Anionic Polymerization of Vinylidene Chloride. I. Susceptibilities of Vinyl Monomers to Initiation by Ionic Catalysis

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The reactivity of the vinyl monomers in the radical polymerization have been theoretically discussed in a number of publications which have dealt with the problem using the molecular orbital method[1,2], the frontier electron theory[3-5], a *Q*-*e* or *q*-ε scheme[6-8], or a polarity parameter[9]. It is considered in ionic polymerization that monomers form an intermediate ionic complex with the catalyst; the mutual relationship between the monomer and the catalyst seems to be more important in ionic polymerization than in free radical polymerization. This paper is intended to make a survey of the susceptibility of vinyl monomers to ionic catalysis.

Theoretical

Susceptibility and *Q*-*e* or *q*-ε Map. — Alfrey and Price have presented polarity (*e*) and resonance (*Q*) factors for vinyl monomers derived from copolymerization data to explain the monomer reactivity ratios; they have reported *Q* and *e* values on thirty one monomers[6,7]. This concept has been theoretically extended and generalized, and a new set of parameter *q* for resonance and ε for polarity has been proposed for one hundred and ten monomers[8]. Walling[10] and Furukawa[11] pointed out that there is a linear relationship between relative reactivities or polarity factor

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[1] M. G. Evans, J. Gergely and E. C. Seaman, *J. Polymer Sci.*, **3**, 886 (1948).

[2] T. Fueno, T. Tsuruta and J. Furukawa, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 1075 (1957).

[3] T. Yonezawa, T. Higashimura, K. Katagiri, S. Okamura and K. Fukui, *Chem. High Polymers* (*Kobunshi Kagaku*), **14**, 533 (1957).

[4] K. Hayashi, T. Yonezawa, C. Nagata, S. Okamura and K. Fukui, *J. Polymer Sci.*, **20**, 537 (1956).

[5] T. Yonezawa, K. Hayashi, C. Nagata, S. Okamura and K. Fukui, ibid., **14**, 312 (1954).

[6] T. Alfrey and C. C. Price, ibid., **2**, 101 (1947).

[7] C. C. Price, ibid., **3**, 772 (1948).

[8] T. C. Schwan and C. C. Price, ibid., **40**, 457 (1959).

[9] C. H. Bamford, A. D. Jenkins and R. Johnston, *Trans. Faraday Soc.*, **55**, 418 (1959).

[10] C. Walling, E. R. Briggs, K. B. Wolfstirn and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1537 (1948).

[11] J. Furukawa and T. Tsuruta, *J. Polymer Sci.*, **36**, 275 (1959).

e and Hammett sigma constants of ionic reaction, and Price[8] has also shown a good linear relation between ε values of styrene derivatives and Hammett sigma constants. Although such a good linearity as this has not been obtained in the case of ethylene derivatives, the effect caused by a substituent of the phenyl group on the double bond of styrene is assumed to correspond to the effect caused by the substituent of ethylene derivatives on their double bond, and the polarity parameter e or ε should reasonably be applied for indicating the ionic reactivity of vinyl monomers in ionic polymerization as well as in radical polymerization.

Although numerous experimental data have been reported on the susceptibilities of various monomers to homopolymerization under anionic, free radical, and cationic conditions, Schildknecht's table[12] is taken here as a reliable reference; here he has classified the susceptibilities of fifty four monomers.

The relationship between the susceptibility and the Q-e values of fourteen monomers obtained from the original Q-e table[7] is illustrated in Fig. 1. Furukawa[11] has presumed that monomers having a large plus e value ($e>1.5$) are likely to be polymerized in an anionic condition; on the contrary, monomers having large negative e values ($e>-1.0$) are likely to be polymerized in a cationic condition. However, it seems rather difficult to explain the behavior of monomers (such as styrene, butadiene and methyl vinyl ketone) which can be polymerized in both radical and ionic conditions. The susceptibility arranged according to Price's new parameter q-ε for twenty two monomers is illustrated in Fig. 2.

In general, cationic polymerization takes place with monomers whose double bond is negatively polarized and has an affinity to electrophillic reagents, whereas the double bond of anionic polymerizable monomers is positively polarized and reacts with nucleophillic reagents. As a first approximation, the magnitude of polarization in an ionic condition seems to correspond to the polarity expressed by the polarity factor e or ε. With the resonance factor Q or q, such a good relationship as ε vs. sigma has not yet been obtained, but the Q or q factor is closely connected with the reactive pi electrons of the vinyl bond, namely, with the electron donating or accepting characters of the vinyl bond, and if the electronic field is so large as to induce the polarization of pi electrons, the magnitude of such electrodynamic polarity here induced may serve to form an ionic complex with an ionic catalyst. Accordingly, the Q or q factor may also be regarded as a reactivity determining factor in ionic reactions, and both the $e(\varepsilon)$ and $Q(q)$ factors may be helpful in explaining

