

Effect of Medium Environment on the Propagating Step in Free-Radical Polymerization

Yougang Mao,^{*,†} Min Wang,[†] Bai Yang,[†] Bogeng Li,[‡] Fei Li,[†] and Jiacong Shen[†]

Key Laboratory for Supramolecular Structure and Spectroscopy of Ministry of Education, Institute of Theoretical Chemistry, Jilin University, Changchun 130023, P.R. China, and State Key Laboratory of Polymerization Engineering, Zhejiang University, Hangzhou 310027, P.R. China

Received: July 24, 2001; In Final Form: January 30, 2002

The Arrhenius parameters of propagating reaction for methyl methacrylate (MMA) and styrene (St) were studied in this paper. For MMA, the Arrhenius parameters monotonically decrease with increasing monomer conversion. At the initial and middle stage of the reaction, the growth of radical chain length is the main reason for these changes. This study has also found the propagation rate coefficient (k_p) changes slowly in this period which shows that k_p is not as sensitive as the Arrhenius parameters to the radical chain length because of the cancellation of the activation energy and frequency factor on k_p . At the final stage, k_p decreases sharply because the activation energy is approximately incline to zero and the propagation is completely controlled by molecular diffusion. Unlike MMA, the Arrhenius parameters for St propagation increase at the initial and middle stage which can be explained by the depression of conformation ratio of R_1 to R_2 , and during the final period, k_p and the Arrhenius parameters all decrease sharply, suggesting that k_p is determined by the molecular interaction between radicals and polymer chain.

Introduction

It has been known that in bulk polymerization processes k_p will change with the increase of monomer conversion. Many investigators, such as Friss and Hamielec,¹ Arai and Saito,² Marten and Hamielec,^{3,4} Soh and Sundberg,⁵ Stickler,⁶ Soh and Sundberg,^{7–10} Arai Kunio,¹¹ Chiu and Soony,¹² Achilles,¹³ Huang and Lee,^{14,15} Tian,¹⁶ Gilbert,¹⁷ etc., have proposed many formulas about k_p to fit this change. They ascribed such change to the variations of the radical medium environment. However, other authors found that, in the same medium environment (at low conversions), there has been much disagreement of apparent values of k_p measured by ESR and by other experimental techniques,^{18–24} even of ESR kinetic data itself for the same system but from different groups.^{25–27} Prof. M. Kamachi and R. G. Robert have ascribed such inconsistency to the selection of the experimental condition.²⁸ It strongly suggests that in addition to the medium environment around the radical which is determined by the chain length and polymer concentration the process of propagating reaction itself (its rate) may affect the k_p value. Because the chain length and rate of propagating reaction will change with the variations of medium environment, such effect on k_p could be observed in the whole process of polymerization and therefore could be studied. To our knowledge, few studies about medium environment and activation energy (frequency factor) of propagating reaction have referred to radical chain length so far.^{28–31} In addition, the previous^{32–34} and our recent studies all demonstrated that the average radical chain length basically grows gradually, accompanied by increasing monomer conversion because termination rates drop rapidly as conversion rises.

According to the Arrhenius equation, $k_p = A \exp(-E/RT)$, the change of k_p was mainly ascribed to the frequency factor.^{1–17} However, it has been observed in our previous studies that the

proportion between the thermal unstable and stable conformations of the radical in some special conditions could be involved in the propagating processes.³⁵ In that case, the change of apparent activation energy with monomer conversion should not be neglected and should be taken into account because of the existence of activation energy difference between those conformations. Especially when the propagating reaction favors to the formation of thermodynamic unstable conformation, k_p will strongly depend on the proportion of the stable and unstable conformation isomers.³⁵ Therefore, the proportion is correlated with not only the relaxation rate of the radical but also the rate of itself, which means it might provide deep insights into the interaction mechanism between propagating reaction and medium environment.

According to the collision theory of chemical reaction, on the other hand, activation energy is the energy difference between the initial state and the transient state of the reaction. If the molecular structure of the radical active center does not obviously change with monomer conversion, activation energy will decrease when the medium environment of the reaction changes from liquid to solid. We think it is because the energy of the initial state increases relatively more rapidly than that of the transient state. In the similar hypothesis, the frequency factor will decrease with conversion and will be mainly dependent on the mobility of radicals and monomer molecules.

A very high concentration of initiator was chosen in this study for the following reasons: The radical chain length will be very short and change significantly with increasing monomer conversion. Therefore, the effects of the radical conformation ratio and chain length as well as the polymer concentration on frequency factor and activation energy for propagation could be easily detected. To obtain the relation between activation energy (or frequency factor) and monomer conversion was another purpose of this study.

To obtain the activation energy and frequency factor at certain monomer conversion, a group of k_p values at the same monomer

* To whom correspondence should be addressed.

[†] Institute of Theoretical Chemistry.

