Macromolecules **1994,** *27,* 1657-1659

Communications to the Editor

Evaluation of the Chain-Length Dependence of the Termination Rate Constant during Radical Polymerization of a Methacrylic Ester

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Received September 10, 1993
Revised Manuscript Received January 13, 1994

Most of the reactions between radicals in solution occur with diffusion-controlled rates. During free-radical polymerization, bimolecular termination, which is a typical diffusion-controlled reaction, is one of the most important steps for controlling the polymerization reactions, but it is quantitatively analyzed with some difficulty because it depends on many polymerization condition factors, e.g., polymer concentration and polymer chain length. The rate-determining step of the termination is a segmental diffusion-controlled one during an earlier regime of polymerization, but it undergoes a change to center-of-mass diffusion and reaction-diffusion-controlled ones, according to the conversion of polymerization.[1] The dependence of the termination rate constant (k_t) on the length of a growing polymer chain has experimentally and theoretically been examined in relation to several termination models.[2-13] However, there are very few experimental reports which extract the chain-length dependence of k_t in a real polymerization system without the influences of any other factors. It is an important problem of great urgency that we accumulate reliable experimental data concerning the chain-length dependence of k_t during in situ polymerization.

We recently reported[14] that, during the radical polymerization of *trans*-4-*tert*-butylcyclohexyl methacrylate (4BCHMA), propagating radical concentrations were determined by electron spin resonance (ESR) spectroscopy for evaluating the propagation rate constant (k_p) and k_t according to the following equations:

$$R_p = -\mathrm{d}[\mathrm{M}]/\mathrm{d}t = k_p[\mathrm{P}^\bullet][\mathrm{M}] \qquad (1)$$

$$R_t = -\mathrm{d}[\mathrm{P}^\bullet]/\mathrm{d}t = k_t[\mathrm{P}^\bullet]^2 \qquad (2)$$

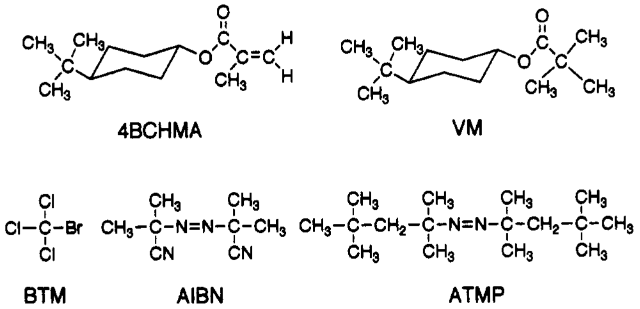
where R_p and R_t are the polymerization and termination rates, respectively, and [M] and [P$^\bullet$] are the monomer and propagating radical concentrations, respectively. At a steady state, R_t is equal to the initiation rate (R_i);

$$\mathrm{d}[\mathrm{P}^\bullet]/\mathrm{d}t = R_i - R_t = 2k_d f[\mathrm{I}] - k_t[\mathrm{P}^\bullet]^2 = 0 \qquad (3)$$

where k_d, f, and [I] are the decomposition rate constant, the initiator efficiency, and the concentration of the initiator, respectively.

This paper deals with the chain-length dependence of k_t. We determined k_p and k_t during an initial stage in several polymerization systems of 4BCHMA initiated with 2,2′-azobis(isobutyronitrile) (AIBN) in benzene at 60 °C (i) at various monomer concentrations and (ii) at various initiator concentrations in the absence of any additives, and (iii) in the presence of *trans*-4-*tert*-butylcyclohexyl pivarate as a viscosity modifier (VM), (iv) in the presence of bromotrichloromethane (BTM) as a chain-transfer agent, and we also analyzed (v) the aftereffect in the photopolymerization with 2,2′-azobis(2,4,4-trimethylpentane) (ATMP) as a photoinitiator (Chart 1).

Chart 1



The polymerization was performed in a sealed glass tube, and the polymer produced was isolated from methanol to determine a polymer yield, i.e., conversion. R_p was determined from an initial slope of the first-order time–conversion relationship in the 0 to ca. 40% conversion region. ESR spectra were recorded on a Bruker ESP 300 spectrometer equipped with an X-band microwave unit and 100-kHz field modulation. All the determinations of [P$^\bullet$] were carried out at a low conversion (below ca. 10%) of polymerization without any corrections with respect to the sensitivity change along with conversion.[14] Radical concentration was calibrated with 1,3,5-triphenylverdazyl as the stable radical. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) were determined by gel permeation chromatography in tetrahydrofuran at 38 °C and calibrated with standard polystyrenes. R_i was determined from the decay of absorbance at 720 nm of the verdazyl added in the polymerization system.

