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Polymerization of Substituted Styrenes by Atom Transfer Radical Polymerization

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ABSTRACT: A series of substituted styrenes were polymerized by controlled/"living" radical polymerization using atom transfer radical polymerization (ATRP), in order to correlate monomer structures with polymerization rate. The effect of substituents is discussed with regard to the Hammett equation. The results show that most of the monomers can polymerize in a controlled way by ATRP; i.e., the apparent polymerization rate is first order with respect to monomer concentration, and molecular weight increases linearly with monomer conversion. The molecular weights obtained fit the theoretical values and polydispersities are relatively low ($M_w/M_n < 1.5$). Monomers with electron-withdrawing (EW) substituents result in better polymerization control and polymerize faster than those with electron-donating (ED) substituents. The apparent polymerization rate constants follow the Hammett equation with $\rho = 1.5$. Further study indicates that the difference of polymerization rates for different monomers can be attributed to both propagation constant, $k_p^•$, and the equilibrium constant, K_{eq}, for atom transfer. Monomers with EW substituents have larger $k_p^•$ and K_{eq} values than those with ED substituents; therefore, EW substituents increase the monomer reactivity and decrease the stability of dormant species, while ED substituents have the opposite effects.

Introduction

Substituents play a significant role in chain polymerization, because polymerizability of a vinyl monomer by a radical, anionic, or cationic mechanism is dependent upon the steric and electronic properties of the substituents. The electronic effect of the substituent manifests itself by altering the electron density of the double bond through inductive and resonance effects and its ability to stabilize the active species, whether it is a radical, anion, or cation. Although substituent effects are not as important in radical reactions ($|\rho| \leq 1$) as they are in ionic reactions ($|\rho| \geqslant 5$),[1−3] radical polymerization is affected by substituents due to the participation of polar effects. The relationship between the polymerization rate and substituents has been well studied. For example, almost 50 years ago, Walling and co-workers[4] concluded from an analysis of free radical copolymerizations that the polymerization rate increases when the alkenes bear electron-withdrawing substituents. Later, Imoto et al.[5] reported that a Hammett relationship could be established in the homopolymerization of p-substituted styrenes, i.e. $\log(k_{px}^•/k_{pH}^•) = \rho\sigma$, ($\rho = 0.6$), in which $k_{px}^•$ and $k_{pH}^•$ represent the absolute propagation rate constant of substituted styrene and unsubstituted styrene, respectively, σ is the Hammett constant of the substituent, and ρ is the reaction constant.

With the recent development of "living" radical polymerization, the study of substituent effects in "living" polymerization systems again attracts great interest. Kazmaier et al.[6] showed that, in the "living" free radical polymerization based on the TEMPO/BPO initiating system, electron-withdrawing groups increase the polymerization rate for substituted styrenes, which is consistent with the conventional radical polymerization.

In the last 2 years, we developed a novel "living" radical polymerization method, atom transfer radical polymerization (ATRP), in which polymers with predetermined molecular weight up to $M_n \approx 10^5$ and polydispersity as narrow as $M_w/M_n \approx 1.04$ have been obtained.[7,8] This method has proved successful for monomers such as styrene, (meth)acrylates, and acrylonitrile.[9−13] From the point of view of both theoretical study and industrial application, it is intriguing to apply ATRP to various substituted styrenes to investigate the correlation between polymerization rate and monomer structure. Furthermore, it is also hoped that such a study might give us a better understanding of the mechanism of ATRP.

In this paper, the kinetic studies of the polymerization of substituted styrenes with a homogeneous and heterogeneous initiating systems are reported, and the effect of substituents is discussed with regard to the Hammett equation: $\log(k_{px}^•/k_{pH}^•) = \rho\sigma$.

Experimental Section

Materials. All the monomers (Aldrich) were purified by passing them through an alumina column to remove stabilizers and then purging them with argon for 15−20 min before polymerization. Diphenyl ether, used as solvent, was also purged with argon for 15−20 min before polymerization. CuBr was purified according to the literature procedure;[14] 2,2′-bipyridine (bipy) was used as received. 4,4′-Di-(5-nonyl)-2,2′-bipyridine (dNbipy) was synthesized by dimerization of 4-(5-nonyl) pyridine with 5% Pd/C.[15] $CuBr_2$ was used as received. Initiator 1-phenylethyl bromide (1-PEBr) was obtained from Aldrich and used without further purification.