[‡] Zhejiang University.

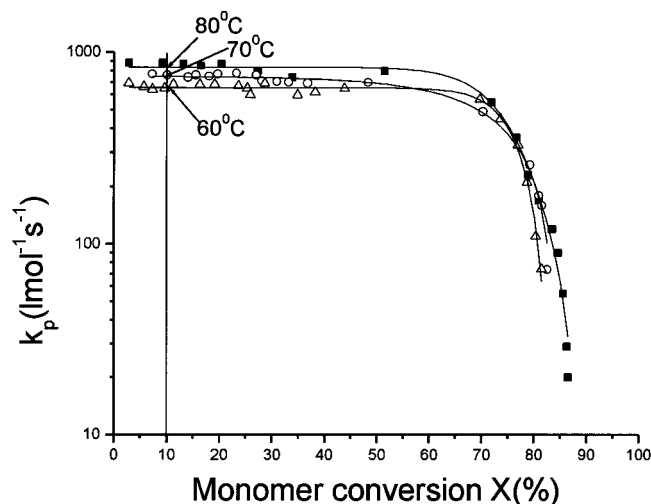


Figure 1. k_p changes with conversion X in bulk polymerization of MMA at three temperatures. $[AIBME]_0 = 0.109$ mol/L. It also presents the method to obtain k_p values of MMA at the same monomer conversion.

conversion but different temperatures must be measured. However, it seems not so easy to measure such a group of k_p values through the experiments. So a method through analysis of k_p values measured by usual experiments was used in this study.

Experimental Section

The measurement of k_p was the same as described in references^{36,37} for MMA and St.

Commercial MMA and St were washed three times with 5 wt. % sodium hydroxide solution, 5 wt. % NaOH, and distilled water, respectively, and dried over a 5 Å molecular sieve and fractionated under reduced pressure. Initiator dimethyl-2,2'-azodiisobutyrate (AIBME) was prepared from 2,2'-azodiisobutyronitrile and purified five times by recrystallization from petroleum ether. Commercial benzoyl peroxide (BPO) was purified by recrystallization from chloroform with methanol.

The polymerizations were carried out in a TM110 cavity on a Bruker ER200D ESR spectrometer at 60–90 °C. The radical concentration was obtained by double integration of the spectra and calibration with the known solution of diphenylpicrylhydrazyl (DPPH) dissolved in MMA and St, respectively. The monomer conversion x was simultaneously followed by a dilatometer. The temperature of the polymerization system was monitored by a thermocouple sealed into the system.

Method for Obtaining the Activation Energy and the Frequency Factor at a Certain Monomer Conversion

The k_p values measured by usual method were shown in Figures 1 and 2. It can be seen that the k_p values for both MMA and St radical change gradually with increasing monomer conversion. No mechanism difference of propagating reaction between MMA and St was observed from the apparent data of k_p . The method for measuring a group of k_p values at the same monomer conversion and different reaction temperatures was shown in Figures 1 and 2. First, we chose a value of monomer conversion, such as 0.1, then a group of k_p values at different temperatures corresponding to this monomer conversion 0.1 could be read from the linking curves of experimental k_p values. When the group of k_p values are acquired, the activation energy and the frequency factor of propagating reaction at that monomer conversion could be calculated according to Arrhenius equation.

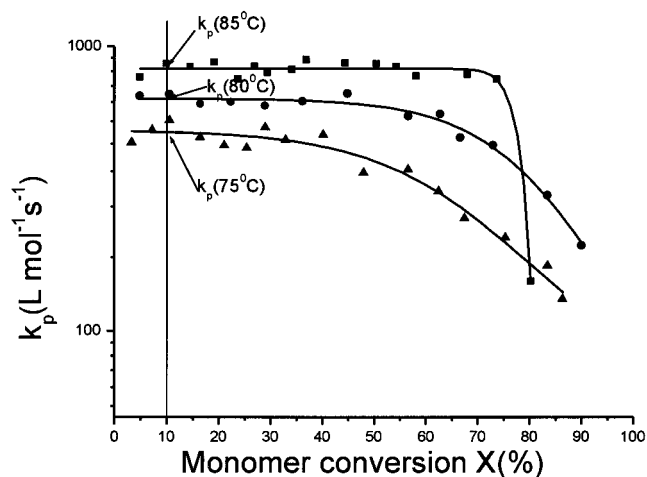


Figure 2. k_p changes with conversion X in bulk polymerization of St at three temperatures. $[BPO]_0 = 0.202$ mol/L. It also presents the method to obtain k_p values of St but the same monomer conversion.

