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Elucidating the Mechanism and Rate Constants in the Cationic Polymerization of Styrene. Limitations of Living Systems

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ABSTRACT: The chemistry and kinetics of various elementary reactions in the cationic polymerization of styrene, including propagation, depropagation, transfer, termination, and initiation, are discussed. The limiting conditions for living systems are then estimated from a master Arrhenius plot of the rate constants of these reactions as a function of temperature. This master plot demonstrates that although polymers with DP $\approx$ 7 might be prepared at 50 °C, polymers with DP $\approx$ 1500 could be prepared by decreasing the temperature to −70 °C. The effect of solvent on the relative contribution of the different reactions is also demonstrated. New "living" systems are similar to classic cationic systems but with better control due to fast initiation and slower polymerization rates as a result of reversible formation of dormant species.

Introduction

Recently, considerable progress has been achieved in the preparation of well-defined polymers by the cationic polymerization of alkenes.[1,2] Some of these systems are called living, since polymers with narrow molecular weight distributions and predetermined molecular weights are prepared under the reported conditions. However, most of these systems produce lower molecular weight polymers; higher molecular weight polymers are prepared only at very low temperatures. For example, we have attempted[3] to prepare high molecular weight polystyrene at room temperature but could not exceed M_n = 15 000 using systems which might provide higher molecular weight polymers at lower temperatures.[4] Thus, some limiting reactions such as transfer reactions must be inherent to cationic polymerizations.[5]

Information on the chemistry and kinetics of the cationic polymerization of styrene and other vinyl monomers is scattered and has not yet yielded a comprehensive mechanistic picture.[6] This paper will collect and systematically analyze the chemistry and kinetic data of elementary reactions in the cationic polymerization of styrene to determine when and to what extent its living polymerization is possible. Although this is determined primarily by propagation and transfer reactions, depropagation, termination, and initiation steps are also important. All of the elementary reactions will be analyzed as a function of reaction temperature, solvent, counterions, and monomer concentration. Combination of these relationships renders a master plot for the cationic polymerization of styrene which shows the limiting conditions for living systems.

Propagation

Carbenium ions add to alkenes very quickly. The rate constant of propagation in the cationic polymerization of styrene initiated by γ-radiation was estimated to be $k_p > 10^6$ mol^{-1} L s^{-1} at 25 °C.[7] However, conventional chemical initiators such as protonic and Lewis acids have much smaller apparent rate constants: $k_p^{app} < 10^1$ mol^{-1} L s^{-1} at 25 °C.[8] This discrepancy was initially ascribed to differences in the reactivities of free ions and ion pairs. However, rate constants of chemically initiated systems calculated from directly observed carbenium ions using stopped flow UV methods were similar to those estimated from γ-radiation: $k_p > 10^5$ mol^{-1} L s^{-1} at 25 °C.[9-11] In this case, the concentration of propagating styryl carbenium ions was estimated by assuming that their extinction coefficient is similar to that of the corresponding carbanion (ϵ = 10 000 mol^{-1} L cm^{-1}), which is probably underestimated since the extinction coefficient of cumyl cations reaches ϵ = 30 000 mol^{-1} L cm^{-1}.[12]

Figure 1 shows the dependence of the rate constants of propagation of styrene, determined by stopped flow UV methods, as a function of temperature. The rate constants in CH_2Cl_2[13] are slightly higher than those in 1,2-dichloroethane.[10] The chlorine atoms of 1,2-dichloroethane are apparently more nucleophilic than those of CH_2Cl_2 and therefore solvate the styryl carbenium ions better, thereby reducing their reactivity.

