Neutral Salt Effects on Cationic Polymerization of *N*-Vinylcarbazole Initiated by Protonic Acids

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ABSTRACT: Cationic polymerization of *N*-vinylcarbazole (VCZ) initiated by perchloric acid or trichloroacetic acid (TCA) in three different solvents (nitrobenzene (NB), ethylene dichloride (EDC), and benzene (Bz)) was studied at 30°C in the presence and absence of neutral electrolytes (tetra-*n*-butylammonium perchlorate (TBP) and tetraethylammonium perchlorate (TEP)). The kinetic quantity determined was the chain-transfer constant to methanol. Since chain-transfer constant is affected by the nature of kinetic chain carrier, the study of neutral salt effects on chain-transfer constants provides useful information on whether the cationic chain carrier is free or ion-paired. Measurements for six combinations of three solvents and two initiators either in the presence of TBP or in its absence afforded the following pieces of information.

(1) The presence of TBP enhanced the chain-transfer constant in polar media. However, no neutral salt effects were observed in benzene, indicating that the growing carbonium ion in benzene is tightly ion-paired and the addition of TBP cannot affect the ionic association.

(2) In EDC, the chain-transfer constants of methanol are very much enhanced by the addition of neutral electrolyte. The results were interpreted assuming that the rate of propagation decreases in the presence of TBP whereas the rate of chain-transfer reaction is relatively unaffected. A study of the deuterium isotope effect using methanol-*d* supports this view.

(3) In NB, the propagating species in the absence of TBP seem to be free carbonium ions since the kind of initiator does not influence the chain-transfer constant. In this system, the growing cation would be strongly solvated and stabilized.

(4) Dependence of the rate of polymerization on neutral salts was also investigated. The rate of polymerization is, however, a complex function of various rate constants and conclusion is difficult.

Chain-transfer constants are very sensitive to the nature of propagating species and their determinations as functions of neutral electrolyte concentration would provide a useful procedure to study the ionic equilibria of the carbonium ion and ion pairs.

KEY WORDS Cationic Polymerization / *N*-Vinylcarbazole / Chain-Transfer Constant / Salt Effect / Deuterium Isotope Effect / Counter Ion / Propagating Species / Ion Pair / Free Ion /

One of the most fundamental problems in cationic polymerization which has not been solved would be the ionic association of propagating carbonium ion. The apparent reactivities of a given monomer cannot be determined *a priori* without considering the effects of the initiator and solvent. Although the solvent might influence the reactivities of monomer as a result of solvation the degree of dissociation of the carbonium ion as a function of solvent polarity

and in some cases, the specific solvation of the carbonium ion are thought to be more important solvent effects than the solvation of monomer. Consequently solvent as well as initiator would influence the nature of the propagating carbonium ion.

The physical state of growing species is certainly a decisive factor which decides various kinetic quantities such as the propagation rate constant, termination rate constant, chain trans-

fer constant, copolymerization reactivity ratios and so on. Due to the lack of suitable experimental procedures, this problem has been discussed only qualitatively on many assumptions. One approach to the study of the nature of the propagating species would be to examine the salt effects on polymerization. The effects of neutral electrolyte in ionic polymerization were first investigated in the living anionic polymerization aimed at the shift of the free ion—ion pair equilibrium.^{1,2} In the case of cationic polymerization, an ideal condition of living polymerization is generally difficult to achieve. The only preceding example is the work by Pepper who claimed to determine the absolute value of k_p for styrene and to distinguish ion paired and free ionic propagating species using the technique of neutral salt effects.^{3,4} In general, however, the rate of cationic polymerization is a complex function of various factors other than the reactivity of the carbonium ion. As indices of reactivity determined by the nature of the propagating species alone, chain-transfer constants and monomer reactivity ratios in copolymerization may be chosen.