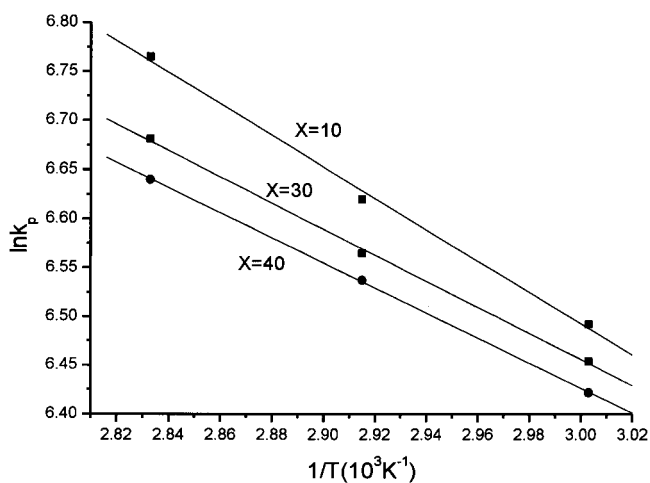


Figure 3. Arrhenius plots for MMA propagation at several monomer conversions.

If the monomer conversion was changed, another group of activation energy and frequency factor values could be obtained. Hence, a series of Arrhenius parameter values at different monomer conversions was available.

The Arrhenius plots of MMA and St radicals at some monomer conversions were shown in Figures 3 and 4. It is clear that the linear relations of k_p vs $1/T$ are quite good. Activation energies and frequency factors at different monomer conversions were shown in Figures 5 and 6.

Results and Discussion

1. PMMA. The changes of activation energy for PMMA radical were shown in Figure 5. It can be explained as follows.

The interaction energy between radical and monomer in the initial state of the propagating reaction is mainly determined by the medium environment around them and will increase with the change of the medium environment from liquid to solid. However, the interaction energy between radical and monomer in the transient state will not increase very much compared with the initial state at the same time. Therefore, the energy difference between initial state and transient state, i.e., the activation energy, will drop when the medium environment of the radical changes from liquid to solid state with the increase of monomer conversion (and accompanying the variation of radical chain length). At the initial stage of the reaction, the radical concentra-

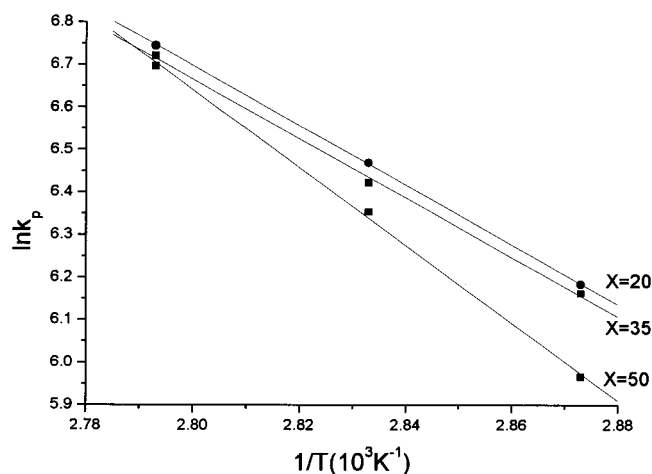


Figure 4. Arrhenius plots for St propagation at several monomer conversions.

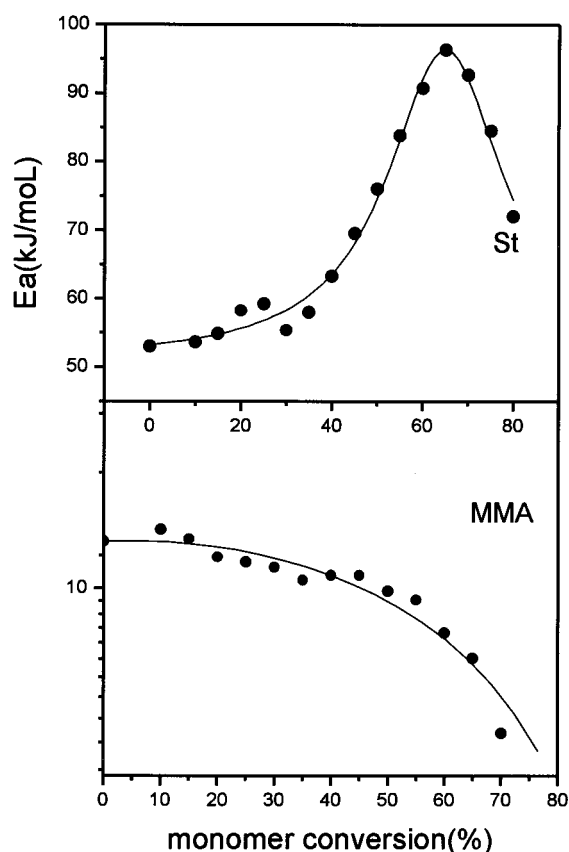


Figure 5. Changes of activation energy for propagation with increasing monomer conversion in the bulk polymerization process of MMA and St.