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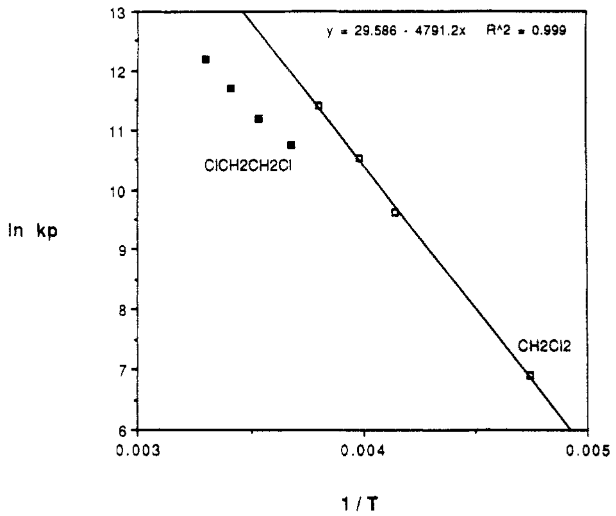


Figure 1. Arrhenius plots of the rate constants of propagation (k_p) of styrene initiated by triflic acid in CH_2Cl_2[13] and in $ClCH_2CH_2Cl$.[10]

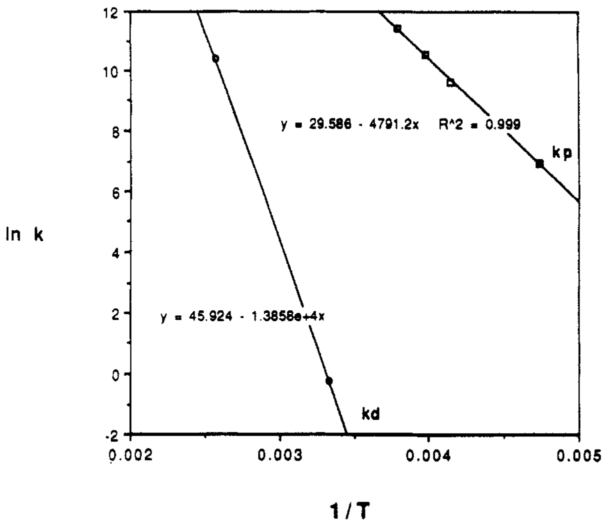


Figure 2. Arrhenius plots of the rate constants of propagation (k_p) of styrene initiated by triflic acid in CH_2Cl_2,[13] from Figure 1, and of depropagation (k_d) calculated from k_p at 25 °C, $[M]_e$,[16] and $\Delta H^\circ{}_p$.[17]

It is difficult to separate the apparent rate constants of ionic propagation into rate constants due to free ions and ion pairs. Estimates from the common ion effect indicate that the ratio $k_p{}^+/k_p{}^\pm < 10$.[9,10] However, the addition of salt to systems initiated by protonic acids may also lead to conjugation of the acid with anions, thereby reducing the concentration of both the acid and the propagating carbenium ions and ultimately yielding lower apparent rate constants. Nevertheless, the ions and ion pairs in some model systems, such as those involving benzhydryl cations[14] and onium[15] ions, are known to have exactly the same reactivity. This is ascribed to equally strong solvation of both free ions and ion pairs. Although reliable values of the absolute rate constants of propagation by ions and ion pairs are not yet available, it suffices to say that the reactivities of ions and ion pairs are similar and the reactivities of ion pairs are not strongly affected by the nature of the counteranion.