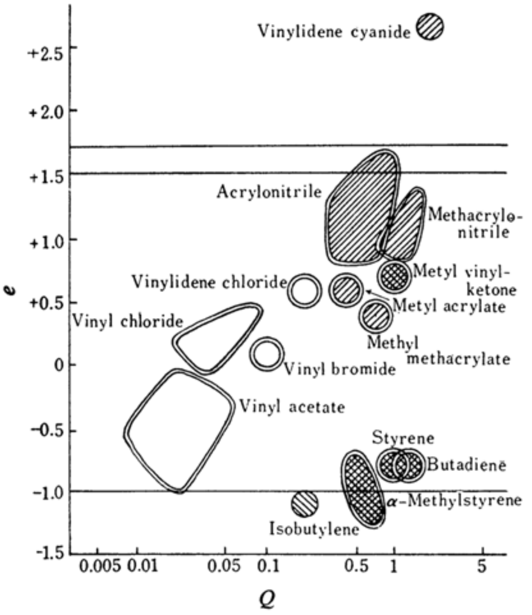

Fig. 1. Relationship between susceptibility and Q-e map. Susceptible to radical ◎, anion ▨ and cation ▤.

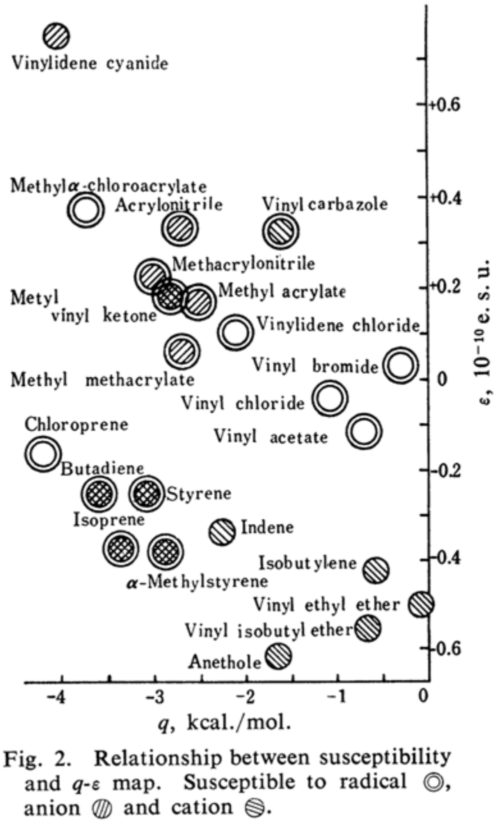

Fig. 2. Relationship between susceptibility and q-ε map. Susceptible to radical ◎, anion ▨ and cation ▤.

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[12] C. E. Schildknecht, *Ind. Eng. Chem.*, **50**, 107 (1958).

the susceptibility of a monomer in an ionic polymerization reaction. Hence, Q-e or q-ε maps can be related to the susceptibilities of vinyl monomers to initiation by an ionic catalyst. Monomers like styrene or butadiene, which has a conjugated double bond, are polymerized by either a cationic or anionic catalyst.

Another factor affecting polymerizability may be steric effect, but the order of its magnitude is difficult to estimate quantitatively. As the matter of fact, the steric factor should be involved implicity in the Q-e or q-ε factors, because the latter factors are experimentally determined.

The propagating macro anions seem to be relatively stable because the living polymer has been obtained in the anionic polymerization of styrene[13]. It is deduced that the larger the value of e (or ε) and Q (or q) of the monomers, the greater the susceptibilities of the monomers toward the ionic catalyst.

The relative susceptibilities can be shown as in Fig. 3 (q-ε map) and Fig. 4 (Q-e map), in which the Q-e values of vinyl ethyl ether[14], vinyl chloride[15], vinylidene chloride[15], acrylonitrile[15], chlorotrifluoroethylene[16] and vinyliden cyanide[17] are added, besides the values listed in Refs. 7 and 8. The values were converted by the following equations,

$$q = -2\times10^{-3}\,T\ln Q - 3.1$$

$$\varepsilon = 1.66\times10^{-12}\,T^{1/2}\,e$$

in which $T=323°\text{K}$. The area of the map is determined from the following monomers: vinylidene cyanide, anethole, 2, 3-dichloro-1, 3-butadiene and diphenylacetylene (Ref. 8).

