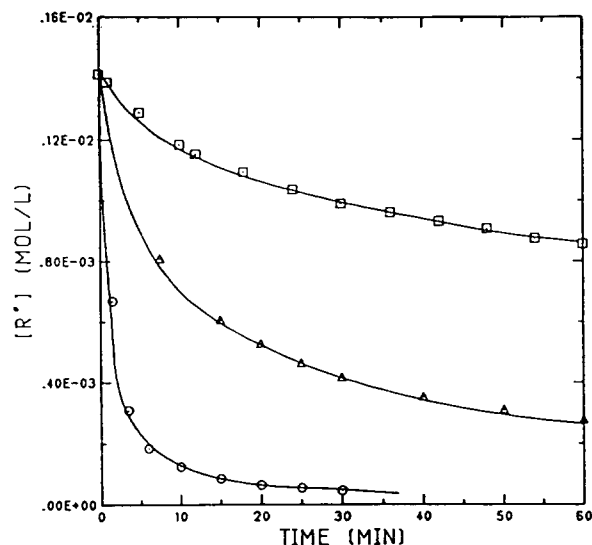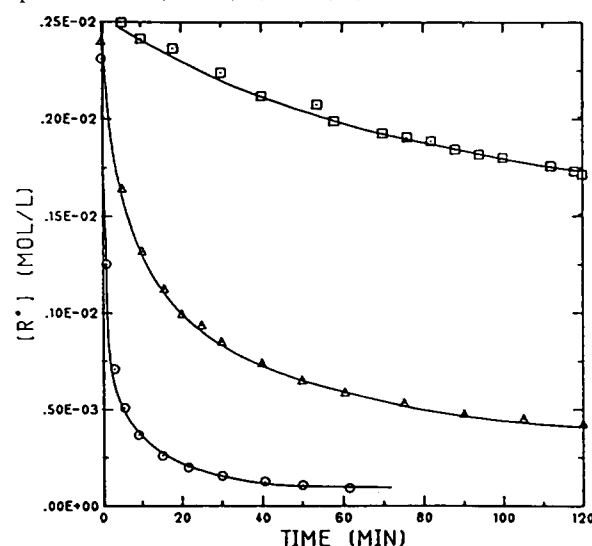

Figure 8 Trapped radical concentration (mol/l) decay *versus* time (min) in post-effect period for MMA/EGDMA (75 wt% EGDMA) polymerized previously for 96 h at 70°C with 2.0 wt% AIBN. Elevated temperatures are ⊙, 180°C; △, 150°C; □, 120°C

Figure 6 Trapped radical concentration (mol/l) decay *versus* time (min) in post-effect period for MMA/EGDMA (25 wt% EGDMA) polymerized previously for 96 h at 70°C with 2.0 wt% AIBN. Elevated temperatures are △, 150°C; □, 120°C; ◇, 105°C

Figure 9 Trapped radical concentration (mol/l) decay *versus* time (min) in post-effect period for pure EGDMA polymerized previously for 96 h at 70°C with 2.0 wt% AIBN. Elevated temperatures are ⊙, 180°C; △, 150°C; □, 120°C

Figure 7 Trapped radical concentration (mol/l) decay *versus* time (min) in post-effect period for MMA/EGDMA (50 wt% EGDMA) polymerized previously for 96 h at 70°C with 2.0 wt% AIBN. Elevated temperatures are ⊙, 180°C; △, 150°C; □, 120°C; ◇, 105°C
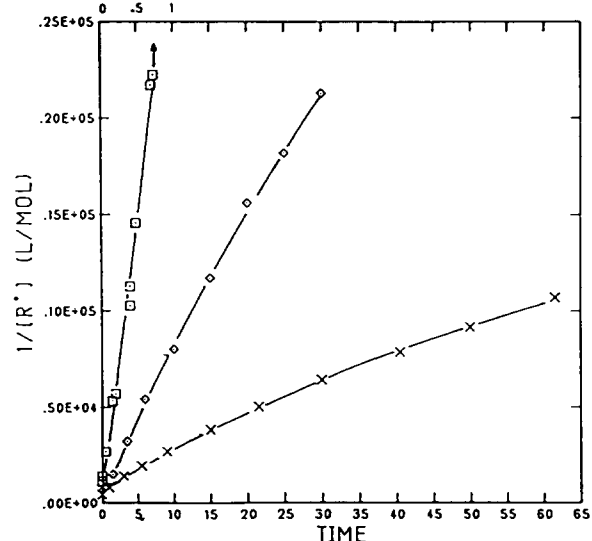