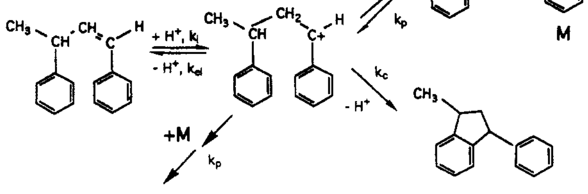
Depropagation

Depropagation in the polymerization of styrene can be neglected at ambient and subambient temperatures. The equilibrium monomer concentration at 25 °C is estimated to be $[M]_e = 10^{-6}$ mol L^{-1}.[16] However, due to the relatively high enthalpy of polymerization ($\Delta H^\circ{}_p = -71$ kJ mol^{-1}),[17] the equilibrium monomer concentration rapidly increases with increasing temperature and approaches the standard 1 M monomer concentration at approximately 280 °C, i.e., the ceiling temperature. Since the ratio of the depropagation and propagation rate constants $k_d/k_p = [M]_e$ is independent of the reaction mechanism and therefore equivalent for radical, anionic, cationic, and coordination processes, an Arrhenius plot of the depropagation rate constants can be constructed when the propagation rate constants,[11] $[M]_e$, and the enthalpy of polymerization are known. That is, the Arrhenius plot of the depropagation rate constants shown in Figure 2 was constructed by first calculating k_d at 25 °C from $k_d = k_p[M]_e$. Since $\Delta H^\circ{}_p = \Delta H^\ddagger{}_p - \Delta H^\ddagger{}_d$, a line was then drawn through this point knowing that the slope of this Arrhenius relation is equal to $\Delta H^\circ{}_p/R - \Delta H^\ddagger{}_p/R$ ($\Delta H^\ddagger = E_a - RT$, $-E_a/R$ being the slope of the plot of ln k_p vs $1/T$).

Transfer by Intramolecular Friedel–Crafts Alkylation To Form Indanyl End Groups

Stopped flow measurements of the carbenium ions in the triflic acid initiated polymerization of styrene revealed that initiation is rapid and that the concentration of carbenium ions steadily increases to a maximum concentration proportional to the product $[HA]^2[M]$.[11,13] The concentration of carbenium ions then decays by a two-stage process. The first fast stage is influenced by the concentration of monomer, whereas the second stage is slow and essentially first order. As discussed in the next section, the first step involves fast deprotonation of the cation (β-proton elimination, k_{tr}) to form unsaturated chain ends. The slower second step is due to intramolecular cyclization (k_c), to form chains with indanyl end groups and protonic acid. Since this step occurs at the end of the polymerization after the monomer is entirely consumed, the acid generated has no more alkene available to protonate and thus results in termination.

Higashimura et al. prepared styrene dimers with unsaturated end groups in high yield at elevated temperatures[18] and then attempted to polymerize them at 50–70 °C.[19] Although β-substituted styrenes with substituents larger than methyl do not readily homopolymerize,[6,8] cyclized trimers and tetramers slowly form, along with minor amounts of linear unsaturated trimers and tetramers. Both the linear trimer and the trimer with indanyl end groups can only form by depropagation of the dimeric carbenium ion to the monomeric carbenium ion and styrene. Styrene can then react with another dimeric carbenium ion to form a trimeric carbenium ion, which undergoes either intramolecular cyclization, elimination, or propagation. Formation of the dimer with indanyl end groups occurs only at the later stages of the reaction and limits the unsaturated dimer conversion to approximately 80%. Since the cyclized dimer is formed in only 20% yield, depropagation must be faster than intramolecular cyclization. The elementary reactions of these model studies are



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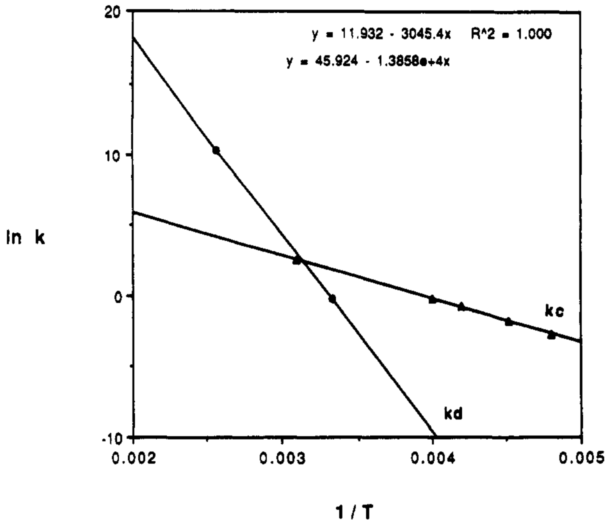

Figure 3. Arrhenius plots of the rate constants of depropagation, from Figure 2, and of intramolecular cyclization (k_c) determined by stopped flow measurements at −20 to −65 °C[13] or calculated by dividing k_d at 50 °C by 4.