Table 1 summarizes typical experimental results of polymerizations of 4BCHMA in systems i–v. During the polymerization of 4BCHMA in the absence of any additives, k_t varied from 1.9 to 0.52 × 10^6 L/mol·s with a change in the monomer concentration (1–2.5 mol/L), but k_p was independent (570 ± 10 L/mol·s). The change in k_t includes both the effects of the chain length of the reacting polymer radicals and the viscosity of the polymerization medium. The difference in the viscosity (e.g., 0.726 cP at [M] = 1 mol/L to 1.47 cP at [M] = 2.5 mol/L (30 °C, at 0% conversion)) also influenced f; f changed from 0.46 to 0.22 with an increase in the viscosity of the solution along with an increase in [M]. Varying [I] resulted in a small change of M_n (system ii), but only a limited range of [I] (more than 10^{-2} mol/L) was available in this work because of the difficulty of precisely estimating [P$^\bullet$] at a lower [I]. To exclude the viscosity effect from system i, we carried out the polymerization in the presence of VM, which is a model compound of the polymer repeating unit (system iii). In the presence of VM, the observed R_p and M_n were higher than those in the absence of VM. This is ascribed to the difference in k_t. Second, we examined the polymerization in the presence of BTM as an effective chain-transfer agent[15] (system iv). By the addition of BTM, a slight

0024-9297/94/2227-1657$04.50/0

Table 1. Typical Results of Radical Polymerization of 4BCHMA with AIBN in Benzene at 60 °C in the Systems i–v

[M], mol/L	10^2[I], mol/L	additive (mol/L)	10^4R_p, mol/L·s	$10^{-4}M_n$	M_w/M_n	$10^{-4}X_n$	$10^7[P^\bullet]$, mol/L	$10^{-2}k_p$, L/mol·s	f	$10^{-6}k_t$, L/mol·s
					System i					
1.0	5	none	2.67	7.5	2.1	5.9	4.9	5.5	0.46	1.9
1.5	5	none	4.64	16.4	2.0	12.8	5.5	5.6	0.43	1.4
2.0	5	none	7.11	30.6	1.7	23.9	6.2	5.7	0.35	0.89
2.5	5	none	9.33	38.5	1.7	30.1	6.5	5.7	0.22	0.52
					System ii					
2.0	2	none	4.54	49.5	1.6	38.7	4.0	5.7	0.35[a]	0.87
					System iii					
1.0	5	VM (1.0)	3.35	10.1	2.0	7.9	5.8	5.8	0.36	1.1
1.5	5	VM (0.5)	5.18	17.0	2.1	13.3	6.0	5.7	0.35[a]	0.95
					System iv					
2.0	5	BTM (0.1)	5.56	2.9	1.8	2.8	4.9	5.6	0.35[a]	1.4
2.0	5	BTM (0.4)	4.71	1.0	1.6	1.0	4.1	5.7	0.35[a]	2.0
					System v					
2.0	5[b]	none		2.7		2.7	20.1			1.4
2.0	1[b]	none		5.4		5.4	16.7			1.2

[a] Assumed to be equal to that at [M] = 2.0 mol/L and [I] = 5×10^{-2} mol/L in system i. [b] Photopolymerization with ATMP.

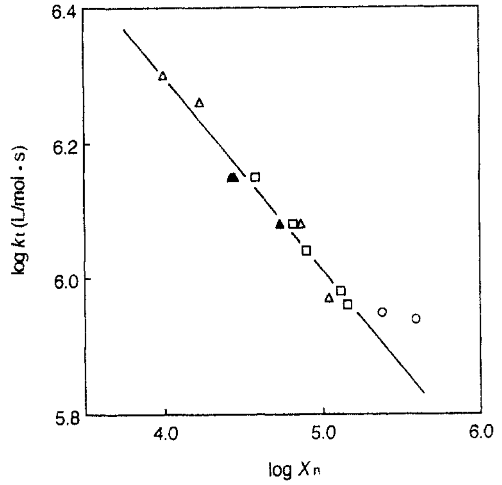


Figure 1. Relationship between log X_n and log k_t in radical polymerization of 4BCHMA in benzene at 60 °C: (○) system ii, (□) system iii, (△) system iv, and (▲) system v (see text).

decrease in R_p was also observed as well as a drastic decrease in M_n, suggesting the chain-length dependent k_t. Subsequently, the aftereffect was also analyzed during the photopolymerization with ATMP (system v) according to eq 4, which is derived by an integration of eq 2;

$$[P^\bullet]_s/[P^\bullet]_t = k_t[P^\bullet]_s t + 1 \qquad (4)$$

where $[P^\bullet]_s$ and $[P^\bullet]_t$ represent $[P^\bullet]$ at a steady state and after t seconds, respectively.