Polymerization. The general procedure for the polymerization was as follows: to a round bottom flask with CuBr and ligand were added the degassed solvent and monomer, followed by the addition of the initiator. A certain volume of sample was taken from the flask using a syringe and then dissolved in THF as a point at zero conversion ($t = 0$). The flask was then immersed in an oil bath thermostated at 110 °C. At timed intervals, the same amount of sample was withdrawn from the flask and dissolved in THF for further analysis.

Characterization. Monomer conversion was determined by GC using a Shimadzu GC-14A with DB-WAX column. Molecular weight and molecular weight distribution were measured using phenogel GPC columns (guard, linear, 1000 and 100 Å). Polystyrene standards were used to calibrate the columns. ^{1}H-NMR study was performed on a 300 MHz Bruker NMR spectrometer using $CDCl_3$ as a solvent, and GC-MS

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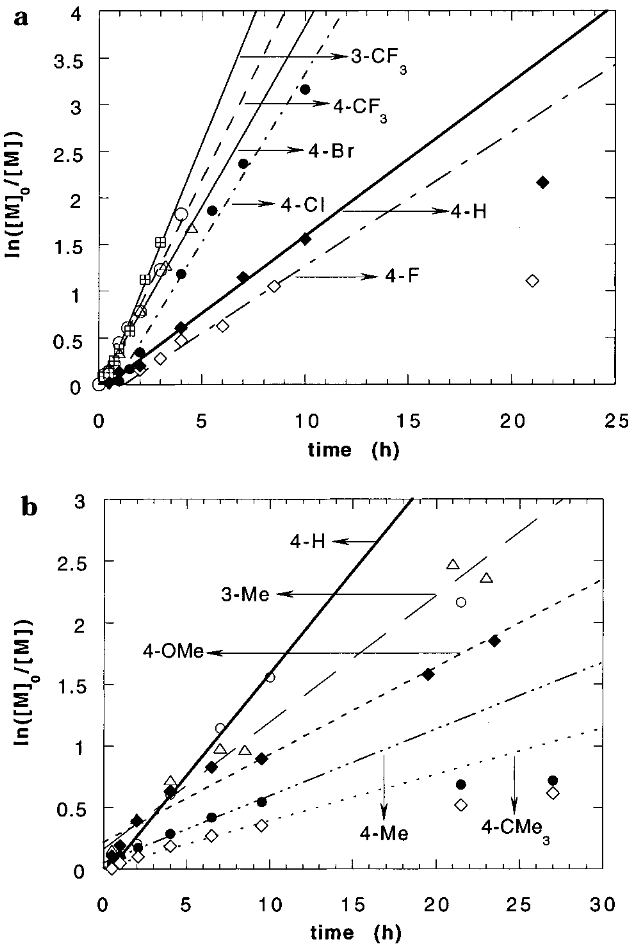


Figure 1. Kinetic plots for ATRP of substituted styrenes in diphenyl ether at 110 °C. $[M]_0 = 4.37$ M and $[M]_0$:[1-PEBr$]_0$:[CuBr$]_0$:[bipy$]_0$ = 100:1:1:3.

Table 1. Various Substituted Styrenes and their σ Values[16]

electron withdrawing (EW)		electron donating (ED)	
monomer	σ	monomer	σ
4-CF_3 sty	0.54	3-Me sty	−0.07
3-CF_3 sty	0.43	4-Me sty	−0.17
4-Br sty	0.23	4-CMe_3 sty	−0.20
4-Cl sty	0.23	4-OMe sty	−0.27
4-F sty	0.06		

measurements were performed on HP 59970 MS ChemStation using THF as the solvent.

Results and Discussion

The substituted styrenes used in this study are listed in Table 1.

General Features of Polymerization. The kinetic plots of the polymerizations are shown in Figure 1. The apparent polymerization rate is first order with respect to monomer concentration in most cases, which means the concentrations of growing radicals are constant. The apparent rate coefficients ($k_p^{app} = -d(\ln[M])/dt$) can be obtained from the slopes of the straight kinetic plots. For some monomers such as styrene, 4-F styrene, 4-Me styrene, and 4-CMe_3 styrene, deviation from linear kinetics occurs at long reaction times due to some side reactions including elimination and termination.[17] Both elimination and termination remove R−X from the reaction. In addition, termination also reduces [Cu^I] and increases [Cu^{II}]. The overall effect results in the deceleration of the polymerization rate. For monomers having smaller propagation constants, the effect of side reactions is more obvious than for monomers having larger propagation constants, and the apparent rate coefficients for these polymerizations were computed from the initial slopes of the kinetic plots. Figure 2 shows the evolution of molecular weights with monomer conversion. Molecular weights increase linearly with monomer conversion in all cases and match with the theoretical values. This indicates fast initiation and a small contribution of transfer under these conditions. The molecular weight distributions are relatively narrow ($M_w/M_n < 1.5$) compared to those of conventional radical polymerizations, as shown in Figure 3. 4-OMe styrene is the only exception, from which no high polymer can be obtained under conventional ATRP reaction conditions.