In this article, the chain-transfer constants to methanol were chosen as reactivity indices. This approach would have the following advantages over the copolymerization method. (1) In the measurements of chain-transfer constants, the physical state of the polymerization system can be kept closely identical since the concentration of chain-transfer agent is in the order of $10^{-3} M$. The determination of monomer reactivity ratios, however, implies the change of monomer feed ratio over a wide range and the physical state of the propagating species would not be identical during a series of measurements. (2) Copolymerization is essentially a comparison of two like reactions, namely the opening of ethylenic double bonds, whereas chain-transfer constants consist of the ratio of two unlike rate constants. Chain-transfer constants are therefore expected to be more sensitive to a minor change in the nature of the propagating species. (3) The accuracy of measurements is in general better for chain-transfer constants than monomer reactivity ratios.

The immediate aim of this study is to obtain information on the reactivities of the polyvinyl-

carbonium ion in different solvents and with different counter ions. The results can then be compared with the results of charge-transfer polymerization of *N*-vinylcarbazole (VCZ). Charge-transfer initiation of cationic polymerization by organic donor-acceptor interaction would produce carbonium ions bearing entirely different counter ions from any conventional cationic polymerizations. Experimental results of photosensitized cationic polymerization of VCZ^{5,6} were interpreted on the assumption of bimolecular dissipation of active species⁷ indicative of the free ionic nature of active species. For understanding the difference between the cationic polymerization *via* charge-transfer interaction and the conventional cationic polymerization, reference experiments are imminently required.

An outline of this research has been published as a short note⁸ and the full details will be described as follows.

EXPERIMENTAL

Materials

The VCZ was recrystallized once from purified *n*-hexane. Nitrobenzene, ethylene dichloride, and benzene (Guaranteed Reagent Grade) were washed by the conventional procedures and distilled at least twice over drying agents before use. The drying agents were calcium hydride for benzene and ethylene dichloride, and barium oxide for nitrobenzene. Trichloroacetic acid (TCA) (G. R. Grade) was used as received. Perchloric acid (63%) was distilled and the azeotropic mixture was used. No attempt at preparing anhydrous perchloric acid was made. Methanol (G. R. Grade) as chain-transfer agent was used after distilling once. Methanol-*d* was purchased in an aliquot and used as received.

Tetraethylammonium perchlorate (TEP) and tetra-*n*-butylammonium perchlorate (TBP) synthesized by Mr. K. Kameoka in this laboratory were used as provided.

Polymerization Procedures and Determination of Chain-Transfer Constants

Polymerization was carried out in a reaction vessel with a glass stopper at 30°C. The monomer solution (0.25 *M*) containing a required amount of chain-transfer agent was added with the initia-

tor solution. Portions of reaction mixture were poured into methanol to precipitate the polymer in appropriate intervals. No special care was taken to conduct the polymerization in an absolutely dry condition. Since VCZ is extremely active for cationic propagation the moisture in the atmosphere has little effect upon polymerization.

The precipitated polymer was filtered, washed well with methanol, and dried. The molecular weight was determined viscometrically⁹ assuming the molecular weight distribution was not affected by the kind of initiators and also by the addition of methanol and/or TBP. The range of molecular weight which can be determined by the viscosity equation is over 10000 (*i.e.*, $[\eta]_{\text{benzene}} > 0.07$). The chain-transfer constant (C) was calculated according to the expression (eq 1), where M_0 and M are the initial and the final monomer concentrations, respectively.

$$1/\overline{DP} = \frac{k_t^{\Sigma X_i}}{k_p} + \frac{k_{tr}^{\text{MeOH}}}{k_p} \frac{\ln M_0 - \ln M}{M_0 - M} [\text{MeOH}] \quad (1)$$

For the VCZ—Bz—HClO₄ system, the simple equation (eq 2) was applied to draw approximate figures of chain-transfer constants.

$$1/\overline{DP} = \frac{k_t^{\Sigma X_i}}{k_p} + \frac{k_{tr}^{\text{MeOH}}}{k_p} \frac{[\text{MeOH}]}{[M]} \quad (2)$$

RESULTS AND DISCUSSIONS

Effects of TBP on the Rate of Polymerization and the Molecular Weight of Polymer

Addition of TBP decreases the molecular weight of polymer. The rate of polymerization decreases when perchloric acid is the initiator. However, TBP acts as an accelerator for the polymerization by TCA in ethylene dichloride or in benzene. The effects of TBP on cationic polymerization may be attributed to the following four factors. (i) Effects of ionic strength. (ii) Exchange of the counter ions of the propagating carbonium ions. (iii) Participation in polymerization as a cocatalyst. (iv) Termination of chain-transfer reactions involving TBP. Since all of these factors would influence the polymerization, definitive analysis of rate data is impossible unless these factors are separable.