The rate constants of cyclization can be estimated from the rate of depropagation. Since the cyclized dimers are formed in 20% yield at 50 °C, the rate constant of cyclization is 4 times slower than that of depropagation at this temperature. Figure 3 shows the Arrhenius plots of the rate constants of depropagation taken from Figure 2 and of the rate constants of intramolecular cyclization. Extrapolation of the rate constants of intramolecular cyclization calculated by stopped flow measurements[13] of the slow stage of the disappearance of carbenium ions at −20 to −65 °C agrees very well with that calculated from the rate constant of depropagation at 50 °C. This consistent mechanistic picture demonstrates that intramolecular cyclization is a transfer reaction when monomer is present since it releases a proton capable of reinitiation and termination once monomer is consumed due to the irreversible disappearance of propagating carbenium ions. IR experiments also demonstrate that 1,2-disubstituted aromatic rings, presumably due to indanyl end groups, are present in the polymers isolated from the stopped flow experiments.

Transfer by β-Proton Elimination

As discussed in the previous section, the concentration of carbenium ions in the triflic acid initiated polymerization of styrene decays in two competitive reactions leading to a two-stage process.[11,13] The rapid first-stage decay is proportional to the decrease in monomer concentration and is due to reversible β-deprotonation of the carbenium ion with formation of unsaturated end groups. Since protonation is reversible, the momentary concentration of cations is proportional to the concentration of double bonds, with most of the double bonds being present as monomer. The first-order rate constant of transfer estimated at the maximum concentration of carbenium ions varies from $k_{tr} = 10^{-1}$ s^{-1} at −65 °C to $k_{tr} = 10^2$ s^{-1} at −32 °C.[20]

The unsaturated dimers of styrene and its derivatives prepared by Higashimura et al. at high temperature are formed under conditions in which β-proton elimination predominates.[18] These model studies demonstrated that unsaturated dimers are formed in higher yield in the presence of protonic acids than they are with Lewis acids. Higher unsaturated oligomers are also formed in concentrations predicted from a simple scheme involving the ratio of the rate constants of transfer to propagation. Table I summarizes the ratios of the rate constants of transfer to propagation determined from the oligomer distribution at 70 °C using different acids. Transfer is highest for the weakest acids, which therefore have the most basic anions. In contrast, the ratios are similar for all of the complex anions derived from Lewis acids. This may indicate that transfer occurs with either solvent or monomer, rather than with the counteranion derived from these Lewis acids.

Table I. Effect of Counterion on the Ratio of the Rate Constants of Transfer to Propagation in Benzene at 70 °C[18]

anion$^-$/LA	Tos$^-$	ClO_4^-	TfO$^-$	$SnCl_4^-$	BF_3OH^-	$AlEtCl_2OH^-$
k_{tr}/k_p, mol L^{-1}	1.4	0.75	0.22	0.11	0.083	0.069

The ratio of transfer to propagation increases substantially with increasing temperature since eliminating reactions usually have higher activation energies than electrophilic addition reactions. This is confirmed in Figure 4,[20,21] in which the difference in the activation energies of transfer by elimination and propagation is $\Delta E_a = 24$ kJ/mol. Table II demonstrates that k_{tr}/k_p is also higher in less polar solvent systems. This is consistent with the expected trend in which the ratio of the rate constants of an ion–ion reaction to an ion–dipole reaction decreases with increasing solvent polarity. That is, ion–ion reactions require more desolvation to reach the transition state than do ion–dipole reactions.

Table II. Effect of Solvent on the Ratio of the Rate Constants of Transfer to Propagation in Styrene Polymerizations with Perchlorate Anion[18]

solvent, 50 °C	C_6H_6	$C_6H_6/(CH_2Cl)_2$	$(CH_2Cl)_2$
k_{tr}/k_p, mol L^{-1}	0.59	0.42	0.11

Transfer to Monomer

Since the ratios of the rate constants of transfer to propagation shown in Table I are similar for all of the complex anions derived from Lewis acids, it appears that transfer occurs in these cases with either solvent or monomer, rather than with counteranion. Sigwalt recently compiled the ratios of the rate constants of transfer to monomer vs propagation for several monomers using a variety of cationic initiating systems.[24] Transfer to monomer also occurs in γ-irradiated systems in which there is no counteranion ($k_{trM}/k_p \approx 0.003$ at −10 °C).[22,23] Figure 5 shows the Arrhenius plots of the rate constants of propagation[13] and of transfer to monomer[23-25] in the polymerization of styrene. Comparison of Figures 4 and 5 demonstrates that transfer to monomer is smaller than transfer to triflate anion. The molecular weights obtained in γ-radiation systems and under "living" conditions are quite similar, confirming that transfer to monomer is impossible to avoid even in systems claimed to be living. Living systems therefore do not stabilize the cation substantially and do not considerably increase the selectivity of propagation over transfer reactions.