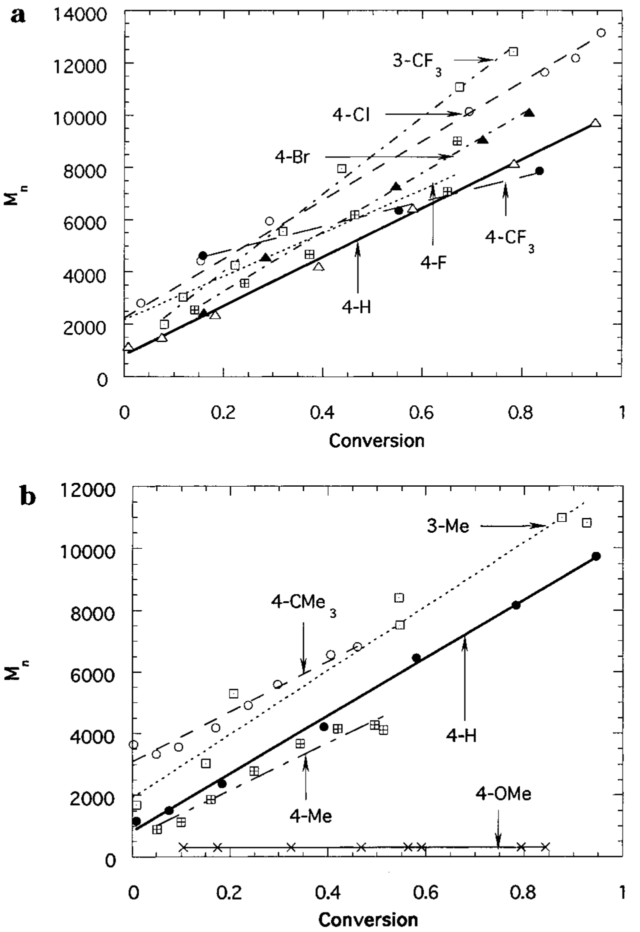


Figure 2. Molecular weights vs monomer conversion for ATRP of substituted styrenes in diphenyl ether at 110 °C. $[M]_0 = 4.37$ M and $[M]_0$:[1-PEBr$]_0$:[CuBr$]_0$:[bipy$]_0$ = 100:1:1:3.

Substituent Effects on Polymerization Rate. As can be seen from Figure 1, monomers with electron-withdrawing substituents polymerize faster than those bearing electron-donating substituents in the order of 3-CF_3, 4-CF_3 > 4-Br, 4-Cl > 4-F, 4-H > 3-Me > 4-OMe > 4-Me > 4-CMe_3. The apparent rate coefficients for each monomer are listed in Table 2.

The results are in agreement with those from conventional radical polymerization[5] as well as previously reported “living” radical polymerization initiated by TEMPO/BPO.[6] In order to get quantitative information, a Hammett plot was made (Figure 4). A linear correlation was obtained between the apparent rate coefficient k_p^{app} and Hammett constants σ for different substitu-

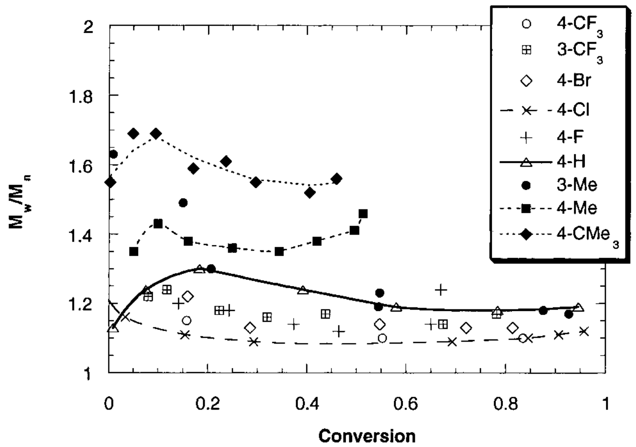


Figure 3. Polydispersities for ATRP of substituted styrenes in diphenyl ether at 110 °C. $[M]_0 = 4.37$ M and $[M]_0$:[1-PEBr]$_0$:[CuBr]$_0$:[bipy]$_0$ = 100:1:1:3.