The retarding effects of TBP on the polymeri-

zation initiated by perchloric acid may be interpreted as the results of increasing ion-paired growing species.

Examples of the time—conversion curves in the presence and absence of TBP are shown in Figure 1—3. Higher concentration of perchloric acid was required to induce polymerization in the presence of TBP and the slope of the time—conversion curve is less steep than that in the absence of TBP.

These results recall the polymerization of styrene initiated by perchloric acid in methylene chloride⁴. The mode of polymerization of styrene—perchloric acid—methylene chloride system is temperature dependent. At -97°C the

Figure 1. Time—conversion curves for the ethylene dichloride—perchloric acid system: 30°C , $[\text{VCZ}] = 0.25\text{ M}$; ○, $[\text{HClO}_4] = 4 \times 10^{-4}\text{ M}$ and $[\text{TBP}] = 0$; ●, $[\text{HClO}_4] = 7 \times 10^{-4}\text{ M}$ and $[\text{TBP}] = 1 \times 10^{-2}\text{ M}$.

Figure 2. Time—conversion curves for the nitrobenzene—TCA system: 30°C , $[\text{VCZ}] = 0.25\text{ M}$; ○, $[\text{TCA}] = 3 \times 10^{-4}\text{ M}$ and $[\text{TBP}] = 0$; ●, $[\text{TCA}] = 3 \times 10^{-4}\text{ M}$ and $[\text{TBP}] = 10^{-2}\text{ M}$.

Figure 3. Time-conversion curves for the benzene-TCA system: 30°C, [VCZ]=0.25 M; ○, [TCA]= 5×10^{-2} M and [TBP]=0; ●, [TCA]= 1×10^{-3} M and [TBP]= 1×10^{-2} M.

polymerization is instantaneous up to a limited conversion depending on the concentration of perchloric acid and further polymerization is not observed whereas at higher temperatures the initial flash polymerization (stage I) is followed by the slow polymerization with a steady rate (stage II). By the addition of TBP, the yield of stage I is greatly reduced whereas the stage II is only partially suppressed indicating that free carbonium ions are the main propagating species in stage I and two propagating species act in the stage II. Although the time-conversion curve in Figure 1 cannot be divided in two stages so distinctly, suppression of the initial fast polymerization by TBP may be interpreted in the same manner as the styrene-perchloric acid-methylene chloride system. Also, the trend of slowing down the initial rate of polymerization is observed for the polymerization in nitrobenzene initiated either by perchloric acid or by TCA. The trend is, however, much smaller in the polar media than in less polar ethylene dichloride or benzene. Also the addition of TBP does not alter the shape of the time-conversion curve so markedly indicating that the contribution of free ionic species or solvent separated ion pairs in which the role of counter ion is of minor importance is dominant (Figure 2).

Dissociation of the growing carbonium ion in benzene is difficult to consider. The addition of TBP causes decreases in the rate of polymerization initiated by perchloric acid whereas the

chain-transfer constant is almost unaffected. This discrepancy could be attributed to salt effects on initiation and termination processes which do not influence the measurement of the chain-transfer constant. Furthermore, TBP in the polymerization initiated by TCA in benzene (Figure 3) might play a role of cocatalyst as judged by the accelerating effects of TBP. TCA is a very weak protonic acid which hardly initiates cationic polymerization by itself. In combination with TBP, there would be a possibility of producing more active initiators.

As a whole, the effects of TBP on the rate of polymerization differ from system to system and much information was not expected. Simpler and clearer explanations on the salt effects would be possible if the propagation process alone can be dealt with. The chain-transfer constants based on eq 1 are independent of the initiation as well as the termination processes and also of the concentration of the growing active species. For example, the termination reaction by TBP is included in the $k_t^{XX_i}$ term in eq 1 and the value of C^{MeOH} will not be affected.