tion is very low, and the local medium environment is mainly determined by radical chain length (Figure 7). In the middle stage, the local medium environment is determined not only by the chain length but also the polymer concentration (Figure 8). However, this is the only suit for the very short chain radical. For the long chain radical, the local medium environment is only dependent on the radical chain length itself (or intramolecular interaction of the radical molecule), because the intramolecular interaction of radicals is much stronger than the intermolecular interaction between radical and polymer molecules. Because most of the radical molecules in this period have enough chain length, their k_p should still be the function of the radical chain length. At the final stage of the reaction,

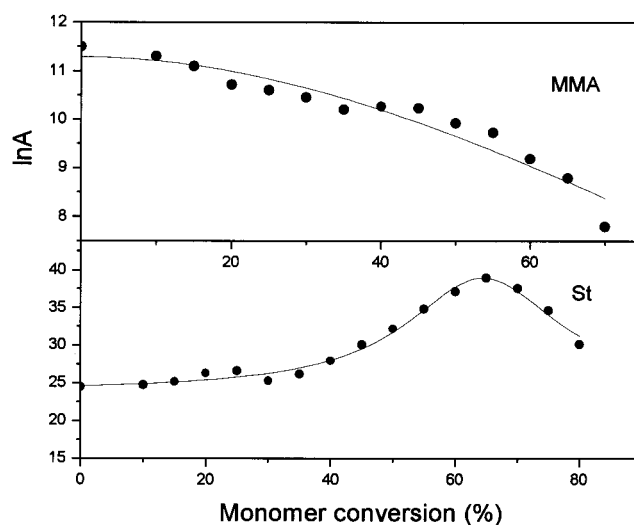


Figure 6. Changes of the frequency factor for propagation with increasing monomer conversion in the bulk polymerization process of MMA and St.

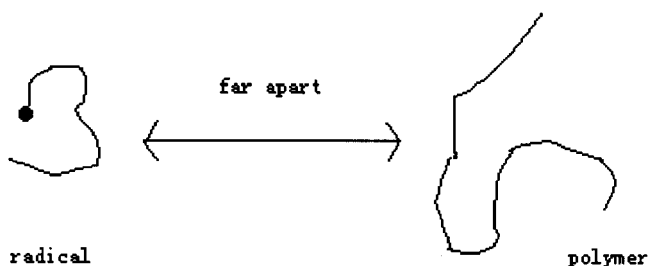


Figure 7. k_p value of the radical determined by the chain length itself, at the beginning stage of the reaction. Therefore, the apparent k_p is determined by molecular weight distribution.

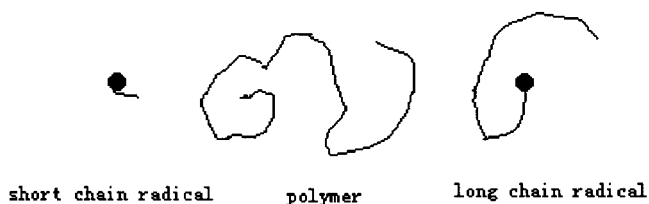


Figure 8. k_p of the long chain radical which is still determined by the chain length itself, at the middle stage of the reaction. However, the short chain radical is determined by not only the radical chain length itself but also the polymer chain.

when the entanglement occurs, the intramolecular interaction is approximately the same as the intermolecular interaction. No matter what, short chain radical or long chain radical will be surrounded by polymer chains. Therefore, the medium environment is mainly dependent on polymer molecules. (Figure 9).

The frequency factor for the MMA radical also decreases with increasing monomer conversion. (Figure 6) It can be ascribed to the depression of the mobility of the radicals and monomer molecules, which will lead to the decrease of collision frequency among them. In the initial and middle stage of the reaction, the decreasing mobility or collision frequency is mainly caused by the growth of radical chain length, because the radical is a large molecule and is more sensitive to the variation of medium environment than the small molecule (monomer). At the final stage, the intermolecular interaction is large enough to affect the mobility of the radical and monomer, so the frequency factor decreases very sharply.

As mentioned above, the increase of the monomer conversion will cause the decrease of activation energy (or the increase of

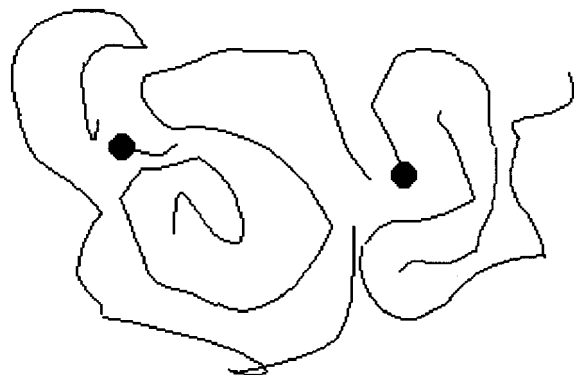


Figure 9. Intramolecular interaction of the radical which is nearly the same as intermolecular interaction between radical and polymer, at the end stage of the reaction. Therefore, the short chain and long chain radicals should have the same k_p .