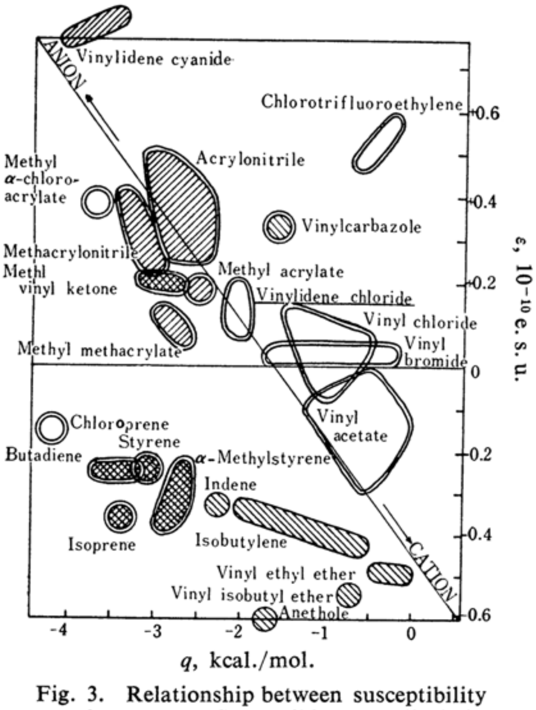

Fig. 3. Relationship between susceptibility and q-ε map. Susceptible to radical ◎, anion ▨ and cation ⊜.

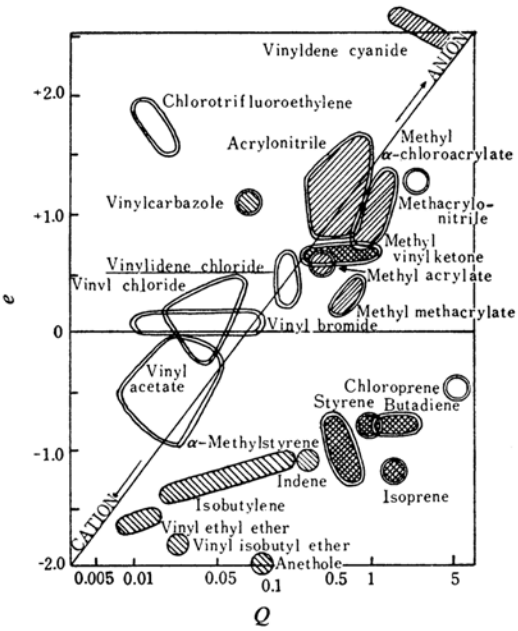

Fig. 4. Relationship between susceptibility and Q-e map. Susceptible to radical ◎, anion ▨ and cation ⊜.

In the map, the diagonal line along which the monomers are distributed shows the relative susceptibilities of monomers to catalysts: at first vinylidene cyanide is located at the upper left corner, followed by acrylonitrile, methacrylonitrile, methyl acrylate, methyl methacrylate (in the order of decreasing susceptibility to anion); styrene, butadiene, isoprene (susceptible to anion, radical and cation and located near the center parallel to the diagonal line); vinylidene chloride, vinyl chloride, vinyl acetate (susceptible to radical); isobutylene, indene, and finally vinyl ether (in the order of decreasing susceptibility to cation). The susceptibility of methyl vinyl ketone (to either cation, radical or anion) and vinylcarbazole (to both radical and cation) are understandable considering that they are located in the central part of the map.

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[13] M. Szwarc, M. Levy and R. Milkovich, *J. Am. Chem. Soc.*, **78**, 2656 (1956).

[14] C. C. Price and T. C. Schwan, *J. Polymer Sci.*, **16**, 577 (1955).

[15] B. R. Thompson and R. H. Raines, idid., **41**, 265 (1959).

[16] N. Kliman and M. Lozàr, *Chem. průmysl.*, **9**, 668 (1959).

[17] H. Gilbert, *J. Am. Chem. Soc.*, **78**, 1669 (1956).

Application of Q-e or q-ε Map. — It is considered that all monomers can be polymerized by either a anionic, radical or cationic catalyst under proper ionic conditions where undesired side reactions between the initiating ion (or its counter ion) and the polar substituents of the monomer can be eliminated as much as possible.

New Polymerization Reaction.—There are a considerable number of monomers which have not been polymerized by ionic reagents. Some of these which are not classified in Ref. 12 are shown in the map, Fig. 5. It can be predicted from the map that cationic polymerization should be possible for such monomers as hexene-1, hexyne-1, *N*-vinylpyrrolidone and stilbene, and for isostilbene, vinyl formate and vinyl acetate with some difficulty. Anionic polymerization will be possible for acrylamide, acrolein, vinylcarbazole, and vinylidene chloride, and either anionic or cationic polymerization of 1,1-diphenylethylene, methyl isopropenyl ketone, methacrolein, acrolein, and 2- and 4-vinylpyridines will be possible. The author has succeeded in the polymerization of vinylidene chloride in anionic mechanism; the details will be reported on in Parts II and III of this report.