Effects of Neutral Electrolytes on the Chain-Transfer Constants to Methanol

The plots of $1/\overline{DP}$ vs. $[\text{MeOH}]$ ($\ln M_0 - \ln M$) ($M_0 - M$) for various systems are shown in

Figure 4. Salt effects on chain-transfer constants of methanol in the nitrobenzene-Perchloric acid system: ○, [TBP]=0; ●, [TBP]= 1×10^{-2} M.

Figures 4—9.

The general trend is the enhancement of C in the presence of TBP. The determined chain-transfer constants are listed in Table I. The linearity of the Mayo's plots is satisfactory with

Figure 5. Salt effects on chain-transfer constants of methanol in the ethylene dichloride—perchloric acid system: $\circ$, $[TBP]=0$; $\bullet$, $[TBP]=1 \times 10^{-2} M$; $\square$, $[TEP]=1 \times 10^{-2} M$.

Figure 6. Salt effects on chain-transfer constants of methanol in the benzene—perchloric acid system; $\circ$, $[TBP]=0$; $\bullet$, $[TBP]=1 \times 10^{-2} M$.

Figure 7. Salt effects on chain-transfer constants of methanol in the nitrobenzene—TCA system: $\bullet$, $[TBP]=0$; $\circ$, $1 \times 10^{-5} M$; $\odot$, $1 \times 10^{-3} M$; $\ominus$, $3 \times 10^{-3} M$; $\oplus$, $5 \times 10^{-3} M$; $\oplus$, $1 \times 10^{-2} M$.

Figure 8. Salt effect on chain-transfer constant of methanol in the ethylene dichloride—TCA system: $\circ$, $[TBP]=0$; $\bullet$, $1 \times 10^{-4} M$; $\odot$, $1 \times 10^{-3} M$; $\ominus$, $3 \times 10^{-3} M$; $\oplus$, $1 \times 10^{-2} M$.

the exception of the TCA—NB systems indicating that methanol behaves as a normal chain-transfer agent and that the possibility of specific interaction of methanol with the growing active species and/or with initiator may be neglected.

As shown in Table II, the salt effect is the largest in ethylene dichloride. On the other

Figure 9. Salt effect on chain-transfer constant of methanol in the benzene-TCA system: ○, [TBP]=0; ●, [TBP]= 1×10^{-2} M.

hand, it does not appear to be found in benzene. The molecular weights of polymers prepared in benzene are so low that the chain-transfer constants determined are of poor accuracy, however. Dissociation of the propagating species and TBP in benzene is highly unlikely and the present results look reasonable in view of the formation of the tight ion-pair in benzene. Furthermore the values of C for the propagating species bearing supposedly different counter ions are not identical (No. 6 and 12 of Table I).

Although the identity of counter ion to the anion part of the initiator could not be proved, the initiator employed is likely to decide the counter ion.

The chain transfer constants determined in ethylene dichloride are also strongly initiator dependent, indicating again that the ion-paired propagating species are predominant (No. 4 and 10 of Table I). However, in the presence of TBP the difference in C between two initiator systems tends to decrease, suggesting that the counter ions in both systems have been converted to the perchlorate anion. In nitrobenzene, the experimental results strongly support the free ionic propagation. The value of C are not influenced by the kind of initiators in the absence of TBP (No. 2 and 8 of Table I) and the enhancement in C caused by TBP is also similar for both initiator systems. Because of its strong solvating power, nitrobenzene is a complexed solvent for cationic polymerization. In appearance, the propagating species behave as free ions whereas the natures of the propagating species in nitrobenzene would be far from "naked". The propagating species would be lapped in the solvation sphere in which the polarized nitrobenzene molecule may play the role of counter ion. This problem will be discussed later.