k_p according to the Arrhenius equation); however, it will simultaneously cause the decrease of the frequency factor (or the decrease of k_p). This means that k_p is not as sensitive to the radical chain length as its activation energy or frequency factor independently because of such cancellation effects, which were supported by the slow variation of k_p at the initial and middle stage of the reaction. Because the radical chain length in this work is shorter compared with others, it is reasonable to deduce that the effect of long chain radical on k_p is smaller than that of short chains, or even it has no effect at all although activation energy and the frequency factor of k_p may change dramatically with growing radical chain length. The following conclusions could be deduced from the discussion above: (1) If the initiator concentration is very low, the average radical chain length will be sufficiently long from the very beginning of the reaction and k_p may keep constant before entanglement occurs. (2) If the short chain radicals appear in polymer concentrated solution, they will have larger frequency factors and smaller activation energies for propagation. Such results mean that k_p must be very large. On the other hand, if the propagation rate in this case is large enough, such as in the auto-acceleration process, the rapid increase of polymer concentration may further reduce the relaxation rate of the macromolecular radical from a thermodynamically unstable state just produced by the propagating reaction to the stable state. So the apparent frequency factor and k_p may rise with increasing monomer conversion. (3) Whether the apparent k_p changes or not, it can be expressed as the function of the average polymerization degree of the radical by means of the relation between active energy (or frequency factor) and radical chain length.

At the final stage of the reaction, because the activation energy is nearly zero, k_p is independent of it and only dominated by the frequency factor (or the mobility of the radical and monomer). In this case, k_p will be diffusion-controlled.

In Figures 5 and 6, the variation of active energy and frequency factor for MMA can be expressed as

$$k_p = A_{\text{mma}} \exp(-E_{\text{mma}}/RT) \quad (1)$$

where

$$E_{\text{mma}} = 12.601\,023 + 0.013\,383\,05X - 0.001\,556\,477\,9X^2 \quad (2)$$

$$\ln A_{\text{mma}} = 11.043\,424 + 0.006\,984\,802\,6X - 6.600\,093\,5 \times 10^{-4}X^2 \quad (3)$$

2. Styrene. As shown in Figure 3, the k_p value of the styrene radical also changes gradually with the increase of monomer conversion. It seems to show that the change mechanism of k_p for St is the same as that of MMA. However, Figure 6 indicates that at the initial and middle stage of the reaction the activation energy for the propagation of the styrene radical increases with increasing monomer conversion, which cannot be explained by the point of view used to explain the propagation of MMA. However, it can easily be clarified by the conformations of styrene. As proposed in our previously studies,³⁵ the propagating radical of St has two innerrotational conformations R_1 and R_2 . The R_1 is the thermodynamically stable conformation and has a smaller activation energy for propagation than R_2 , because R_1 has a larger spinning electron density in its α carbon atom, which leads to the effect of propagating reaction on the conformation ratio of R_1 to R_2 because the relaxation between R_1 and R_2 favors the formation of R_1 and the propagating reaction favors the formation of R_2 (or R_2 is a kinetically stable conformation). For a short chain radical, the interchange rate between R_1 and R_2 through innerrotation is quite larger than the propagation rate. So that R_1 is the major conformation. For a long chain radical, the rate of the interchange becomes quite small. If the rate of the propagating reaction in this case is large enough, the rapid increase of polymer concentration may further reduce the relaxation rate between R_1 and R_2 ; therefore, the propagating rate may be larger than the relaxation rate, and R_2 will become the major conformation. It means that the conformation ratio of R_1 to R_2 (R_1/R_2) in this case is dominated by propagating reaction. In our experiments, at the initial stage of the reaction, because the initiator concentration was very high, most of the radicals were short chains and had the R_1 conformation. Therefore, apparent k_p had smaller activation energy. With the increase of monomer conversion, the average chain length of the radical grew, and the relaxation rate between R_1 and R_2 decreased gradually. On the other hand, the propagating reaction became more and more rapid, and finally, the auto-acceleration process happened. Then the conformation ratio of R_1 to R_2 would decrease with conversion. The experiment result that the apparent activation energy increased identified this deduction. Figure 6 shows that the frequency factor also increases with conversion. This indicates that the frequency factor of R_2 is larger than that of R_1 . This is consistent with the fact that R_2 has higher conformation energy than R_1 . The gradual depression of apparent k_p in this period demonstrates that the k_p value of R_2 is smaller than that of R_1 .