Figure 10 Reciprocal of radical concentration (l/mol) *versus* time (min) in post-effect period at 180°C for MMA/EGDMA polymerized previously for 96 h at 70°C with 2.0 wt% AIBN. EGDMA levels are □, 50 wt%; ◇, 75 wt%; ×, 100 wt%
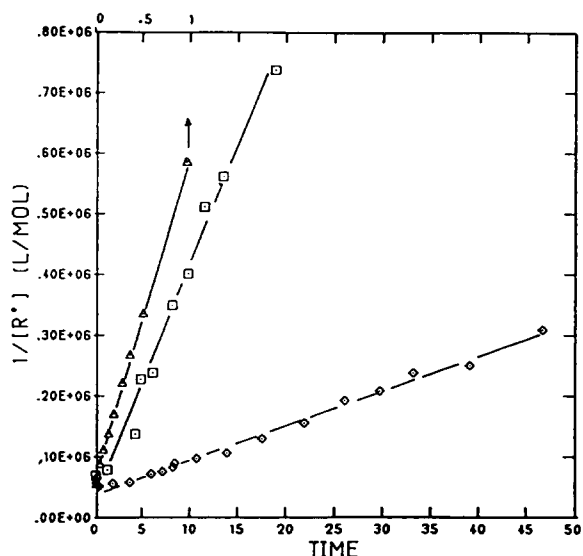
Figure 11 Reciprocal of radical concentration (l/mol) *versus* time (min) in post-effect period for MMA polymerized previously for 120 h at 70°C with 2.0 wt% AIBN. Elevated temperatures are △, 150°C; □, 120°C; ◇, 105°C
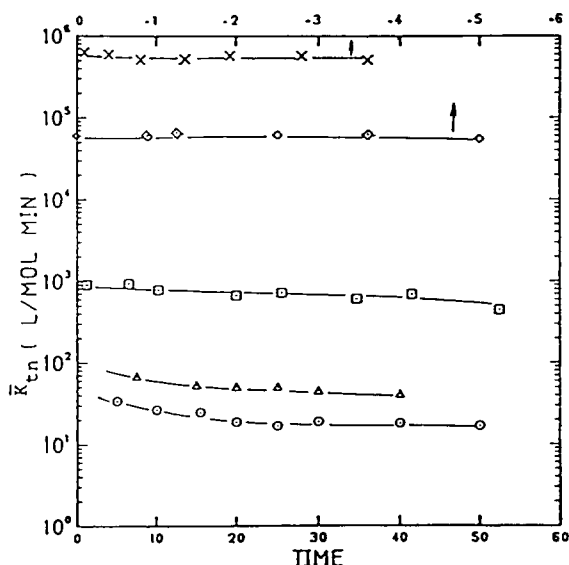

Figure 12 Termination rate constants (l/mol min) *versus* time for the post-effect period at 150°C for MMA/EGDMA polymerized previously for 96 h (120 h for pure MMA) at 70°C with 2.0 wt% AIBN. EGDMA levels are ○, 100 wt%; △, 75 wt%; □, 50 wt%; ◇, 25 wt%; ×, 0 wt%

periods, e.g. a maximum change of 0.06 in double bond conversion was observed (from 0.63 to 0.69) for the samples of 100 wt% EGDMA at 180°C. Clearly, for such small decreases in $[M]$, equation (8) cannot explain the decreases in $\bar{K}_{tn}$ observed.

