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Quasiliving Carbocationic Polymerization. XI. An Interpretation of Solvent Effects by Donor and Acceptor Numbers

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ABSTRACT

Counteranion/solvent interactions (counteranion solvation) profoundly influence each and every elementary step of carbocationic polymerizations and are just as important as the commonly emphasized cation/solvent interactions (cation solvation). Counteranion solvation and carbocation solvation have been characterized by Gutmann's acceptor number AN and donor number DN, respectively. Analysis of earlier data leads to the conclusion that the effect of

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monomer concentration on the rate, molecular weight, and molecular weight distribution obtained in cationic olefin polymerizations in "polar" solvents are in fact due to subtle changes in solvent concentration. Indeed, olefin monomers behave as "nonpolar" solvents and by changing the monomer concentration the character of the medium may profoundly change. It is further concluded that quasiliving polymerizations cannot be achieved in batch operations because the conditions that prevail in the initial charge, although possibly suitable for quasiliving polymerizations, must continuously change with the diminishing monomer concentration, i.e., by continuously changing the solvent character of the system. In contrast, in continuous systems initial conditions in the charge suitable for the attainment of living or quasiliving conditions can be maintained even for long periods of time by continuously replenishing the consumed monomer. By the use of these concepts, heretofore unexplained observations made in the course of quasiliving polymerization studies have been accounted for and, beyond this, new insight into solvation phenomena in cationic polymerizations is generated.

INTRODUCTION

The first and basic requirement of living and quasiliving polymerizations is that the concentration of active sites must remain constant during the experiment, R* = constant. In addition, in order to obtain linearly increasing molecular weights and to maintain narrow molecular weight distributions with increasing monomer consumption, chain transfer to monomer must be absent or at least strongly depressed.

The first requirement that R* = constant can be readily achieved in living anionic systems or in free radical systems under steady-state conditions, and specifically in carbocationic systems in terminationless polymerizations. Terminationless carbocationic polymerizations prevail when termination (i.e., the collapse of the propagating cation counteranion pair by halogenation) and reionization are in equilibrium, and sufficient time is available for complete monomer consumption:

$$\sim\!\!-\mathrm{C}^{\oplus}\mathrm{MtX}^{\ominus}_{n+1} \rightleftharpoons \sim\!\!-\mathrm{C{-}X} + \mathrm{MtX}_n \qquad (1)$$

$$\sim\!\!-\mathrm{C}^{\oplus} + \mathrm{C{=}C} \rightleftharpoons \sim\!\!-\mathrm{C{-}C{-}C}^{\oplus} \qquad (1a)$$

By careful selection of the initiating system (cationogen initiator/Friedel-Crafts acid MtX_n coinitiator combination), monomer, solvent, and temperature, conditions can be found for Equilibrium (1) to exist. The position of Equilibrium (1) is strongly influenced by the nature of the monomer/solvent combination and by the MtX_n used. Ionization will be favored by increasing the stability of both the carbocation and the counteranion, and by solvating these species.

As to the second requirement, i.e., to eliminate or strongly reduce chain transfer to monomer, it can also be achieved by careful selection of reaction conditions. Several systems have been identified [1-5] in which the nature of the solvent determines the course of chain transfer reactions, and by suitably selected solvent(s) or solvent mixture(s), and concentrations chain transfer can be strongly depressed.

Thus, under carefully selected conditions, specific carbocationic systems have been shown readily to yield quasiliving kinetics; however, quasiliving conditions can only prevail in continuous systems and not in batch systems. While specific conditions conducive for the attainment of quasiliving polymerization mechanisms may be achieved momentarily in batch systems, they cannot be maintained for any length of time because with advancing conversions the monomer/solvent concentration will continuously change in favor of the solvent. Due to the continuous shift in the monomer/high AN solvent concentration during a batch polymerization, the concentration and/or charge separation of active centers may change, therefore the rate of propagation and chain transfer may also change and living conditions may never be maintained. In contrast, under continuous conditions, by continuously replenishing the consumed monomer, the initial monomer/solvent concentration ratio in the charge conducive for the attainment of living polymerizations can be maintained and prolonged for long times.