Table I. Summary of experimental results

Expt no.	Polymerization system	Dielectric constant	Conversion in the presence of TBP	Effects of methanol on conversion ^b	$C \times 10^2$ $\left(\frac{k_{tr}^{CH_3OH}}{k_p \times 10^2} \right)$	C/C_{TBP}
1	NB-HClO ₄ -TBP ^a	35.7	Decreased	No effect	28.9	0.24
2	NB-HClO ₄			Maximum conversion at [CH ₃ OH]= 5×10^{-3} M	6.9	
3	EDC-HClO ₄ -TBP ^a	10.4	Decreased	Slight retardation	100	0.097
4	EDC-HClO ₄			Retardation	9.7	
5	Bz-HClO ₄ -TBP ^a	2.3	Decreased	Retardation	about 50	about 1
6	Bz-HClO ₄			Retardation	about 50	
7	NB-TCA-TBP ^a	35.7	Slightly decreased	Maximum conversion at [CH ₃ OH]= 2×10^{-2} M	33	0.20
8	NB-TCA			Maximum conversion at [CH ₃ OH]= 1×10^{-2} M	6.6	
9	EDC-TCA-TBP ^a	10.4	Increased	Almost no effect	60	0.016
10	EDC-TCA			Acceleration	0.97	
11	Bz-TCA-TBP ^a	2.3	Greatly increased	Retardation	about 6	about 1
12	Br-TCA			Retardation	about 5	

^a [TBP]= 10^{-2} M.

^b The maximum conversion of methanol is 4×10^{-2} M.

All experimental results in Table I were interpreted on the assumptions of the free ion—ion pair equilibrium and the exchange of counterions. Several assumptions on which the discussion was constructed should now be examined. Firstly, the roles of undissociated salt and of the cationic part of the salt have been exempted from discussions. Attention was paid to the behavior of dissociated salt where as the fraction of undissociated salt is considerable in ethylene dichloride and even more so in benzene. Using tetraethylammonium perchlorate as a neutral electrolyte in ethylene dichloride, the determined C from Figure 5 is the same as that shown in Table I, No. 9, indicating that the reactivities of propagating species are decided by the anion alone. Secondly, the role of methanol might not be confined to the chain-transfer agent alone. Specific solvation of active species by methanol might lead to deceiving conclusions. In addition, the effects of methanol on polymer yields are complicated suggesting methanol to be a cocatalyst. However, as the plots in Figures 4–11 are reasonably straight, there would be no objections on the present analysis.

Now the question arises as to why C for the free ionic propagation species is smaller than that for the ion-paired propagating species. The mechanistic clarification of propagation and chain-transfer reactions is needed to answer this question.

The modes of propagation reaction based on the present discussions are schematically expressed by eq 3–5.

In nitrobenzene

In ethylene dichloride

In benzene

Deuterium Isotope Effects on Chain-Transfer Constant to Methanol- d

The neutral salt effects on C should be originated from the different dependences of chain-transfer and propagation reactions on the nature of growing carbonium ions. The values of k_p for free ionic and ion-paired propagation have been a point of disputation. The comparison of catalyzed cationic polymerization with radiation-induced ionic polymerization¹⁰ would render the estimation that the free ionic propagation is 10^4 – 10^5 times faster than the propagation of ion-paired species for the polymerization of styrene. The present experimental results, consequently, require that the value of k_{tr} for the ion-paired and the free ionic active species are different to a lesser extent in comparison to these two modes of propagation processes. The rate determining step of propagation reaction of VCZ would be the attack of the carbonium ion on the ethylenic double bond by analogy to the propagation reaction of styrene¹¹ whereas the chain-transfer reaction to methanol consists of two processes, namely the attack of the carbonium ion on the oxygen of methanol, and the subsequent elimination of the hydroxyl proton. Provided that the elimination process is rate-determining, the chain-transfer reaction would be less sensitive than the propagation reaction to the nature of the attacking carbonium ion.