On the other hand, the second explanation is based on the assumption that there exists an appreciable concentration of oligomeric radicals which, at elevated temperatures, gain mobility. These radicals may terminate with the radicals bound on the gel structure. The latter are likely to be wandering around their crosslinking nodes. A prerequisite for modelling this termination process is the full understanding of chain length dependent diffusion of oligomeric radicals in a crosslinked polymer matrix. Unfortunately, this type of diffusion is not well understood. The existing theories, such as the free volume theory[36] and the reptation theory[37] have not been extended and evaluated for crosslinked systems.

Another simple explanation is to assume that the reacting mass is heterogeneous in terms of the radical environment, some are surrounded by a large number of polymeric segments and thus have a lower level of free volume in their vicinity while others have relatively more free volume. An increase in temperature increases the free volume and releases a fraction of the trapped radicals while the remainder of the radicals are still trapped in the polymer matrix. For this situation, equation (6) can be rearranged as follows[38] (a derivation of equation (9) may be found in the Appendix),

$$\frac{t}{[R^{\cdot}]_0 - [R^{\cdot}]} = \frac{t}{[R^{\cdot}]_0 - [R^{\cdot}]_{tr}} + \frac{1}{K'_{tn}\{[R^{\cdot}]_0 - [R^{\cdot}]_{tr}\}^2} \quad (9)$$

where $[R^{\cdot}]_0$ is the initial radical concentration, $[R^{\cdot}]_{tr}$ is the final concentration of trapped radicals, and $\bar{K}'_{tn}$ is the termination rate constant for the active radicals. A plot of $t/\{[R^{\cdot}]_0 - [R^{\cdot}]\}$ *versus* t should give a straight line. *Figure 13* shows two examples (the coefficient of determination reaching 0.999). The trapped radical concentration and the active radical termination rate constant can be estimated from the slope (S) and intercept (I) as follows

$$[R^{\cdot}]_{tr} = [R^{\cdot}]_0 - S^{-1} \quad (10)$$

and

$$\bar{K}'_{tn} = S^2/I \quad (11)$$

Figure 14 presents these termination rate constants for active radicals *versus* EGDMA weight fraction and temperature and clearly shows the influence of crosslinking on active radical termination rate constants. *Figure 15* shows the same termination rate constants *versus* the reciprocal of absolute temperature. The activation energies for the five EGDMA levels under investigation are listed in *Table 1*. The values are of the order of 10 kcal/mol. Obviously, such a strong temperature dependence cannot be for chemically controlled radical bimolecular termination (usually about 1 kcal/mol). *Figure 16* shows trapped radical concentrations calculated using equation (10). The
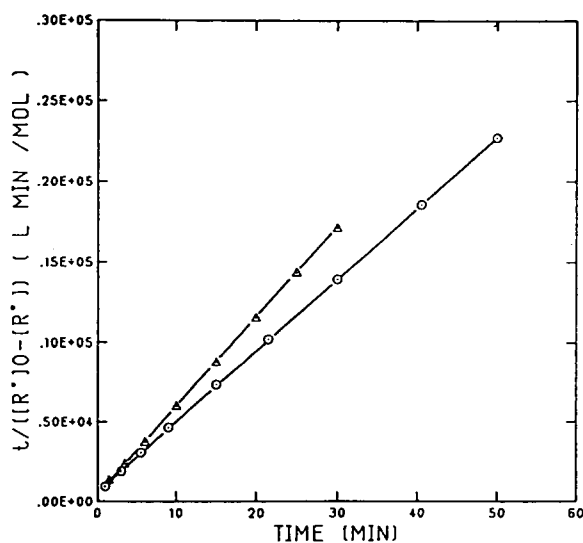