Table 2. Apparent Rate Coefficients in ATRP and Absolute Propagation Rate Constants of Substituted Styrenes

substituent	σ^d	k_p^{app} (s^{-1}) × 10^4 [a]	k_p^{app} (s^{-1}) × 10^5 [b]	$k_p^\bullet$(mol^{-1} L s^{-1})[c]
4-CN	0.66			219
4-CF$_3$	0.54	1.25	5.47	
3-CF$_3$	0.43	1.44		
4-Br	0.23	1.06		186
4-Cl	0.23	0.97	2.56	150
4-F	0.06	0.39		
4-H	0.00	0.44	1.50	110
3-Me	-0.07	0.28		
4-Me	-0.17	0.16	0.36	84
4-CMe$_3$	-0.20	0.10		
4-OMe	-0.27	0.21		71

[a] Heterogeneous system at 110 °C. $[M]_0 = 4.37$ M, $[M]_0$:[1-PEBr]$_0$:[CuBr]$_0$:[bipy]$_0$ = 100:1:1:3. [b] Homogeneous system with 5% added CuBr$_2$ at 110 °C. $[M]_0 = 4.37$ M; $[M]_0$:[1-PEBr]$_0$:[CuBr]$_0$:[dNbipy]$_0$:[CuBr$_2$]$_0$ = 100:1:1:3:0.05. [c] Absolute propagation rate constant at 30 °C.[18] [d] σ: ref 16.

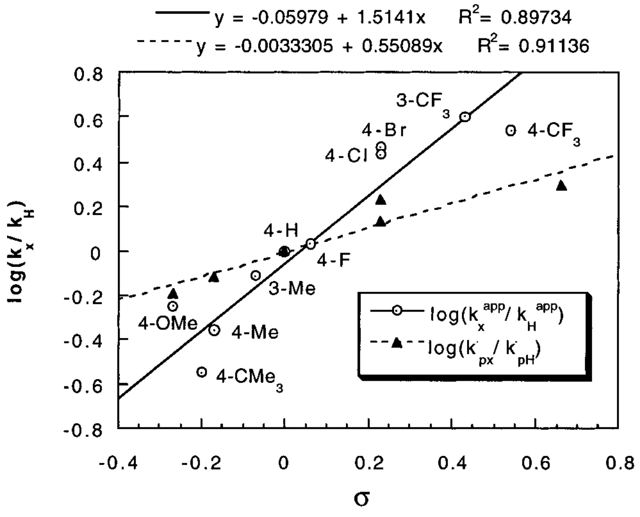


Figure 4. Hammett plots for k_p^{app} in heterogeneous ATRP of substituted styrenes (○), and for absolute $k_p^\bullet$ in conventional polymerization of substituted styrenes (△).[19]

ents, as in the case of conventional radical polymerization of para-substituted styrenes. However, the value of ρ for ATRP ($\rho \approx 1.5$) was much greater than the ρ value of the conventional systems ($\rho \approx 0.6$, Figure 4). The difference between these two values results from the fact that the two ordinates are different. In conventional radical polymerization, the correlation was established with regard to the absolute propagation rate constant $k_p^\bullet$, rather than the apparent rate coefficient k_p^{app} which additionally comprises the concentration of growing radicals.

The rate law for ATRP can be derived from eq 1, in which growing radicals, $P_n^\bullet$, are reversibly generated from the dormant alkyl halides, P_n–X. The activation process requires catalysis by a Cu^I species, whereas X–Cu^{II} deactivates reversibly the growing radicals. An equilibrium is established between the dormant species and the growing radicals, and the equilibrium constant K_{eq} can be expressed by eq 2. In eq 2, since the

$$P_n\text{–}X + Cu^I \underset{k_{deact}}{\overset{k_{act}}{\rightleftharpoons}} P_n^\bullet + X\text{–}Cu^{II} \qquad (1)$$

$$P_n^\bullet \xrightarrow{k_p^\bullet} + M$$

$$K_{eq} = k_{act}/k_{deact} = [P_n^\bullet][X\text{–}Cu^{II}]/[P_n\text{–}X][Cu^I] = [P_n^\bullet][Cu^{II}]/[I]_0[Cu^I] \quad (2)$$

equilibrium is strongly shifted to the left side, the concentration of the dormant species is very close to the initial initiator concentration and can be regarded as $[P_n\text{–}X] \approx [I]_0$. The apparent rate coefficient can then be defined by eq 4. Thus, k_p^{app} for ATRP is determined