To obtain information on the rate-determining step, the deuterium isotope effect on the chain-transfer constant was investigated using methanol- d . Results are shown in Figures 10 and 11. The calculated deuterium isotope effect for the VCZ–TCA–EDC system ($C^{\text{MeOH}}/C^{\text{MeOD}}$) is 2.6. This value is in the reasonable range of deuterium isotope effects observed for this type of reaction. The value of k_H/k_D for acid-base reactions involving bond scissions of C–H and C–D is around 2.7 in general and in some cases, approaches 10. For the reactions involving scissions of O–H or N–H bonds, although the values of k_H/k_D fluctuate more, they would be comparable to the reactions with C–H bond scission.¹²

The deuterium isotope effect is good support for the postulate that C for the free carbonium

Figure 10. Deuterium isotope effects on chain-transfer constants in the ethylene dichloride—TCA system: $\circ$, plots for CH_3OD , $[\text{TBP}]=0$; $\bullet$, plots for CH_3OH , $[\text{TBP}]=0$; $\square$, plots for CH_3OD , $[\text{TBP}]=1 \times 10^{-2} \text{ M}$; $\blacksquare$, plots for CH_3OH , $[\text{TBP}]=1 \times 10^{-2} \text{ M}$.

Figure 11. Deuterium isotope effects on chain-transfer constants in the nitrobenzene—TCA system: $\circ$, plots for CH_3OD , $[\text{TBP}]=0$; $\bullet$, plots for CH_3OH , $[\text{TBP}]=0$; $\square$, plots for CH_3OD , $[\text{TBP}]=1 \times 10^{-2} \text{ M}$; $\blacksquare$, plots for CH_3OH , $[\text{TBP}]=1 \times 10^{-2} \text{ M}$.

ion is less than that for the ion-paired carboxonium ion. The difference between propagation

and chain-transfer processes may be expressed by reactions 6–8.

The deuterium isotope effect in the EDC—TCA system disappears when TBP is added. In the presence of TBP, the reactivity of the propagating species decreases and therefore the rates of both reactions 6 and 7 decrease whereas the rate of reaction 8 would be independent of the nature of the propagating species. In a relative scale, reaction 7 becomes faster than reaction 8. The value of C approaches 1 indicating the rate of attacking VCZ and methanol are nearly comparable. This is a support for reaction 7 to be the rate determining step.

In nitrobenzene, the deuterium isotope effect was not observed either in the presence or absence TBP. A probable interpretation is to assume an increased rate of reaction 8 in nitrobenzene. It is reasonable to consider that the highly polar medium facilitates the elimination of proton from the dipolar methoxy group. Furthermore, the solvated propagating species would be less reactive, which brings about an additional factor to convert the rate-determining step from reaction 8 to reaction 7.

Investigation of the deuterium isotope effect leads to the conclusion that the upper limit of the rate constant of the chain-transfer reaction is determined by reaction 8 and consequently, the value of C decreases with increasing reac-

Table II. Deuterium isotope effect

Reaction system	$C^{\text{MeOD}} \times 10^2$	$C^{\text{MeOH}}/C^{\text{MeOD}}$
EDC—TCA	0.37	2.6
EDC—TCA—TBP	66	1.0
NB—TCA	33	1.0
NB—TCA—TBP	7.6	0.9

tivity of the propagating species.

The observed deuterium effects are tabulated in Table II.

Dependence of C in the Concentration of TBP

The equilibrium between free ion and ion pairs is governed by the concentration of TBP. The equilibrium constants and therefore the degree of dissociation should be functions of the dielectric of solvent as well as of the salt concentration.

The values of C as calculated from the plots of Figures 7 and 8 with varying concentrations of TBP are shown in Figure 12. Since the salt effects are very small, the experiments in benzene were not attempted. Although the dissociation constants of TBP have not been determined under identical conditions of the present polymerization systems, relevant dissociation constants of tetra-*n*-butylammonium salts are tabulated in Table III.¹³ These values determined in a solvent fall in the same order of magnitude

indicating that the difference in anion is of secondary importance in deciding the dissociation constants. The sequence of the dissociation constants of salts with different anions determined in a certain solvent holds also in different solvent systems. The dissociation constant of TBP would therefore be close to 10^{-2} in nitrobenzene and in the order of 10^{-4} in ethylene dichloride. Assuming the dissociation constant of the growing carbonium ion to be not greater than that of TBP, the dissociation of the growing carbonium ion would be small in ethylene dichloride whereas the dissociation would be almost complete in nitrobenzene. The degree of dissociation is a function of the concentration of active species. In the present concentration range of initiator the free dissociation of propagating species in nitrobenzene seems to be an acceptable assumption even if all initiator molecules are converted to the growing species.