In a quasiliving polymerization the overall rate of polymerization R_p is equal to the rate of monomer addition A, and the prevailing monomer concentration is very low:

$$R_p = A = k_p[M][R^{\oplus}] \tag{2}$$

and

$$[M] = \frac{A}{k_p[R^{\oplus}]} \tag{3}$$

where $[R^{\oplus}]$ is the concentration of the active centers. According to Eq. (3), an increase of the monomer addition rate increases the monomer concentration linearly. In a number of quasiliving experiments however, we observed that above a certain monomer addition rate monomer accumulated in the system, i.e., the monomer concentration was not a constant very low value as expected from Eq. (3). According to these observations, the monomer concentration influences the course of quasiliving polymerization in a more complex manner than previously commonly assumed. The observed monomer accumulation can be explained by assuming that due to changes in the monomer/solvent ratio the concentration of the active centers and/or the rate constant of propagation decreases.

The purpose of this article is to explain these phenomena in terms of solvent effects and, more ambitiously, to discuss solvent effects on the course of cationic polymerizations in general.

DISCUSSION

Recent insight into the detailed mechanism of quasiliving polymerization and an extensive search of the literature of cationic polymerization has convinced us that: (A) Solvent/counteranion interactions are at least as important as solvent/carbocation interactions and affect all the elementary steps of cationic polymerizations, and (B) changes in monomer concentration profoundly affect the above interactions by simultaneously changing the solvent concentration; indeed, the monomer behaves as its own solvent.

The nature and the concentration of the solvent and the monomer will help determine whether a polymerization system can acquire living or quasiliving character. Solvent and monomer should be characterized in an identical manner and their interactions with the carbocation and counteranion should be given the same weight. We propose to view the solvent and the monomer (as a solvent) in cationic polymerizations in terms of the "coordination model" developed for the chemistry of ionic reactions in nonaqueous solvents [6-10] and to characterize the media by Gutmann's acceptor number (AN) and donor number (DN) [11]. We now turn to a discussion of elementary steps in carbocationic polymerizations with special attention to solvent interactions by the use of these parameters.

Reversibility of Termination

The reversibility of termination as described by Eq. (1) is determined by the respective stabilities of the carbocation and counteranion, and by the extent of their separation. If the solvent is a strong donor and a weak acceptor, the cations will be highly solvated, whereas the anions will remain relatively unsolvated and therefore rather reactive. If the solvent is a strong acceptor, the anions will be solvated and the cations will remain unsolvated, i.e., reactive [11]. A combination of a donor solvent and an acceptor solvent will favor charge separation, and both the cation and the counteranion will be stabilized. Ion separation will also be favored by increasing the dielectric constant of the medium [11]. Thus Equilibrium (1) will be shifted toward the left by the use of solvents or solvent mixtures of high specific coordinating ability and high dielectric constant. For example, charge separation will be larger in nitromethane than in methylene chloride because the donor number of the former solvent is larger than that of the latter ($DN_{CH_3NO_2} = 2.7$ and $DN_{CH_2Cl_2} = 0$) while their acceptor numbers are essentially identical ($AN_{CH_3NO_2}$

= 20.5 and $AN_{CH_2Cl_2}$ = 20.4). Also, the larger dielectric constant of CH_3NO_2 than CH_2Cl_2, i.e., $\epsilon_{CH_3NO_2} = 35.87$ and $\epsilon_{CH_2Cl_2} = 9.8$, will further facilitate charge separation. Thus CH_3NO_2 will stabilize both the carbocation and the counteranion by specific coordination and nonspecific solvation; CH_2Cl_2 will stabilize only the counteranion by coordination, and both charges to a relatively modest degree by nonspecific solvation. Similarly, by changing the solvent from CH_2Cl_2 to CH_3NO_2 the ion dissociation constant K_d increases from 10^{-5} to 10^{-3} M in the polymerization of THF at 25°C [12]. In the acetyl perchlorate initiated polymerization of p-chlorostyrene the fraction of free ions is 26, 38, and 82% in pure CH_2Cl_2, and in 1/15 and 1/7 v/v CH_3NO_2/CH_2Cl_2 solvent mixtures, respectively [13].