Figure 13 Plot of $t/([R^{\cdot}]_0 - [R^{\cdot}])$ (1 min/mol) against t (min) in the post-effect period at 180°C for MMA/EGDMA with EGDMA levels: ○, 100 wt%; △, 75 wt%. The samples were polymerized previously for 96 h at 70°C with 2.0 wt% AIBN
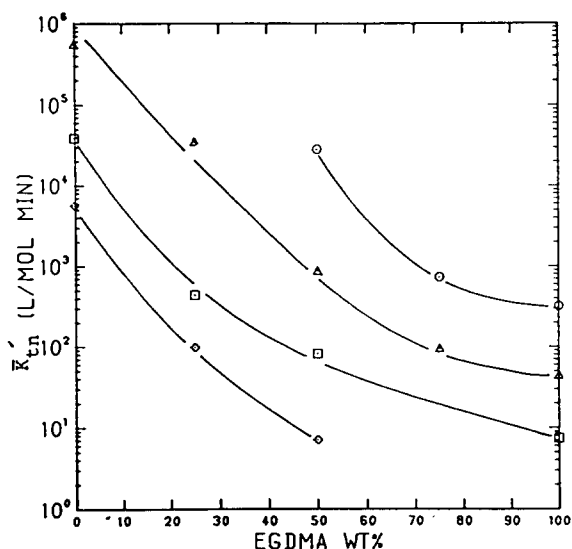
Figure 14 Termination rate constants (l/mol min) of active radicals *versus* EGDMA concentration level (wt%) for MMA/EGDMA at limiting conversion of 70°C and 2.0 wt% AIBN. Temperatures are ⊙, 180°C; △, 150°C; ▣, 120°C; ◇, 105°C
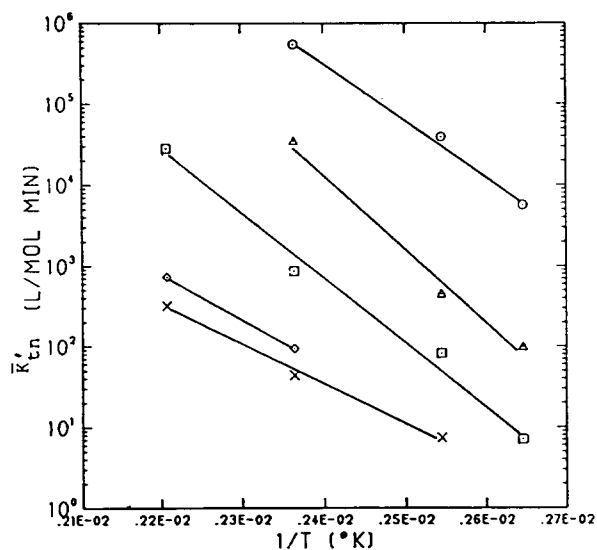

Figure 15 Termination rate constants (l/mol min) of active radicals *versus* reciprocal of absolute temperature (K^{-1}) for MMA/EGDMA with EGDMA levels: ⊙, 0 wt%; △, 25 wt%; ▣, 50 wt%; ◇, 75 wt%; ×, 100 wt%, at terminal conversions of 70°C and 2.0 wt% AIBN

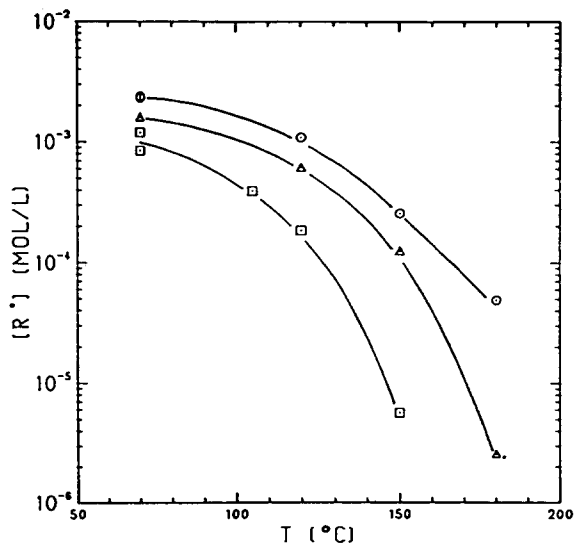**Figure 16** Trapped radical concentration (mol/l) as function of temperature (°C) for MMA/EGDMA with 2.0 wt% AIBN and EGDMA levels: ⊙, 100 wt%; △, 75 wt%; ▣, 50 wt%