Termination

Termination is not a typical reaction in the cationic polymerization of styrene while monomer is still present, and quantitative conversions are often obtained. Nevertheless, termination may occur by the following routes. Added nucleophiles and nucleophilic impurities may abstract β-protons or react with growing carbenium ions to form stable onium ions. Nucleophiles may also complex with Lewis acids to form less reactive or even inactive complexes. However, onium ion formation may be reversible if the nucleophile is a weak base. In this case, the lifetime of the carbenium ions is reduced, resulting in lower

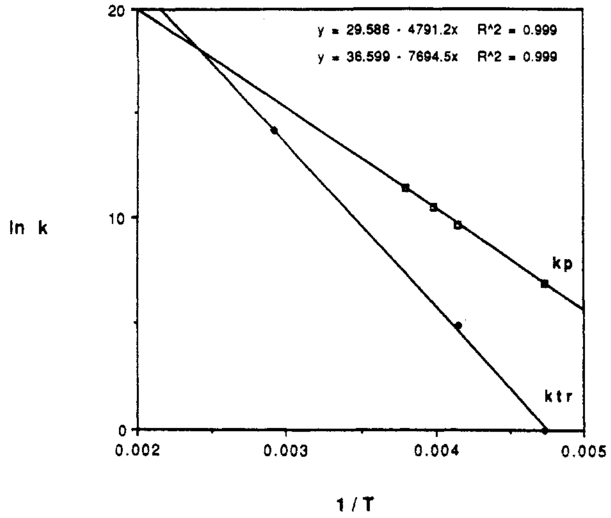

Figure 4. Arrhenius plots of the rate constants of propagation (k_p) of styrene initiated by triflic acid in CH_2Cl_2[13] and of transfer by elimination to counteranion.[20,21]

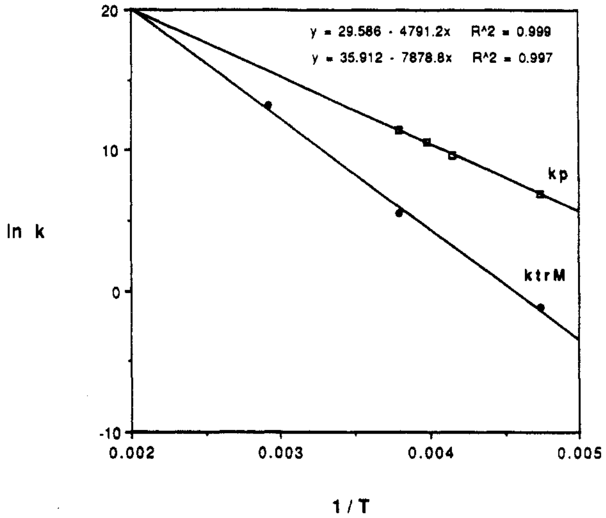

Figure 5. Arrhenius plots of the rate constants of propagation (k_p) of styrene initiated by triflic acid in CH_2Cl_2[13] and of transfer by elimination to monomer.[25]

polydispersities in systems that suffer from slow exchange of active species.[26,27] The addition of a small amount of nucleophile will also reduce the polymerization rate, making it easier to control.