In the less dissociative solvent of ethylene

Figure 12. Chain-transfer constants of methanol as functions of the TBP concentration: $\circ$, polymerization in nitrobenzene initiated by TCA; $\bullet$, polymerization in ethylene dichloride initiated by TCA.

Table III. The limiting values of dissociation constants of tetra-*n*-butylammonium salts (25°C)¹³

Salt	Solvent		
	Nitrobenzene	Ethylene dichloride	Acetone
TBP	—	1.53×10^{-4}	9.58×10^{-3}
$(n\text{-C}_4\text{H}_9)_4\text{N}^+ \cdot \text{NO}_3^-$	25.0×10^{-3}	1.18×10^{-4}	5.46×10^{-3}
$(n\text{-B}_4\text{H}_9)_4\text{N}^+ \cdot \text{Br}^-$	16.2×10^{-3}	—	3.29×10^{-3}
$(n\text{-C}_4\text{H}_9)_4\text{N}^+ \cdot \text{picrate}$	—	1.94×10^{-4}	22.3×10^{-3}

dichloride, the value of C approaches a limiting value at the concentration of TBP about $10^{-3} M$ showing that the dissociation constant of the growing carbonium ion is small. Beyond this concentration of TBP, the growing carbonium ions are thought to carry the exclusively perchlorate anion as a counter ion.

Free Ion, Ion Pair, and Their Reactivities

The present approach based on neutral salt effects seems to be promising. Within its limits pieces of evidence have been obtained showing that the propagating carbonium ion is free in nitrobenzene, ion-paired in benzene and in the mixed state in ethylene dichloride. However, the present technique cannot provide information on the nature of the counter ion originated from the initiator. The experiments with different counter ions can be designed using neutral electrolytes with various inorganic as well as organic anions. A study on salt effects of various ammonium, phosphonium or arsenium salts is a future problem.

The importance of solvent effects on the reactivity of the carbonium ion should not be overlooked. In nitrobenzene, although all results are in favour of free ionic propagation, the reactivities of the propagating species look quite different from those in the radiation-induced free ionic polymerization in absolutely dry systems. Firstly, the present system is relatively inert to impurities whereas the radiation-induced cationic polymerization is known to be extremely sensitive to a trace amount of basic materials. Secondly, the rate of propagation seems to be much slower in nitrobenzene. If the value of k_p estimated by the scavenger method in radiation-induced cationic polymerization could be applied to the present polymerization system, the rate of polymerization should have been much larger. This postulate is based on the expected higher concentration of active species in the present nitrobenzene system in comparison with the radiation-induced polymerization as judged by the concentration of the initiator. The radiation-induced cationic polymerization of styrene in hydrocarbon solvent and the present polymerization system in nitrobenzene would therefore provide two extreme cases of free ionic propagation. The following conclusion may be

drawn.

Case 1. Nitrobenzene system

Strong solvation by solvent $\Rightarrow$ stabilization of free ion $\Rightarrow$ free ion is easily formed but less reactive.

Case 2. In hydrocarbon

Weak solvation $\Rightarrow$ naked and unstable free ion $\Rightarrow$ free ion is difficult to obtain but extremely reactive. Although numbers of examples for comparison are limited, it is the authors impression that the discussions on the reactivities of free ion and ion-paired species are significant only for a fixed solvent system.

In this article, the problem of solvent separated ion pairs was neglected. When the influence of the anion is small due to solvent molecules between the cation and anion, the solvent separated ion pair would be included in the category of "free ion". Consequently, the terminologies of "ion pair" and "free ion" in this article should be understood as expressing the physical states in which the cation is strongly and scarcely controlled by the counter ion, respectively.

Discussions on the nitrobenzene system are immediately useful for the interpretation of photosensitized charge-transfer polymerization of VCZ which is expected to be essentially free ionic since no initiator is added. Detailed interpretation of this unique photopolymerization is now in progress using the technique of salt effects and will be published elsewhere.

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