The AN and DN of n-hexane are both zero, i.e., ionization will be more extensive in pure CH_2Cl_2 than in CH_2Cl_2/n-C_6H_{14} mixtures. Indeed, conversions were over 90% when p-tert-butylstyrene (ptBuSt) monomer was added in a steady slow stream to a cumyl chloride/BCl_3 system in pure CH_2Cl_2 [14]; however, conversions decreased precipitously when various CH_2Cl_2/n-C_6H_{14} mixtures were used. As shown by the data in Fig. 1, conversions decreased in the presence of in-

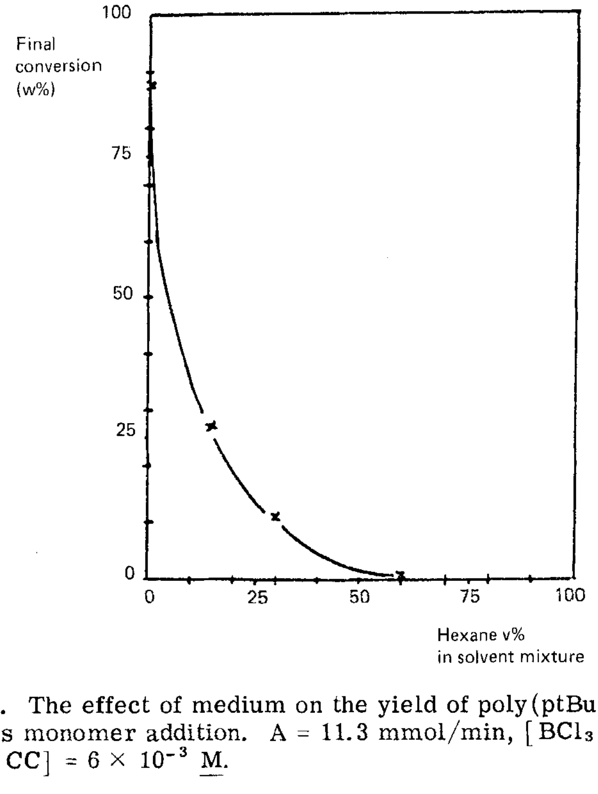

FIG. 1. The effect of medium on the yield of poly(ptBuSt) using continuous monomer addition. A = 11.3 mmol/min, [BCl_3] = 2.5 × 10^{-2} M, [CC] = 6 × 10^{-3} M.

creasing amounts of $n\text{-}C_6H_{14}$. This surprisingly strong effect of the solvent composition on conversions reflects the shift of Equilibrium (1) toward the right, i.e., toward the "dormant" chlorinated species, by increasing the $n\text{-}C_6H_{14}$ content.

The data presented in Fig. 1 together with the phenomenon in general may be explained by the following chain of thought. Let us assume that counteranion $G^{\ominus}$ solvation by solvent S involves the following equilibria:

$$G^{\ominus} + S \rightleftharpoons G^{\ominus}S_1 \qquad K_1 = \frac{[G^{\ominus}S_1]}{[G^{\ominus}][S]} \tag{4}$$

$$G^{\ominus}S_1 + S \rightleftharpoons G^{\ominus}S_2 \qquad K_2 = \frac{[G^{\ominus}S_2]}{[G^{\ominus}S_1][S]} \tag{5}$$

$$\vdots \qquad\qquad \vdots$$

$$G^{\ominus}S_{n-1} + S \rightleftharpoons G^{\ominus}S_n \qquad K_n = \frac{[G^{\ominus}S_n]}{[G^{\ominus}S_{n-1}][S]} \tag{6}$$

where n is the highest number of the CH_2Cl_2 molecules that surrounds $G^{\ominus}$, and K_1, K_2, . . . , K_n are equilibrium constants of the different solvation stages. Thus the ratio of concentrations of solvated and unsolvated counteranions can be expressed by