$$R_p = -d[M]/dt = k_p^\bullet\,[P_n^\bullet]\,[M] = k_p^\bullet K_{eq}[I]([Cu^I]/[Cu^{II}])[M] \quad (3)$$

$$k_p^{app} = -d(\ln[M])/dt = k_p^\bullet\,[P_n^\bullet] = k_p^\bullet K_{eq}[I]_0([Cu^I]/[Cu^{II}]) \quad (4)$$

by four factors: absolute propagation rate constant $k_p^\bullet$, equilibrium constant K_{eq}, concentration of the initiator, and the concentration ratio of Cu^I to Cu^{II}. Since the initiator concentration was held constant for polymerization of all monomers, k_p^{app} must be dependent on the other three factors. The enhancement of k_p^{app} with σ could therefore be caused not only by $k_p^\bullet$ but also by K_{eq} or [Cu^I]/[Cu^{II}] or all of them.

The larger slope for k_p^{app} than for $k_p^\bullet$ in Figure 4 indicates that monomers with electron-withdrawing substituents must have a larger K_{eq} or a larger [Cu^I]/[Cu^{II}] or both.

In order to treat these two factors separately, polymerizations in homogeneous media using dNbipy as the ligand were undertaken. First, 5% of Cu^{II} was added as a solution of CuBr$_2$/dNbipy in diphenyl ether to each system before polymerization so that the ratio of [Cu^I]/[Cu^{II}] could be regarded as constant for different systems. The Hammett plot obtained was parallel to that for the heterogeneous system (bipy as the ligand) (Figure 5). This indicates that the [Cu^I]/[Cu^{II}] varied insignificantly and made a small contribution to the increase of k_p^{app} with σ in heterogeneous ATRP. Therefore, the larger ρ value in ATRP can be mainly attributed to K_{eq}. In other words, monomers with electron donating substituents have a greater K_{eq} than monomers with electron donating substituents.

The next question is, *why* do monomers with electron-donating substituents have a greater K_{eq}? Thermodynamically, a greater K_{eq} could originate from either a more stabilized $P_n^\bullet$, or a weaker P_n–X bond.

Some insight into the stability of polymeric radicals is provided by analysis of the values of propagation rate constants and monomer reactivities from copolymeri-

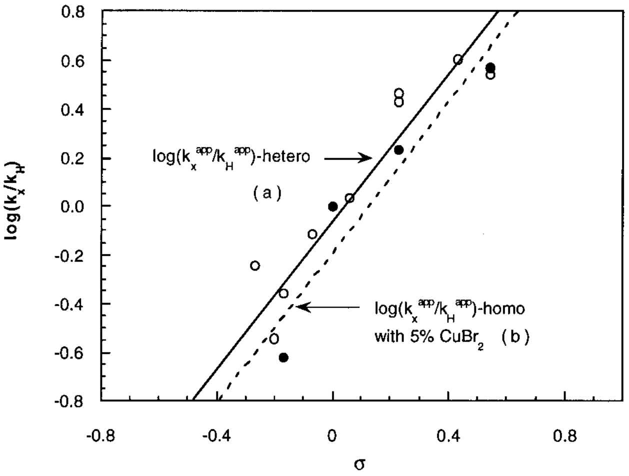


Figure 5. Linear correlations for substituted styrenes: (a) k_p^{app} for the heterogeneous system in ATRP; (b) k_p^{app} for the homogeneous system in ATRP.

Table 3. Monomer Reactivity Ratios and Derived Quantities for the Copolymerization of Styrene (M_1) with Substituted Styrenes (M_2)[18]

substituent	σ^{14}	r_1	r_2	$1/r_1$	$\log(1/r_1)$
4-CN	0.66	0.28	1.16	3.57	0.553
3-CF3	0.43	0.603	0.806	1.66	0.220
4-Br	0.23	0.695	0.99	1.44	0.158
4-Cl	0.23	0.74	1.025	1.35	0.130
4-I	0.18	0.62	1.61	1.61	0.208
4-H	0	1	1	1	0
4-Me	−0.17	0.83	0.96	1.20	0.0792
4-OMe	−0.27	1.16	0.82	0.86	−0.066

zation data. The propagation rate constant is a function of monomer reactivity and radical reactivity; hence, it is possible to get some information about radical reactivities by comparing monomer reactivities and $k_p^{\bullet}$ of different substituted styrenes. In copolymerization, if a standard monomer (M_1, e.g. styrene) is copolymerized with a series of other monomers, e.g., substituted styrenes (M_2's), the reciprocals of the monomer reactivity ratio ($1/r_1 = k_{12}/k_{11}$) describe the relative reactivities of the substituted styrenes toward the styryl radical. We arbitrarily chose styrene as the standard monomer because it is a part of the same monomer family and because of the availability of literature data.