Complex MtX_{n+1}^- counterions may decompose to form covalent species and Lewis acid. Depending on the nature of the ligand X, this termination reaction may be reversible. Anions containing chloride and bromide ligands such as $SnCl_5^-$, $SbCl_6^-$, $SnBr_5^-$, BCl_4^-, and BBr_4^- usually decompose reversibly. However, the momentary concentration of propagating carbenium ions is much lower than that of dormant covalent species, which leads to lower polymerization rates and more controlled polymerizations. Reversible systems that are in fast exchange in comparison to propagation provide living systems with narrow molecular weight distributions.[26]

Finally, termination may occur due to the formation of carbenium ions which are too stable and sterically too crowded to initiate polymerization. In this case, transfer by β-proton elimination or intramolecular cyclization occurs first, followed by rearrangement to the more stable carbenium ion. Thus, termination may be suppressed if transfer is eliminated. The more stable cations are often highly delocalized, with indanyl, allyl, or even polyene sequences.

Initiation

Although rate constants of propagation, depropagation, transfer to monomer, and intramolecular cyclization do not depend strongly on the nature of the counterion, that of initiation obviously does. Stopped flow measurements demonstrated that protonic acid initiated systems are very complex due to the formation of acid aggregates, with subsequent conjugation of the acid with counterions to form HA_2^- anions. In stopped flow polymerizations, the monomer solution is mixed with an initiator solution just before entering the observation cell. Since the higher aggregates that are initially present have a lower probability of forming in the presence of monomer, the initiation rate reaches a maximum at a carbenium ion concentration proportional to $[HA]^2$. This indicates that subsequent initiation occurs through the dimeric acid.[13]

In contrast, Lewis acids rarely initiate polymerization alone and require a true initiator such as a protonic or alkylating reagent. The best and simplest systems are based on alkylating reagents that mimic the growing species. For example, 1-phenylethyl halide models the macromolecular growing species present in the cationic polymerization of styrene, and the rate of initiation with this compound should therefore be similar to that of propagation. 1-Phenylethyl chloride has the additional advantage that it can be studied in some model reactions such as exchange and racemization, from which the rate of ionization is determined. If the rate of initiation is faster than that of propagation and if side reactions are absent, living polymers with low polydispersities are formed. If initiation is slow, it is not possible to control the molecular weight and the polydispersity of a living system broadens to a limiting value of $M_w/M_n > 1.3$.[28]

Master Plot and Limitation of Living Systems

The molecular weight of systems with instantaneous initiation and with transfer is defined by

$$1/DP_n = [I]_0/\Delta[M] + k_{trM}/k_p \qquad (2)$$

when transfer to monomer occurs and by

$$1/DP_n = [I]_0/\Delta[M] + k_{tr}/k_p[\ln([M]_0/[M])/\Delta[M]] \qquad (3)$$

when unimolecular transfer dominates, such as to counterion or to another reagent to form indanyl end groups. The intercept of a plot of the reciprocal degree of polymerization as a function of the reciprocal monomer concentration is therefore equal to k_{trM}/k_p when transfer to monomer dominates; the slope is proportional to the ratio of the initial initiator concentration to the amount of reacted monomer. If unimolecular transfer dominates, a plot of the reciprocal degree of polymerization as a function of $\ln([M]_0/[M])/\Delta[M]$ will yield k_{tr}/k_p as the slope and $[I]_0/\Delta[M]$ as the intercept.

According to eq 2, the molecular weight should increase with conversion in the case of transfer to monomer. In the case of unimolecular transfer described in eq 3, the molecular weight may not increase with conversion since the rate of transfer does not decrease with conversion although the rate of propagation does. Equations 2 and 3 demonstrate that the molecular weights are limited in both cases by the ratio of the rate constants of propagation and transfer, and only limited molecular weights may be possible even at the lowest possible initiator concentration. Both equations can be simplified by assuming an infinitely small initiator concentration and high conversion to calculate the maximum obtainable DP. In this case, the upper DP limit is defined simply by the ratio of the rate