$$[G^{\ominus}S_n]/[G^{\ominus}] = K[S]^n \tag{7}$$

where

$$K = \prod_{i=1}^{n} K_i \tag{8}$$

According to Eq. (7), counteranion solvation is very strongly affected by the solvent concentration (n-th power) and the ionization equilibrium. In Eq. (7), K is determined by the nature of solvent, i.e., by AN and DN. In view of the exponential dependence of solvation on solvent concentration, the data depicted in Fig. 1 become understandable. By increasing the amount of $n\text{-}C_6H_{14}$ in the system, the concentration of CH_2Cl_2 (AN = 20) decreases, and thus ion separation decreases exponentially. As a rule, hydrocarbon monomers (whose AN is expected to be low) should behave similarly in solvents of high AN in general. Monomer accumulation observed in certain quasiliving systems when the monomer addition rate was higher than an optimum value [15, 16] may also be due to the exponential nature of anion solvation by high AN solvent. By increasing the rate of monomer addition, the concentration of the monomer will increase according to Eq. (3) and the relative concentration of the high AN solvent will decrease, and as a consequence the extent of counteranion solvation will decrease. As a result, the equilibrium of reversible termination will shift somewhat toward the dormant species (Eq. 1). In this manner the number of active centers and/or the rate constant of propagation will decrease which in turn leads to an even stronger monomer accumulation and to a further decrease in the rate of propagation. Thus it is understandable that, beyond an optimum addition rate, monomer suddenly starts to accumulate with a concomitant strong decrease in conversions. This effect was also observed in the quasiliving polymerization of indene and ptBuSt in CH_2Cl_2 [15].

By decreasing the high AN solvent concentration, the nature of the ions is expected to change as the ion pair passes through different solvation stages; for example, from free ions to contact ion pairs or dormant species. Such changes must affect the rate constant of propagation and those of different chain transfer reactions.

Monomer accumulation was also observed in the quasiliving cumyl chloride/BCl_3/α-methylstyrene system when the monomer addition rate was too high [14]. According to the GPC traces of poly(α-methylstyrene) samples withdrawn during a polymerization at -50°C, shown in Fig. 2, the nature of active centers changes with monomer concentration. At a critical monomer concentration level a new peak appears in the GPC spectrum. The appearance of the new peak is delayed when the polymerization is faster and monomer accumulation is slower (experiment at -70°C, shown in Fig. 3).

Similar monomer concentration effects have been observed in conventional batch polymerization of styrene [17] and ptBuSt [15] in CH_2Cl_2 using CF_3SO_3H and cumyl chloride/BCl_3 initiator systems, respectively. In these experiments the monomer was added in one rapid dose to solutions containing the active centers. In these batch experiments monomodal molecular weight distribution could be obtained only at very low monomer concentrations; at higher monomer concentrations multimodal molecular weight distributions were obtained (by GPC). Evidently at low monomer concentrations, i.e., in systems where the monomer/solvent ratio changes only slightly during polymerization, the ionicity of the system changes only slightly (no change in GPC traces). However, at higher monomer concentrations, due to the consumption of higher amounts of monomer, the ionicity of the medium changes which in turn may affect k_p and $k_{tr,M}$, and would cause the multimodal distributions to appear by GPC.

The Effect of Solvent on the Propagation Rate

In a medium in which the active centers are mainly in contact ion pair form (low AN and DN), the polymerization will be relatively slow