Table 3 lists the literature data on reactivity ratios for monomers used in this study.

The logarithms of the relative reactivities of substituted styrenes toward the unsubstituted styrene radical ($\log 1/r_1$) are plotted against Hammett's σ values. A linear plot is obtained with $\rho \approx 0.5$, as shown in Figure 6. Similar results could be found in Walling et al.'s work 50 years ago,[19] except that some σ values were slightly different from those currently accepted.[16] The straight line ($\log 1/r_1 \sim \sigma$) is nearly parallel to the plot of $\log(k_p^{\bullet}/k_H^{\bullet})$ against σ, which implies that the increase of $k_p^{\bullet}$ with σ is more affected by the reactivities of the monomer than the reactivities of radicals. In other words, substituents have a minor effect on the reactivity of the styrene type radical.

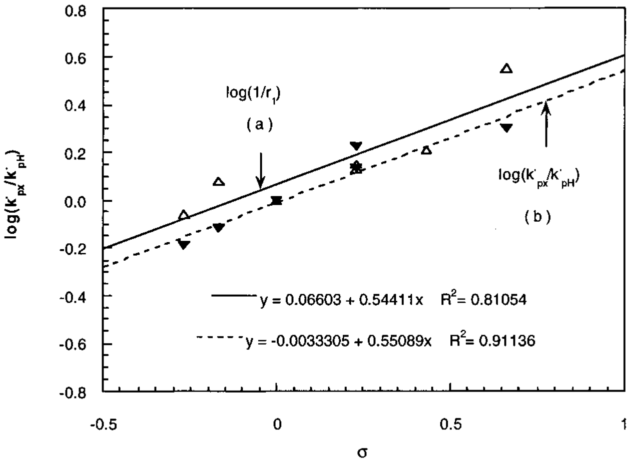


Figure 6. Linear correlations for substituted styrenes: (a) monomer reactivities $1/r_1$; (b) propagation rate constant $k_p^{\bullet}$.

This conclusion seems unusual, but it is compatible with the results from several other studies.[20-23] For example, both electron-withdrawing and electron-donating groups tend to stabilize the benzyl radical, and the stabilization energy is independent of the electronic nature of the substituent.[23] In a model study of polymerization, Fischer et al.[24] investigated the addition of benzyl radicals to alkenes. It was found that *p*-OCH_3; *p*-CH_3; *p*-F; and *p*-CN-substituted benzyl radicals react with various alkenes at similar rates. On the other hand, variations in the energy of the alkene LUMO (lowest unoccupied molecular orbital) resulting from the substituent affect the addition of the radical more than corresponding changes in the radical SOMO (singly occupied molecular orbital) energy.

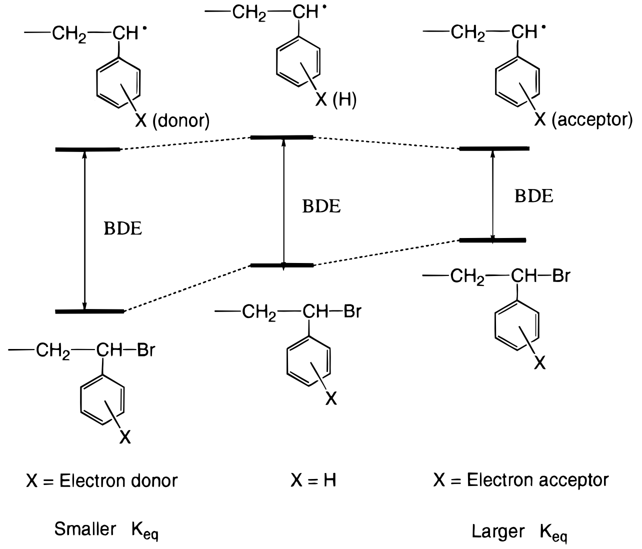
Usually, the order of substituents in affecting radical reactivity is the opposite of their order on monomer reactivity, and the effect of a substituent on the radical is often larger than its effect on the monomer. Thus $k_p^{\bullet}$ decreases in the sequence of VAc ≈ MA > MMA > styrene, because the radical reactivity decreases more strongly than the increase in monomer reactivity. The reason why the benzyl radical behaves differently lies in its unique structure. The benzyl radical is planar, and its SOMO is delocalized over the whole molecule because of the interaction of the π orbital on the CH_2 moiety with the molecular orbitals of the benzene fragment.[25] Therefore this radical is more stabilized than most other radicals. The low polar effect caused by delocalization consequently reduces the substituent effect on the radical. Consequently, for the reactions involving benzyl radicals, substituent effects on the reactivities of molecules are often larger than those for the radicals.