Table 1 Activation energies for termination rate constants of active radicals at elevated temperatures for different levels of crosslinker

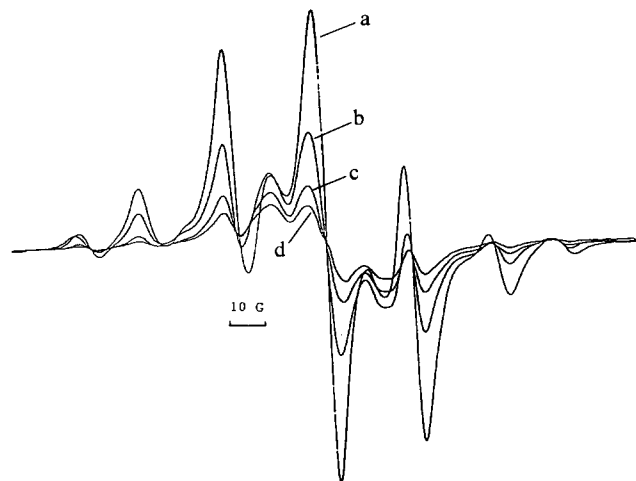| EGDMA (wt%)	0	25	50	75	100
E (kcal/mol)	13.87	18.36	15.61	11.30	9.60

Figure 17 E.s.r. spectra recorded in post-effect period at 180°C for MMA/EGDMA with 75 wt% EGDMA. Operation conditions: microwave frequency 9.45 GHz, modulation frequency 100 kHz, modulation amplitude 3.2 Gpp, power 20 dB, gain 2×10^4 and reaction time (a) 0 min 00 s, (b) 1 min 30 s, (c) 3 min 30 s, (d) 6 min 00 s

concentrations fall dramatically with increase in temperature at all levels of crosslinker.

A final point worth mentioning is that the e.s.r. signals in the post-effect period experience some structural changes. *Figure 17* gives an example. It can be seen that the height ratio of the central line over the neighbour inner line falls significantly in the post-effect period. This change in e.s.r. spectra reflects some changes in radical conformation and likely reactivity. Such information is essential to a better understanding of polymerization mechanisms and kinetics. A model simulation study of spectra for both active and trapped radicals is underway.

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APPENDIX

Equation (9) has been derived by Dole[38] as follows. In general, the consumption of any reactant, C, in a bimolecular reaction, can be expressed as,

$$\frac{dC}{dt} = -KC^2 \tag{A1}$$

Integrating equation (A1) with the initial condition $C = C_0$ at $t = 0$ yields

$$(1/C) - (1/C_0) = Kt \tag{A2}$$

Expressing equation (A2) explicitly in terms of C, one obtains

$$C = C_0/(1 + C_0 Kt) \tag{A3}$$

This can be rearranged to yield

$$C_0 - C = CC_0 Kt \tag{A4}$$

Substituting equation (A3) into the right-hand side of equation (A4), inverting and multiplying by time, t, one obtains

$$\frac{t}{C_0 - C} = \frac{t}{C_0} + \frac{1}{KC_0^2} \tag{A5}$$

Now, specifying C to be the concentration of active radicals at time t and C_0 to be the initial concentration of active radicals

$$C_0 = [R^{\bullet}]_0 - [R^{\bullet}]_{tr} \tag{A6}$$

$$C = [R^{\bullet}] - [R^{\bullet}]_{tr} \tag{A7}$$

and substituting equations (A6) and (A7) into equation (A5) one obtains

$$\frac{t}{[R^{\bullet}]_0 - [R^{\bullet}]} = \frac{t}{[R^{\bullet}]_0 - [R^{\bullet}]_{tr}} + \frac{1}{\bar{K}'_{tn}\{[R^{\bullet}]_0 - [R^{\bullet}]_{tr}\}^2}$$