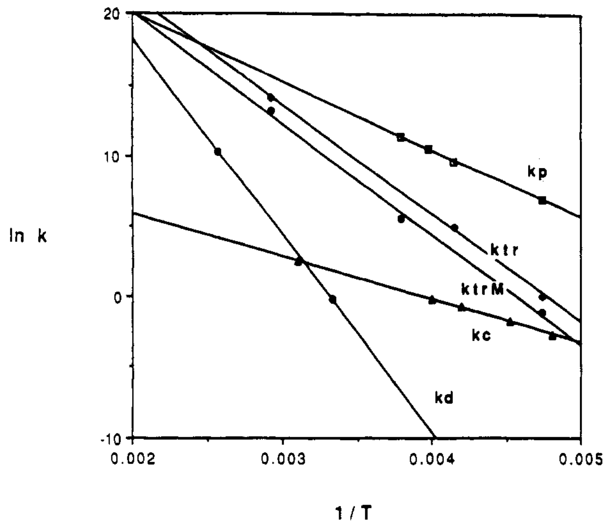

Figure 6. Master plot for the triflic acid initiated polymerization of styrene in CH_2Cl_2.

constants of propagation and transfer if transfer to monomer dominates; however, in reality DP must always be lower than k_p/k_{trM} or k_p/k_{tr} since the ratio $[I]_0/\Delta[M]$ cannot be ignored.

Figure 6 compiles all of the data discussed in this paper. The Arrhenius plots of the rate constants of propagation (p), depropagation (d), and transfer to counterion (tr), monomer (trM), and aromatic rings with indanyl formation by cyclization (c) provide the following conclusions.

1. The activation energies decrease in the order $E_d \gg E_{trM} \approx E_{tr} > E_p > E_c$.

2. The rate constants under standard conditions, i.e., $[M]_0 = 1$ mol/L, at temperatures lower than 50 °C decrease in the order $k_p > k_{tr} > k_{trM} > k_c > k_d$. The rates of propagation and transfer to monomer will be lower at lower monomer concentrations since both reactions are bimolecular; all others are unimolecular and will not be affected by monomer concentration.

3. The formation of indanyl end groups becomes increasingly more important at lower temperatures, until it becomes the most important transfer reaction below -85 °C. Therefore, the ratio of the rate constants of propagation and all other transfer reactions will continuously increase with decreasing temperature until intramolecular cyclization becomes important; the ratio k_p/k_{tr} or rather k_p/k_c then becomes smaller at lower temperatures. Thus, -85 °C may be the optimum temperature to obtain the highest molecular weight polystyrene by cationic polymerization; molecular weights may again decrease at temperatures lower than -85 °C due to intramolecular cyclization. Of course, quite high molecular weight polymers will be formed at low temperatures.

4. There are currently no data indicating that "living" systems behave better than classic cationic systems. Although transfer to counteranion may be reduced or even eliminated using γ-radiation or initiators with complex anions, transfer to monomer and intramolecular cyclization still occur. However, less basic counteranions such as triflate will decrease k_{tr} relative to that with more basic anions such as tosylate and increase the molecular weight. In addition to selection of a better counteranion, a specific solvent or solvating agent may also increase the selectivity slightly toward propagation and therefore increase the upper limit of molecular weights. Nevertheless, even a 2-fold increase in selectivity (k_p/k_{tr}) corresponds to less than 1 kcal/mol improvement in the difference in activation energies of propagation and transfer, which is difficult to attribute to any specific factor. In other systems, additives reduce the molecular weight. For example, the addition of ethyl acetate as a cation "stabilizer" to the polymerization of isobutyl vinyl ether reduces the molecular weight 2-3-fold.[29]

5. The master plot shown in Figure 6 is typical of polymerizations in CH_2Cl_2 and solvents of similar polarities. Whenever possible, the rate constants were calculated or taken from literature values of triflic acid initiated polymerizations of styrene in CH_2Cl_2. In other cases, it was necessary or more appropriate to estimate the desired rate constants using data obtained in benzene and/or with Lewis acid or γ-irradiated initiation. The resulting master plot is therefore not meant to report absolute rate constants but rather to demonstrate the trends in the various rate constants as a function of temperature to demonstrate the effect of different polymerization conditions. Nevertheless, the following variations with changing solvent polarity should be considered, especially when the master plot is translated to other solvent systems. Ion-ion reactions such as transfer to counterion will be strongly accelerated in less polar solvents. Ion-dipole reactions may be slightly faster in less polar solvents. Since propagation, depropagation, transfer to monomer, and intramolecular cyclization all involve ion-dipole reactions, they are usually affected in the same way by solvent polarity. Thus, lower molecular weights may occur in less polar solvents if molecular weight is controlled by transfer to counterion.