This is in fact the case in ATRP. The stabilities of different substituted polystyryl radicals are more or less the same compared to the change of bond dissociation energy (BDE) of C−X in the dormant molecules, polystyryl halides, caused by substitution. It is the decrease in the BDE of C−X by electron-withdrawing substituents that accounts for the larger K_{eq} in these monomers rather than in monomers with electron-donating substituents and hence causes the additional enhancement of apparent polymerization rate coefficient with σ. The energy graph in Scheme 1 provides a qualitative picture of the substituent effects on polymerization rates in ATRP of substituted styrenes.

A further explanation for Scheme 1 is given as follows: in the dormant species P−X, the polarized C−X bond gives the carbon a partial positive charge. Thus electron-donating substituents on the benzene ring help stabilize the charge and lower the energy of the molecule. On the other hand, an electron-withdrawing substituent increases the energy of the molecule by destabilizing the partial positive charge and consequently enhances the bond dissociation energy.

Similar results can be found in the literature where the substituent effect on the bond dissociation energies

Scheme 1



of substituted benzyl bromides has been studied.[26] The linear Hammett plot of ΔBDE vs σ with a slope of $\rho = -5.5$ indicates that electron-withdrawing substituents weaken the C$-$Br bond relative to the unsubstituted species. It is interesting to notice that another study by Wayner[27] has shown that the Hammett slope for substituted toluenes is smaller but positive ($\rho \approx 2.0$), which means the substituents have the opposite effect on the C$-$H bond cleavage. Since the same type of radicals, substituted benzyl radicals, are generated in both studies, the opposite trends of BDE variation can only be attributed to the parent molecules. This again supports our conclusion that substituents have a larger effect on covalent molecules than on benzyl radicals.

Recently, the Xerox group published their second paper on the studies of substituted styrenes in the nitroxide mediated free radical polymerization.[28] A Hammett correlation with a slope of 1.45 was established for this system. The ρ value similar to ours indicates that the effects of the substituents on stabilizing the bromo-ended polystyryl and the TEMPO-ended polystyryl are more or less the same.

It should be pointed out that the comparison between $k_p^{\bullet}$ vs σ and $1/r_1$ vs σ is based on the available literature data only. The data are limited, and some were acquired many years ago by the rotating sector method rather than by a more modern pulse laser polymerization technique.[29] It should also be mentioned that the $k_p^{\bullet}$ values were measured at 30 °C, r_1 values were measured at 60 °C, and k_p^{app} values were obtained at 110 °C. Obviously, temperature plays an important role in determining all these values and may even change the trend if different monomers have different activation energy of propagation (E_p). However, according to the data available in literature, it seems that E_p does not change much from electron-withdrawing substituent to electron donating substituent. For example, E_p for 4-Br styrene is 31.8 kJ/mol,[5] for 4-methylstyrene is 31.8 kJ/mol,[5] and for styrene itself is 32.5 kJ/mol.[30]

Substituent Effect on Polydispersities. As shown in Figure 3, the polydispersities for all the polystyrenes obtained by ATRP are relatively low and decrease with conversion and increasing chain length. This is typical for polymerization systems with relatively fast exchange between active and dormant species. In a system with a low concentration of active species and lack of transfer, the relationship between polydispersity (DP_w/DP_n), chain length (DP_n) and conversion (p) is[31]

$$DP_w/DP_n = 1 + 1/DP_n + ([I]_0 - [I])\,(k_p^{\bullet}/k_{deact}[Cu^{II}])(2 - p)/p \quad (5)$$