The conformation ratio depends on the relaxation rate between R_1 and R_2 , as well as the propagating rate (or k_p and radical concentration). Because the relaxation rate, k_p , and radical concentration all correlate with the radical chain length, the effect of the conformation ratio on k_p can be regarded as another way for the radical chain length to influence k_p . Furthermore, we call it the indirect effect of the radical chain length on k_p in order to distinguish the direct effect discussed for MMA system.

In Figures 5 and 6, we can obtain experimental expressions of apparent k_p :

$$k_p = A_{\text{st}} \exp(-E_{\text{st}}/RT) \quad (4)$$

where

$$E_{\text{st}} = 53.623\,558 + 0.021\,374\,83X + 1.350\,192\,2 \times 10^{-4}X^2 + 1.570\,665\,2 \times 10^{-4}X^3 \quad (5)$$

$$\ln A_{\text{st}} = 24.743\,675 + 0.006\,345\,407\,1X + 1.247\,596\,7 \times 10^{-4}X^2 + 5.123\,957\,8 \times 10^{-5}X^3 \quad (6)$$

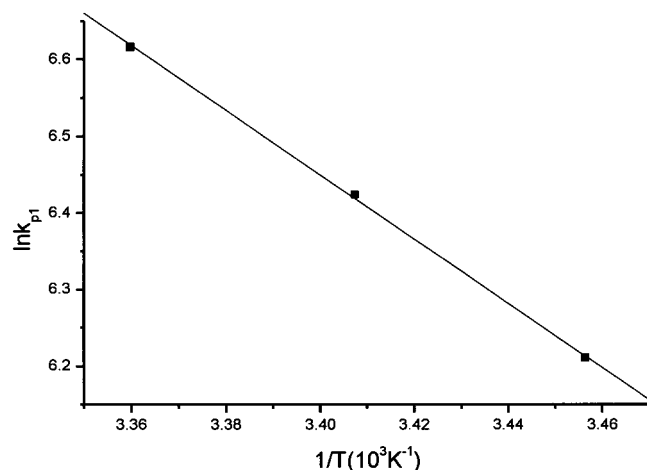


Figure 10. Arrhenius Plots of conformation R₁ for the styrene radical.

Assuming that the propagating rate coefficients of R₁ and R₂ are k_{p1} and k_{p2} respectively, then the apparent k_p should be

$$k_p = \alpha_1 k_{p1} + \alpha_2 k_{p2}, \quad \alpha_1 = \{[R_1]/([R_1] + [R_2])\}, \\ \alpha_2 = \{[R_2]/([R_1] + [R_2])\} \quad (7)$$

[R₁] and [R₂] are the concentration of R₁ and R₂, and respectively, α_1 and α_2 are the concentration fraction of R₁ and R₂, respectively. If α_1 and α_2 are dominated by conformation energy, they should be

$$\alpha_1 = \frac{\exp\left(\frac{\Delta E_{21}}{RT}\right)}{1 + \exp\left(\frac{\Delta E_{21}}{RT}\right)} \quad (8)$$

$$\alpha_2 = \frac{1}{1 + \exp\left(\frac{\Delta E_{21}}{RT}\right)} \quad (9)$$

where ΔE_{21} , the conformation energy difference between R₁ and R₂, was calculated to be 3.09 kJ/mol.³⁵

As discussed previously, at the initial stage of the reaction when the initiator concentration is high enough or the chain length of the radical is short enough, the concentration ratio of R₁ to R₂ is dominated by conformation energy difference between R₁ and R₂; therefore, the apparent k_p can be expressed by eqs 7–9. In the middle stage of the reaction when the radical chain length is long enough, the concentration ratio of R₁ to R₂ should be dominated by the propagating reaction. The ESR study of the St radical has shown that the major conformation in the period of auto-acceleration was R₂.³⁵ Therefore, the apparent k_p value corresponding to the maximum apparent activation energy in Figure 5 is assigned to k_{p2} . It can be expressed as

$$k_{p2} = A_2 \exp(-E_2/RT) \quad (10)$$

where $A_2 = 8.1464 \times 10^{16} \text{ L mol}^{-1} \text{ s}^{-1}$ and $E_2 = 96.338 \text{ kJ/mol}$. Furthermore, k_{p1} values at 85, 80, and 75 °C can be also calculated from eqs 7–9 and three apparent experimental k_p values. Then, $A_1 = 1.010 \text{ } 175 \text{ } 585 \text{ } 78 \times 10^9$ and $E_1 = 42.01 \text{ kJ/mol}$ are available through the Arrhenius equation (see Figure 10). The linear relation is quite good.

