Effects of Tetra-n-butylammonium Perchlorate on the Chain Transfer Constants in the Cationic Polymerization of *N*-Vinylcarbazole

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Summary Determination of chain transfer constants of methanol in the cationic polymerization of *N*-vinylcarbazole in the presence and absence of $Bu^n_4NClO_4$ provides a new method to study free-ion and ion-pair mechanisms of propagation.

THE problem of free-ion and ion-pair mechanism in cationic polymerization has been a point of dispute for some time. One approach to this problem would be to study the effects of neutral salts on cationic polymerization. Free-ion propagation is expected to be suppressed by the addition of neutral salts and the changes in kinetic patterns would provide useful indices for distinguishing these two mechanisms. Recently, the polymerization of styrene in methylene chloride initiated by anhydrous perchloric acid was investigated from the point of view of salt effects.[1] On the basis of the rate and molecular-weight determinations it was demonstrated that free ionic species dominate the propagation in the flash polymerization at low temperatures, and play only a secondary role at higher temperatures.[2]

Discussions on the rate of polymerization appear straightforward provided that the polymerization is "*living*". However, such ideal conditions are usually difficult to achieve. The present author concentrated on the chain transfer constant which is controlled only by the nature of the propagating species for a given combination of monomer, chain transfer agent, and solvent. The reason for choosing *N*-vinylcarbazole (VCZ), notorious for its complicated polymerizabilities, was to obtain information on counter-ion effects on cationic polymerization of the monomer, which can then be compared with the results of charge transfer polymerization. Cationic propagating species induced by an organic donor–acceptor system would produce counterions different from any conventional cationic polymerizations induced by Lewis acids or protonic acids.

Chain transfer constants to methanol (*C*) under various conditions were determined (Table). The molecular weight of poly-VCZ was determined viscometrically[3] assuming the molecular weight distribution was not affected by the addition of methanol and/or $Bu^n_4NClO_4$(TBP). It was confirmed that the changes in initiator concentration and the substitution of TBP with Et_4NClO_4 did not affect the value of *C*. Consequently, the effects of neutral salt (Table) should be considered as results of affecting the free-ion–ion-pair equilibrium and exchanging counter-ions. The following remarks can be made on the experimental results.

(i) Addition of salt causes an enhancement of *C*. The enhancement is most prominent in ethylene dichloride. (ii) In nitrobenzene, the values of *C* are independent of the kind of initiator (compare Nos. 1, 2, 7, and 8 of the Table), indicative of the free ionic propagation in the absence of salt. (iii) The values of *C* depend very much on the kind of initiator in ethylene dichloride and benzene. These two solvents would favour ion-pairing propagating species in comparison with nitrobenzene. (iv) In the presence of a neutral salt in ethylene dichloride (compare Nos. 3 and 9 in Table), the values of *C* depend only slightly on the kind of initiator, indicating that both propagating species of Nos. 3 and 9 mostly accompany perchlorate counter-ions. (v) In benzene, a neutral salt effect is scarcely observed (Nos. 5, 6, 11, and 12 in Table). Tight ion pairs in the nonpolar solvent would not exchange the counter-ions originating from initiators. (vi) Determination of *C* as a function of [TBP] in ethylene dichloride and nitrobenzene indicates that *C* reaches a limiting value at [TBP] = 3×10^{-3}M in ethylene dichloride, whereas it continues to increase with the TBP concentration in nitrobenzene at salt concentrations as high as 10^{-2}M. (vii) The value of *C* for free ionic species is smaller than that for ion-paired species. This postulate seems reasonable, since the chain transfer process consists of two unit reactions, namely the attack of carbonium ion on the oxygen of the alcohol and subsequent scission of the O–H bond, whereas the propagation process is the single step of opening the vinyl bond. The scission of the O–H bond will not be influenced by counter-ions as much as the addition of carbonium ion. Provided that the O–H bond scission participates in the rate-determining step, the decrease in k_p would be larger than that in k^{MeOH}_{tr} brought about by converting a free ionic propagating species into an ion-paired species. In support of this, the deuterium isotope effect on *C* was observed to be 2·6 when CH_3OD was used as a chain transfer agent in the $C_2H_4Cl_2$–CCl_3CO_2H system (No. 10 in the Table).

Chain transfer constants for methanol

No.	Polymerization system	[Initiator] M	C (k^{MeOH}_{tr}/k_p) $\times 10^2$
1	$PhNO_2$–$HClO_4$–TBP	$1 \cdot 5 \times 10^{-5}$	28·9
2	$PhNO_2$–$HClO_4$	$2 \cdot 5 \times 10^{-6}$	6·9
3	$C_2H_4Cl_2$–$HClO_4$–TBP	7×10^{-4}	100
4	$C_2H_4Cl_2$–$HClO_4$	4×10^{-4}	9·7
5	C_6H_6–$HClO_4$–TBP	1×10^{-3}	(50)[b]
6	C_6H_6–$HClO_4$	5×10^{-4}	(50)[b]
7	$C_6H_5NO_2$–CCl_3CO_2H–TBP	3×10^{-4}	33
8	$C_6H_5NO_2$–CCl_3CO_2H–TBP	3×10^{-4}	6·6
9	$C_2H_4Cl_2$–CCl_3CO_2H–TBP	1×10^{-3}	60
10	$C_2H_4Cl_2$–CCl_3CO_2H	1×10^{-3}	0·97
11	$C_6H_6CCl_3CO_2H$–TBP	1×10^{-3}	(6)[b]
12	C_6H_6–CCl_3CO_2H	5×10^{-2}	(5)[b]

[a] [VCZ] = 0·25 M, 30°. When TBP was added, the concentration was 1×10^{-2}M.

[b] The molecular weight of polymer was too low for accurate measurements.

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[1] B. MacCarthy, W. P. Millrine, and D. C. Pepper, *Chem. Comm.*, **1968**, 1442.

[2] D. C. Pepper, personal communication (1969).

[3] K. Ueberreiter and J. Springer, *Z. phys. Chem.* (*Frankfurt*), 1963, **36**, 299.