6. The master plot shown in Figure 6 can be used as a guide to the synthetic limits of the cationic polymerization of styrene with triflate counteranions. Degrees of polymerization ($\sim k_p/k_{tr}$) of only around 7 can be obtained at 50 °C. This limiting degree of polymerization increases to approximately 100 at -20 °C. At -70 °C, degrees of polymerization above 1000 are possible. Higher DPs could be obtained with complex counterions or with γ-radiation where transfer to monomer limits the molecular weights (DP $\sim k_p/k_{trM}$), with approximately DP = 25, 350, and 7000 formed at the corresponding temperatures.

Conclusions

Figure 6 clearly demonstrates that high molecular weight polymer is favored by decreasing temperature due to the increasing ratio of the rate constants of propagation to transfer. The master plot and the relative positions of the Arrhenius relationships can also be manipulated by changing other reaction conditions to favor either high or low molecular weight polymers. For example, assuming that transfer occurs primarily by transfer to counteranion, it is best to work at low temperature in a polar solvent using a high initial monomer concentration and an initiator with the least basic counteranion possible to obtain high molecular weight polymer. The use of both a high initial monomer concentration and a polar solvent will favor propagation over transfer to counteranion. On the other hand, if one needs to synthesize dimer,[18] it is best to work at high temperature in a nonpolar solvent using a low initial monomer concentration and an initiator with a basic counteranion. In this case, the rate of transfer to counteranion is increased relative to that of propagation.

Master plots of the Arrhenius relationships of the elementary reactions in other polymerizations should also be helpful in defining the best reaction conditions for synthesizing a desired molecular weight polymer. The synthesis of a polymer with precisely controlled end groups, molecular weights, and narrow molecular weight distribution requires $\Delta[M]/[I]_0 \approx 0.01k_p/k_{tr}$ or at least $\Delta[M]/$

$[I]_0 < 0.1k_p/k_{tr}$. For example, there should be no significant deviation from an expected molecular weight of DP = 1000 if $k_p/k_{tr} > 10^4$. However, k_p/k_{tr} must be greater than 10^6 to obtain DP = 100 000. Determining k_p/k_{tr} is useful for predicting the synthetic limits not only for cationic polymerizations but presumably also for anionic, radical, metathesis, and other polymerizations.

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(21) The rate constant of transfer by elimination to counteranion (k_{tr}) at 70 °C in the triflic acid initiated polymerization of styrene was estimated from the rate constant of propagation (k_p) in CH_2Cl_2 at 70 °C from Figure 4 and from the ratio $k_{tr}/k_p = 0.22$ at 70 °C in benzene reported in ref 18.

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(23) The small differences in molecular weights reported in ref 22 in benzene vs in the bulk styrene polymerization must be due to chain transfer to monomer since the ratio of the rates of propagation to unimolecular chain transfer should be affected by monomer dilution. The ratio k_{trM}/k_p can then be estimated from $1/DP = [I]_0/\Delta[M] + k_{trM}/k_p$, which reduces to $1/DP = k_{trM}/k_p$ in the absence of initiator and at high conversion.

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(25) The rate constant of transfer to monomer (k_{trM}) at 70 °C was estimated from k_p in CH_2Cl_2 at 70 °C from Figure 5 and the mean value of the ratios k_{trM}/k_p at 70 °C reported in ref 18 for the three Lewis acid coinitiated polymerizations of styrene in benzene. The rate constant of transfer to monomer (k_{trM}) at −10 °C was estimated from k_p in CH_2Cl_2 at −10 °C[13] and k_{trM}/k_p at −10 °C calculated from ref 22.[23] The rate constant of transfer to monomer (k_{trM}) at −62 °C was estimated from k_p in CH_2Cl_2 at −62 °C[13] and k_{trM}/k_p at −60 °C reported in ref 24 for the $TiCl_4$ initiated polymerization of styrene in CH_2Cl_2.

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