The activation energy of the R₁ conformation obtained above, 42.01 kJ/mol, as well as the apparent activation energy in this work at the beginning stage of the reaction, 50 kJ/mol (see Figure 5), are both higher than the IUPAC accepted value (32.51

kJ/mol).²⁴ The higher apparent activation energy (50 kJ/mol) can be ascribed to the lower conformation ratio of R₁ to R₂. However, the higher activation energy of R₁ (42.01 kJ/mol) cannot be ascribed to the same reason. Prof. Kamachi also observed an activation energy value (25 kJ/mol)²⁸ which is lower than the IUPAC accepted value and hard to explain by the conformation ratio. This suggests that there should be other factors that would affect the activation energy for the propagation of styrene radical. It is likely that the direct effect mechanism of chain length on the activation energy and frequency factor as discussed for the MMA radical plays the main role. In this case, the longer the chain length of the radical is, the lower the activation energy. This is consistent with the fact that when the initiation concentration is very high the radical chain length in this work must be shorter than those of other authors' experiments. It means that the frequency factor and activation energy of the styrene radical depends on both the conformation ratio of R₁ to R₂ (or the indirect effect of chain length on k_p) and the chain length of the radical itself (the direct effect). It is also the reason the k_p of styrene depends on the selection of the experimental condition. Therefore, the radical chain length (or average polymerization degree) should be the fundamental and important factor in the initial and middle stage of the propagating reaction for St.

When the monomer conversion is about 70%, both apparent activation energy and frequency factor reach the maximum and then decrease quickly with the increasing monomer conversion. Two possible reasons are as follows. (i) When the monomer concentration is low enough, the conformation ratio of R₁ to R₂ will begin to rise and gradually be dominated by conformation energy. Therefore, apparent activation energy and frequency factor will decrease because both the activation energy and the frequency factor of R₁ are smaller than those of R₂. However, accompanying the increasing conformation ratio of R₁ to R₂, the apparent k_p should increase because the k_p of R₁ is larger than that of R₂. This is not consistent with the experimental result. Therefore, the sharp decrease of apparent k_p cannot be ascribed to the change of the conformation ratio. However, it does not mean that the conformation ratio keeps constant, actually, it will change and the major conformation of St will gradually become R₁. (ii) The polymer concentration is large enough, and some extent of entanglement occurs. Furthermore, as expected for MMA, activation energy, frequency factor, k_{p1} , and k_{p2} will all decrease with increasing monomer conversion, leading to the depression of apparent k_p . Obviously, the second explanation is feasible, and the sharp depression of apparent k_p indicates that, in this period, k_p is dominated by the medium environment of radicals.

Conclusions

The decrease of the activation energy and frequency factor of k_p for the MMA radical with the increasing monomer conversion can be explained by the changes of chain length and medium environment. At the initial and middle stage of the reaction, the changes are mainly attributed to the increase of the intramolecular interaction between the active center and the radical chain, which is caused by the growth of chain length, and this effect of the radical chain length on k_p is called the direct effect. However, the variation of k_p in this period is not as obvious as that of the activation energy and frequency factor because of the cancellation of them on k_p . At the final stage of the reaction, the depression of k_p is mainly ascribed to the increase of the intermolecular interactions between the radicals and polymer molecules. It indicates that the activation energy

in this period is nearly incline to zero, so that the propagating reaction is diffusion-controlled.

The Arrhenius parameters of apparent k_p for the styrene radical are not only dependent on the radical chain length and medium environment but also on the conformation ratio of R_1 to R_2 . Because the radical chain length can also influence the conformation ratio of R_1 to R_2 , its effect on k_p can be regarded as the indirect effect of radical chain length on k_p . In the initial and middle stage of the reaction when the initiator concentration is very high or the radical chain length is short enough, the apparent activation energy and frequency factor are mainly determined by the conformation ratio. However, when the initiator concentration is very low or the radical chain length is long enough, the apparent activation energy and frequency factor are mainly determined by the chain length of the R_1 conformation. At the final stage of the reaction when the intermolecular interaction between radicals and polymer molecules becomes the major interaction, the change of apparent k_p should be ascribed to the frequency factor of k_{p1} of conformation R_1 . Furthermore, k_{p1} is also diffusion-controlled.

Whether apparent k_p changes or not, it can be expressed as the function of the average polymerization degree of the radical (or radical chain length) because of the effect of the radical chain length on the activation energy and frequency factor.

Acknowledgment. This work was subsidized by the Special Funds for Major State Basic Research Projects (G1999064803) and by National Natural Science Foundation of China (No. 29734130). We also thank the State Key Laboratory of Theoretical and Computational Chemistry for financial supports.