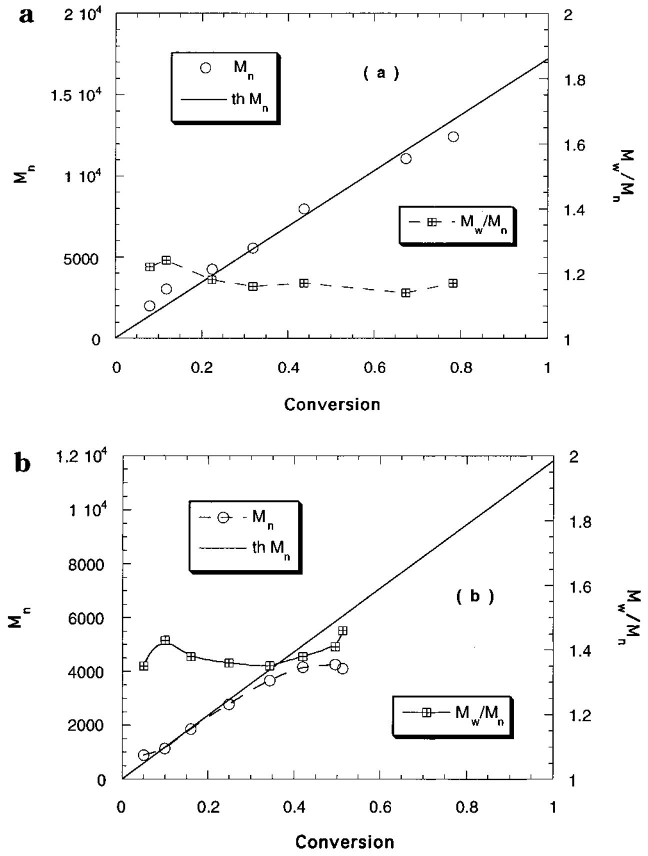


Figure 7. Comparison of ATRP for (a) 3-CF_3 styrene and (b) 4-CH_3 styrene in diphenyl ether at 110 °C. $[M]_0 = 4.37$ M and $[M]_0$:[1-PEBr]$_0$:[CuBr]$_0$:[bipy]$_0$ = 100:1:1:3.

Therefore a longer chain length and a higher conversion will lead to a lower polydispersity. On the other hand, chain transfer may become increasingly significant with the increase of molecular weights. As a result, the polydispersity may increase after its initial decrease. This is also shown in Figure 3. For some systems with electron-donating groups such as 4-Me styrene and 4-CMe_3 styrene, the effect of chain transfer is evident much earlier than for other monomers.

Another feature of ATRP of substituted styrene is that the polymers bearing electron withdrawing groups have lower polydispersities than those bearing electron donating groups. This may possibly be due to two reasons: either the former systems have less transfer, or the solubility of Cu^{II} in the former system is higher. If the latter case is true, the increased concentration of Cu^{II} in electron-withdrawing systems will increase the deactivation rate of growing radical and result in a narrower molecular weight distribution according to eq 5.

Combining the results from both the polymerization rate and polydispersity, we conclude that ATRP works better for styrenes with electron-withdrawing substituents than with electron-donating substituents. The former ones not only polymerize faster but also result in better molecular weight control in the sense of lower polydispersity and less contribution of chain transfer. This can be shown more clearly in Figure 7 by comparing the polymerization of 3-CF_3 styrene and 4-Me styrene.

Polymerization of 4-OMe Styrene. The only exception among all the monomers studied is 4-OMe styrene. In this case, no high polymer was formed by ATRP, even if the monomer was consumed relatively rapidly (85% conversion after 24 h). The resulting products consist of oligomers, as observed by GPC. ^{1}H-NMR study indicates that the major reaction is transfer to form unsaturated dimer, trimer, tetramer, etc. Dimer was proved to be the dominant species by GC-MS measurement. The significant transfer suggests a cationic mechanism for 4-OMe styrene. Instead of homolysis of the C−Br bond to form a radical, the electron donating methoxy group may direct the reaction toward the heterolysis of C−Br bond to generate a cation. Another possibility is that the formed *p*-methoxystyryl radical is oxidized to a carbocation by Cu^{II} species in an electron transfer process. At higher temperatures, unsaturated dimer and trimer as the major products resulting from transfer reaction were detected by GPC. The signals of the olefinic protons were observed in ^{1}H-NMR at 6.3 ppm.

Conclusion

In summary, atom transfer radical polymerization can be successfully adapted to the synthesis of substituted polystyrenes with controlled molecular weights and narrow polydispersities. The overall polymerization rate varies with different substituents by following the Hammett relation with $\rho = 1.5$. Such substituent effects are due to the fact that both the equilibrium constant for atom transfer reaction, K_{eq}, and the absolute propagation rate constant, $k_{p^\cdot}$, increase for monomers with electron-withdrawing substituents. In the presence of strong electron donating substituent such as methoxyl group, the active growing species can even change to a possible cationic nature.

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