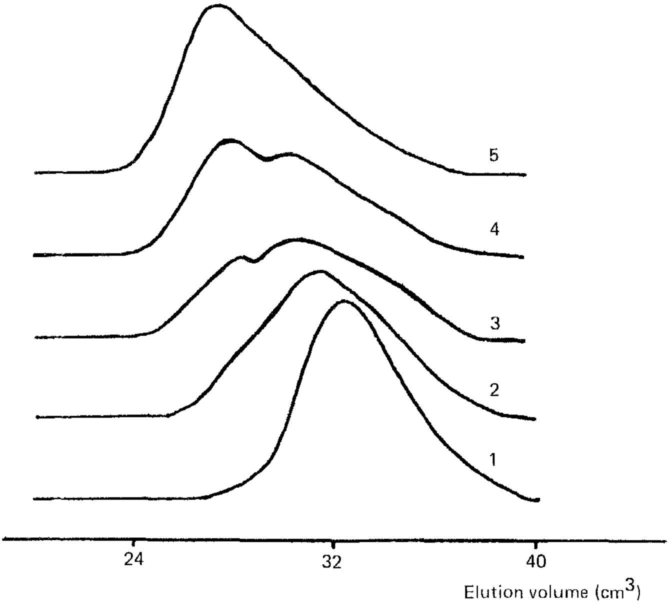

FIG. 2. The effect of increasing monomer concentration on the polymerization of α-methylstyrene using continuous monomer addition. T = 50°C, conversion = 78%, A = 31 mmol/min, [BCl_3] = 2.5×10^{-2} M, [CC] = 7×10^{-3} M. [M]: Curve 1 = 2 min, 0.034 M; Curve 2 = 4 min, 0.068 M; Curve 3 = 6 min, 0.136 M; Curve 4 = 8 min, 0.271 M; Curve 5 = 10 min, 0.542 M.

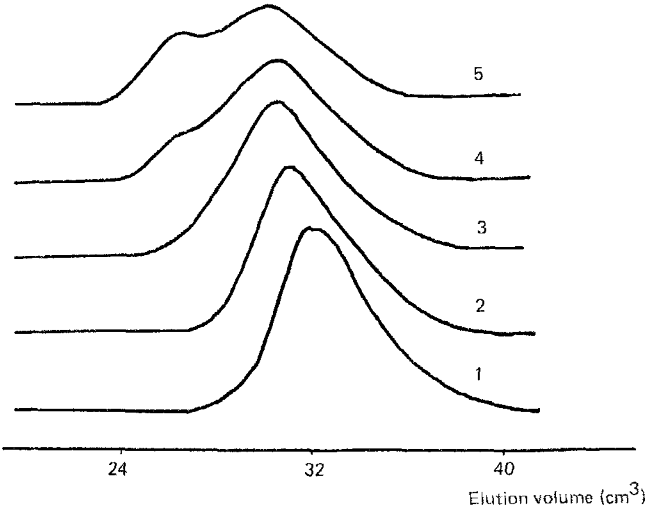

FIG. 3. The effect of increasing monomer concentration on the polymerization of α-methylstyrene using continuous monomer addition. T = -70°C, conversion = 86%, A = 31 mmol/min, [BCl_3] = 2.5×10^{-2} M, [CC] = 7×10^{-3} M. [M]: Curve 1 = 2 min, 0.022 M; Curve 2 = 4 min, 0.043 M; Curve 3 = 6 min, 0.086 M; Curve 4 = 8 min, 0.172 M; Curve 5 = 10 min, 0.345 M.

because the monomer has to be inserted between strongly interacting ions. By separating the ion pair and stabilizing the counteranion by solvation with a high AN species, that is, by increasing the acceptor nature (accepticity) of the medium, the interaction between the carbocation and the counteranion will be weakened, the activation energy of propagation will decrease, and the rate of propagation will increase. It is well known that cationic polymerizations proceed much faster by free ions than by ion pairs [18-21]. In contrast, by increasing the donicity of the solvent (high DN), the rate of propagation may decrease because of the strong interactions between the carbocation and donor molecules. Solvents having very high donor numbers (e.g., $DN_{\text{diethyl ether}} = 19$) may even prevent carbocationic polymerizations from occurring.

The effect of solvent DN and AN's is illustrated by Kagiya et al.'s [22] data (Table 1). These authors have investigated the cationic polymerization of 2-phenyl-2-oxazoline initiated with 2-phenyl-2-oxazolinium perchlorate and observed that the rate constant of propagation, k_p, increases with decreasing nucleophilicity of the solvent; however, they did not find any correlation between k_p and the dielectric constant of the solvent [22]. Since k_p must reflect the extent of ion separation, we theorized that there must be a correlation between k_p and AN and/or DN. By increasing the AN of the medium, i.e., by counteranion solvation, the equilibrium between ion pairs and free ions should shift toward ion separation and propagation should accelerate. The plot of ln k_p versus AN shown in Fig. 4 constructed by the use of Kagiya et al.'s data seems to bear out this postulate. In the same vein, solvent (media) with increasing DN's are expected to reduce k_p by complexing with the propagating carbocation although they would increase ion separation. Figure 5 shows the ln k_p versus DN plot constructed by the use of Kagiya et al.'s data. Except for one data point, this linear correlation seems also to corroborate our theory.