References and Notes

- (1) Friss, N.; Hamielec, A. E. *Am. Chem. Soc. Symp. Ser.* **1976**, *24*, 82.
- (2) Arai, K.; Saito, S. *J. Chem. Eng. Jpn.* **1976**, *9*, 302.
- (3) Marten, F. L.; Hamielec, A. E. *Am. Chem. Soc. Symp. Ser.* **1979**, *104*, 43.
- (4) Marten, F. L.; Hamielec, A. E. *J. Appl. Polym. Sci.* **1982**, *27*, 489.
- (5) Soh, S. K. *J. Appl. Polym. Sci.* **1982**, *25*, 2993.
- (6) Stickler, M.; et al. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 2243.
- (7) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1299.
- (8) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1315.
- (9) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1331.
- (10) Soh, S. K.; Sundberg, D. C. *J. Polym. Sci., Polym. Chem. Ed.* **1982**, *20*, 1345.
- (11) Arai, K. *J. Chem. Eng. Jpn.* **1978**, *42*, 300.
- (12) Chiu, W. Y.; Soony, D. S.; et al. *Macromolecules* **1983**, *16*, 348.
- (13) Achilias, D.; et al. *J. Appl. Polym. Sci.* **1988**, *35*, 1303.
- (14) Huang, Y. J.; Fan, J. D.; Lee, L. J. *J. Appl. Polym. Sci.* **1987**, *33*, 1315.
- (15) Huang, Y. J.; Lee, L. J. *AIChE J.* **1985**, *31*, 1585.
- (16) Tian, Y. The Kinetics of bulk polymerization of MMA. Ph.D. Thesis, Jilin University, Jilin, P. R. China, 1988.
- (17) Russel, G. T.; Napper, D. H.; Gilbert, R. G.; et al. *Macromolecules* **1988**, *21*, 2133.
- (18) Bubak, M.; Garcia-Rubio, L. H.; Gilbert, R. G.; Napper, D. H.; Guillot, J.; Hamielec, A. E.; Hill, D.; O'Driscoll, K. F.; Olaj, O. F.; Shen, J.; Solomon, D.; Moad, G.; Stickler, M.; Tirrell, M.; Winnik, M. A. *J. Polym. Sci., Polym. Lett. Ed.* **1988**, *26*, 293.
- (19) Bubak, M.; Gilbert, R. G.; Russell, G. T.; Hill, D. J. T.; Moad, G.; O'Driscoll, K. F.; Shen, J.; Winnik, M. A. *J. Polym. Sci., Polym. Chem. Ed.* **1992**, *30*, 851.
- (20) Aleksandrov, H. P.; Genkin, V. N.; Kitai, M. S.; Smirovna, J. M.; Sokolov, V. V. *Kvantovaya Elektron. (Moscow)* **1977**, *4*, 976.
- (21) Olaj, O.; Bitai, I. *Angew. Makromol. Chem.* **1987**, *155*, 177.
- (22) Davis, T. P.; O'Driscoll, K. F.; Piton, M. C.; Winnik, M. A. *Macromolecules* **1989**, *22*, 2785.
- (23) Bubak, M.; Gilbert, R. G.; Hutchinson, R. A.; Klumperman, B.; Kuchta, F. D.; Manders, B. G.; O'Driscoll, K. F.; Russell, G. T.; Schweer, J. *Macromol. Chem. Phys.* **1995**, *196*, 3267.
- (24) Hutchinson, R. A.; Paquet, D. A.; McMinn, J. H.; Beuermann, S.; Fuller, R. E.; Jackson, C. *DEHEMA Monogr.* **1995**, *131*, 467.
- (25) Lau, W.; Westmoreland, D. C.; Novvak, R. W. *Macromolecules* **1987**, *20*, 457.
- (26) Zhu, S.; Tian, Y.; Hamielec, A. E.; Eaton, D. R. *Macromolecules* **1990**, *23*, 1144.
- (27) Yamada, B.; Kageoga, M.; Otsu, T. *Polym. Bull.* **1992**, *28*, 75.
- (28) Tonge, M. P.; Kajiwar, A.; Kamachi, M.; Gilbert, R. G. *Polymer* **1998**, *39*, 2305.
- (29) Tryson, G. R.; Shultz, A. R. *J. Polym. Sci. Polym. Phys. Ed.* **1979**, *17*, 2059.
- (30) Anseth, K. S.; Wang, C. M.; Brown, C. N. *Macromolecules* **1994**, *27*, 650.
- (31) Gridnev, A. A.; Ittel, S. D. *Macromolecules* **1996**, *29*, 5864.
- (32) Yoon, W. J.; Choi, K. Y. *Polymer* **1992**, *33*, 4582.
- (33) O'Shaughnessy, B.; Yu, J. *Macromolecules* **1994**, *27*, 5067.
- (34) Kumar, V. R.; Gupta, S. K. *Polymer* **1991**, *32*, 3233.
- (35) Mao, Y.; Song, R.; Zheng, Y.; Shen, J. *Macromolecules* **1994**, *27*, 6746.
- (36) Shen, J.; Tian, Y.; Wang, G.; Yang, M. *Makromol. Chem.* **1991**, *192*, 2669.
- (37) Shen, J.; Wang, G.; Zheng, Y.; Yang, M. *Makromol. Chem., Macromol. Symp.* **1992**, *63*, 105.