All experimental data obtained in the four systems ii–v gave the chain length–k_t relationship shown in Figure 1. Here the chain length of the propagating radical (X_n) was estimated from M_n of the resulting polymer[16,17] with the assumption that the frequency ratio of proportionation to recombination termination is 0.36 to 0.28.[18] The data obtained from system i deviate from the relationship in the figure because the viscosity conditions in that system are not identical to those in systems ii–v.

In the region of $10^4 < X_n < 10^5$,

$$k_t = AX_n^{-0.28} \qquad (5)$$

where A is the constant. The slope of the line is very close to the chain-length dependence in the intermolecular reactions in dilute solution of polystyrene (poly(St)) by means of the triplet probe method by Horie and Mita[8] and of poly(oxyethylene) by pulse radiolysis by Schnabel and co-workers[5] and is somewhat larger than the values in spatially intermittent polymerization by Mahabadi,[10] i.e., −0.15 and −0.24 for methyl methacrylate (MMA) and St in the bulk, respectively. These values are different from the one (−0.6) expected for the translational diffusion of the center of mass of the whole chain, suggesting the importance of diffusion of segments. For $X_n > 10^5$, the experimental plots deviate from the linear relationship of eq 5 to the upper side. According to the model of Benson and North[4] for the segmental diffusion-controlled termination, k_t is expected to be independent of the chain length of the polymer radical when the chain length is sufficiently large, but we could reach no constant value of k_t in this work because of the limit of the determination of $[P^\bullet]$ at the present conditions and apparatus for ESR measurements. The critical point around 10^5 of X_n may be related to an alteration of the termination mode, e.g., onset of an entanglement between the segments of the propagating polymer radicals. Norisuye and Fujita[19] reported that an excluded-volume effect of the poly(MMA) chain in a good solvent appears in the region of the molecular weight above 2×10^4. Tamai et al.[20] described a picture of a poly(MMA) chain of contour length L = 100 nm as a projection of representative instantaneous contours of a helical wormlike Monte Carlo chain. Since the poly(4BCHMA) chain is less flexible than the poly(MMA) chain because of the steric hindrance of the side alkyl groups, the effect of entanglement is expected to appear at a higher molecular weight than poly(MMA). At the present time, we have no quantitative interpretation for the slope of −0.28 in eq 5 with respect to the termination mechanism, e.g., a style of the segment diffusion, a segment size, and an effect of chain entanglement.

Thus, we succeeded in the evaluation of the chain-length dependence of k_t during the radical polymerization of 4BCHMA in benzene at 60 °C by using the ESR method. Further detailed analysis of the polymerization behavior of 4BCHMA from a kinetic aspect will be reported elsewhere.[21] Molecular characterization of the poly(4BCHMA) chain in solution is now in progress.

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(16) For systems i–iii, $X_n = \{(1 + p)/2\}M_n$ where p is the probability for disproportionation termination (i.e., $1 - p$ is for recombination). In the presence of BTM (system iv), $X_{n,CT}$ was calculated with the equation $X_{n,CT} = \{(1 + p)/2\}M_{n,0}[\{(1 + p)/2\}(M_{n,0}/M_{n,CT}) + \{(1 - p)/2\}]^{-1}$ where $M_{n,0}$ and $M_{n,CT}$ are the number-average molecular weight in the absence and presence of a chain-transfer agent, respectively. In the photopolymerization (system v), since primary radical termination occurs predominantly because of a high concentration of the primary radical, X_n is equal to M_n.

(17) In a strict sense, eq 2 should be described as follows because of the chain-length distribution of both propagating radicals:[1] $R_t = \sum_i\sum_j k_{t,ij}[P_i^\bullet][P_j^\bullet]$ where $[P_i^\bullet]$ and $[P_j^\bullet]$ are the concentrations of the i- and j-meric free radicals. In this work, however, we deal with k_t and $[P^\bullet]$ as the average one.

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