These observations suggest that in order to increase the rate of propagation in carbocationic polymerizations the accepticity of the solvent has to be increased, i.e., high AN solvents should be used. Indeed, it has been demonstrated in cationic polymerizations of various vinyl and heterocyclic monomers [23] that in the presence of strong electron acceptors the polymerization rate and the molecular weight increased. The electron acceptors used in these experiments, e.g., tetracyanoethylene, are predicted to have very large AN and low DN's (data are unavailable in the literature).

As mentioned above, the monomer may perform as its own solvent. The effect of monomer concentrations on the polymerization of styrene derivatives in the presence of several Bronsted acids has been studied in CH_2Cl_2 [24, 25], and it was shown that with increasing monomer concentration k_p decreases and the nature of active centers changes.

TABLE 1. The Propagation Rate Constants for the Polymerization of 2-Phenyl-2-oxazoline Initiated with 2-Phenyl-2-oxazolinium Perchlorate in Different Solvents [22]

Solvent	ϵ	k_p	$\ln k_p$	AN[a]	DN[a]
Di-n-propyl ether	4.3	0.14	-1.97	3.9	19.2
N,N-Dimethylacetamide	36.7	0.69	-0.37	13.6	27.8
Ethyl acetate	6.0	0.85	-0.16	9.3	17.1
Anisole	3.4	1.04	0.04	-	-
Acetonitrile	49	1.75	0.56	18.9	14.1
Nitrobenzene	34.8	2.09	0.74	14.8	4.4
Nitroethane	28.1	4.24	1.44	20.5	2.7

[a] Data from Ref. 11.

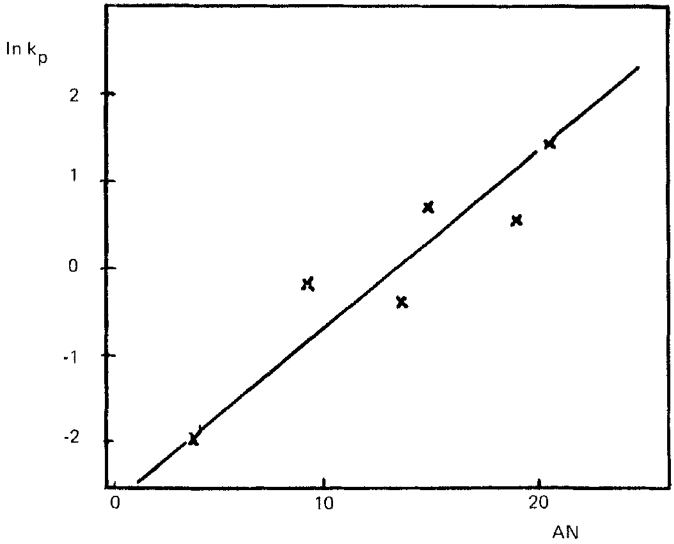

FIG. 4. Correlation between the logarithm of the propagation rate constant and AN (data from Ref. 22, see Table 1).

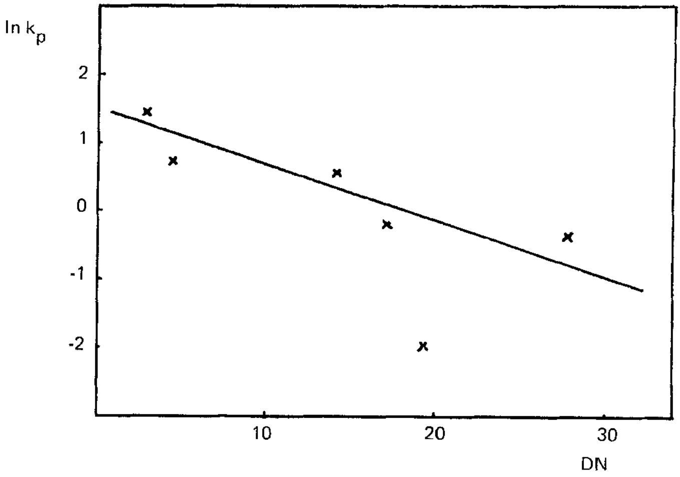

FIG. 5. Correlation between the logarithm of the propagation rate constant and DN (data from Ref. 22, see Table 1).