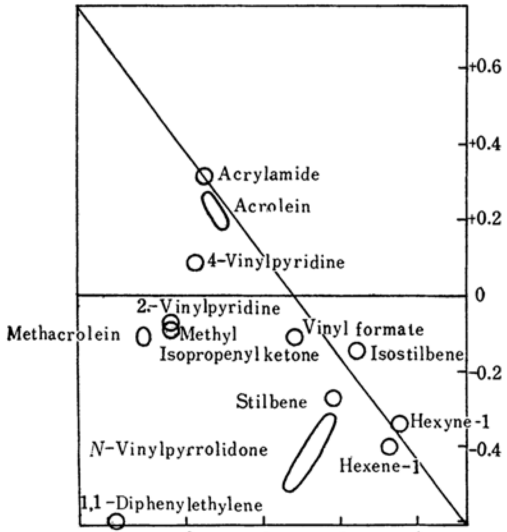

Fig. 5. Locations of several monomers in q-ε map.

Ionic Copolymerization.—Data of the monomer reactivity ratios in ionic polymerization[18,19] are very interesting since the relative reactivity of monomers in the ionic reaction can be estimated from them. Although data are less available and are more uncertain than in the case of radical copolymerization, it can be seen qualitatively that in cationic copolymerization the monomer reactivity ratios of the monomer seated near the lower right corner are larger than the comonomer, and in anionic copolymerization the monomer reactivity ratios of the monomer located near the upper left corner are larger than the comonomer; the arrow in Figs. 6 and 7 shows the monomers whose monomer reactivity ratios are larger in the pair. The case of styrene-vinyl acetate is

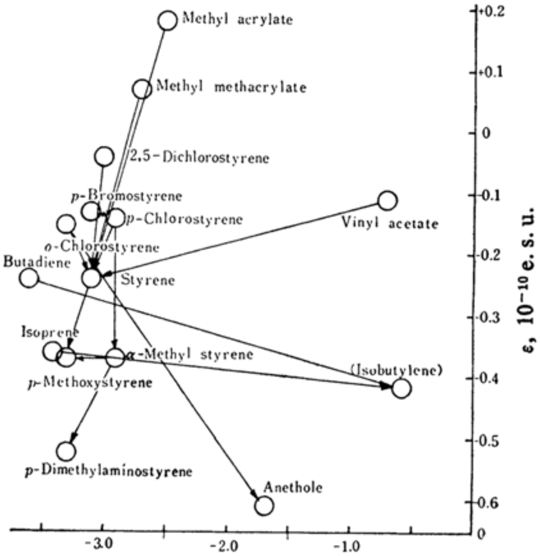

Fig. 6. Relative reactivities of monomers in cationic copolymerization.

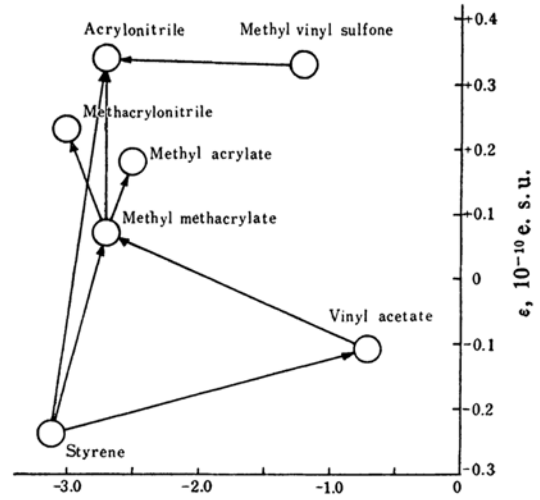

Fig. 7. Relative reactivities of monomers in anionic copolymerization.

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[18] D. C. Pepper, *Quart. Rev.*, **8**, 88 (1954).

[19] N. L. Zutty and F. J. Welch, *J. Polymer Sci.*, **43**, 445 (1960).

somewhat abnormal, for in this case both r_1 and r_2 are far smaller than unity. It is possible to predict the relative tendency between two monomers which enter into copolymerization under an ionic condition, and the results on the anionic copolymerization of vinylidene chloride, which will be reported on in Part III, will present an experimental evidence of this scheme.

Summary

The relative reactivities of vinyl monomers under ionic conditions have been discussed using a Q-e or q-ε map. It has been deduced that the larger the value of the polarity factor e (or ε) and the resonance factor Q (or q) of the monomer, the greater the susceptibility of the monomers to ionic catalysis. The possibility of new ionic polymerization reaction and the relative reactivity of monomers in ionic copolymerization have been discussed. As the result of this scheme, it seems that the anionic polymerization of vinylidene chloride is possible.

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