Penczek reported [26] that in the batch polymerization of THF in CCl_4, k_p increases with decreasing monomer concentration and the observed dependence was interpreted in terms of a solvent effect. Chmelir showed that the initial rate of polymerization of styrene by triflic acid in CH_2Cl_2 is controlled by the initial monomer concentration in a complex manner. According to this author, nondissociated catalyst rapidly forms an inactive complex with the monomer which is in equilibrium with other active species (ion pairs, free ions, and triple ions) [27].

Evidently the rate of cationic propagation can be increased by the use of solvents having large AN's. Preferentially the olefin concentration should be low and it should not change during polymerization. Such conditions can be achieved by continuous feeding of the monomer at an optimum rate of addition, i.e., by the use of the quasiliving technique.

Chain Transfer to Monomer

Evidence is accumulating that chain transfer to monomer, whatever the detailed mechanism [28-30], is facilitated by the proximity of the counteranion to the propagating cation. In line with this, pseudocationic systems, i.e., systems in which the counteranion is very close or even linked to the propagating center, are dominated by chain transfer to monomer and therefore yield very low molecular weights [36]. At the other extreme are systems in which counteranions as such do not even exist (γ-ray [33], nuclear chemical induced polymerizations [31,32]) or are physically removed in a different phase (complex chemical initiators [34, 35]). The common denominator between the latter systems is that the counteranion is far removed from the vicinity of the propagating sites which therefore become highly reactive or "free." Free carbenium ions are highly reactive (faster propagation) and are not assisted by the counteranion in transfer processes. Enhanced propagation and diminished transfer result in increased molecular weights [28].

By solvating the counteranion by high AN species and carrying out the polymerization in a nonnucleophilic medium (low DN solvent), the counteranions are removed from the close vicinity of the carbenium ion and chain transfer is suppressed. As a general rule, in media of high accepticity, low donicity, and preferentially high dielectric constant, the carbocation will be relatively free and therefore reactive, and the rate of propagation will be high. In such media, due to the high accepticity of the solvent, counteranions will be strongly stabilized and therefore removed from the carbocation, and thus chain transfer will be strongly depressed.

For example, the isobutyl vinyl ether/$AgSbF_6$/p-dicumyl chloride [1] and methyl vinyl ether/$AgSbF_6$/p-dicumyl chloride [2] systems at low temperatures in CH_2Cl_2 show strong quasiliving character. The number-average molecular weights increase linearly with the weight of added monomer, and narrow molecular weight distributions are obtained. The number of polymer chains remains unchanged during the early stages of reactions, indicating the absence of chain transfer in this solvent. However, in n-heptane or in toluene, where the counteranion is much less stabilized and thus may participate in chain transfer reactions, the number of polymer chains increases steadily during the reaction, indicating extensive chain transfer. Similarly the styrene/cumyl chloride/BCl_3 system shows quasiliving character in CH_2Cl_2 [3] and the number of polymer molecules remains unchanged during the entire reaction, indicating the absence of chain transfer. In contrast, several attempts to carry out the same polymerization in n-C_6H_{14}/CH_2Cl_2 mixtures failed although the monomer concentration was maintained low to prevent changes in ion separation due to monomer accumulation.

Due to the extreme ease of chain transfer by unimolecular intramolecular self-alkylation (i.e., indane-skeleton formation) in the case of styrene and its derivatives, the data obtained with these monomers have to be interpreted as somewhat special cases. Thus, in the course of our early attempts to obtain quasiliving polymerizations with styrene and derivatives, it was repeatedly observed that when the monomer addition rate was too low, indene formation invariably ensued. Evidently under these conditions the rate of propagation became too slow and the probability for the undesirable chain transfer by indane formation could not be avoided. Most likely the extent of this reaction is a function of the average lifetime of the carbocation. By increasing the lifetime (stability) of the cation either by the use of electrondonating substituent (p-tert-butyl or α-methyl) or by CH_2Cl_2 will therefore result in indane-skeleton formation. It is of interest in this context that among the three monomers, styrene, ptBuSt, and α-methylstyrene, the first one which is expected to produce the least stable carbocation yields the highest molecular weight product while the other two yield increasingly lower molecular weights and increasing extents of indane formation under the same conditions [3, 15].

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