Polymer(Korea). Published by the Polymer Society of Korea
Vol. 12, No. 8, 1988

중합 억제제의 반응성 연구

— 스티렌 중합에 있어서 다환 방향족 할로겐 화합물 —

박 동 규·김 양*
경성대학교 이과대학 화학과·*부산대학교 자연과학대학 화학과
(1988년 5월 26일 접수)

Reactivity Studies of the Polymerization Retarders

— Polycyclic Aromatic Halogen Compounds in Styrene Polymerization —

Dong Kyu Park and Yang Kim*
Department of Chemistry, Kyung Sung University, Pusan 608-020 Korea
**Department of Chemistry, Pusan National University, Pusan 609-390 Korea*
(Received May 26, 1988)

요 약 : 다환 방향족 할로겐 화합물을 2,2′-azobisisobutyronitrile(AIBN)을 개시제로 하여 스티렌 중합의 억제제로 사용하였다. 중합 억제 반응 실험은 진공($\sim 10^{-5}$mmHg)하에서 조심스럽게 용액중의 기체를 제거한 후 vacuum dilatometer로써 반응 속도를 측정하였다. 사용한 12개의 억제제 중 4개가 억제 효과를 보였다. 그리고 스티렌 중합시 얻어진 실험 결과는 Fukui의 frontier electron density법으로 고찰하였다. 그 결과는 다음과 같다. 1) 45℃에서 억제제를 넣지 않고 AIBN과 스티렌 만의 반응 속도는 $-\frac{d\ln[M]}{dt}=R_0=8.855\times10^{-3}[AIBN]^{1/2}$ percent per sec로 표시할 수 있었다. 2) 2-bromoanthracene의 K_X값은 anthracene의 K_X값보다 컸었다. 3) Meso 위치를 갖고 있지 않은 다환 방향족 할로겐 화합물은 스티렌 중합시 억제 효과를 나타내지 않았다. 4) 1-chloroanthracene와 2-chloroanthracene의 K_X값은 anthracene의 K_X값보다 적었다. 5) 억제제의 S_r(혹은 S_r') 값은 억제제의 반응성을 잘 나타내 주었다. 다환 방향족 할로겐 화합물의 S_r값과 S_r'값은 1.31과 0.94 이상의 값을 갖는 물질들이었다.

Abstract : The polycyclic aromatic halogen compounds have been used as retarders for the 2,2′-azobisisobutyronitrile (AIBN) catalyzed polymerization of styrene. All retardation experiments were carried out under vacuum ($\sim 10^{-5}$ mmHg) with a carefully degassed solution. The rate was measured dilatometrically. Four of twenty compounds tested showed retardation effects. The obtained reactivity data of styrene polymerization were examined in the light of the Fukui's frontier electron density method. The results are as follows : 1) The unretarded rate was determined as : $-\frac{d\ln[M]}{dt}=R_0=8.855\times10^{-3}[AIBN]^{1/2}$ percent per sec. 2) The K_X value of 9-bromoanthracene is larger than that of anthracene. 3) The compounds not possessing the mesomeric position do not shown any retarding effect for styrene polymerization. 4) The K_X values of 1-chloroanthracene and 2-chloroanthracene

are smaller than that of anthracene. 5) The Sr(or Sr′) value of the retarder, generally, explained reasonably the reactivities of the retarders. The Sr and Sr′ values of the polycyclic aromatic halogen compounds which show retardation effect are larger than about 1.31 and 0.94, respectively.

INTRODUCTION

One of the principle characteristics of free radical chain reactions is that their rates can be drastically reduced (even stopped) by the addition of less than stoichiometric amounts of certain materials to the reacting system. Among the materials known to inhibit or retard such processes are aromatic amines and phenols, aromatic nitro compounds and some of the condensed compounds. It is apparent that the extent to which the over all rate is altered might be conceived as a measure of the reactivities of the additive molecules. In order to place such reactivities on a quantitative basis theoretically and empirically, it is desirable to investigate kinetics of a reaction for which a rate constant can be easily determined. The rate constant should be the one for the reaction step removing the additive from the reacting system.

In 1950, Bartlett and Kwart[1] and Kice[2] have carried out measurements on the effects of additives on the vinyl polymerization rate by means of a dilatometric technique rendered highly precise by the large volume changes accompanying the reaction. This aspect of dilatometry and the very elegant and successful kinetic treatment which Kice devised for the retarded methyl methacrylate (MMA) polymerization makes this system a prior an ideal one for the present purposes. Kubin[3] and Ihrig et al[4] have studied a variety of retarders including phenols and aromatic amines. Ihring and Sood[5] have investigated the effects of the condensed ring hydrocarbons on the retardation and inhibition of styrene and MMA polymerization. The polymerization rates were also measured dilatometerically.

Futhermore, Kim[6] has studied the effects of twenty retarders of various heterocyclic nitrogen compounds on the AIBN catalyzed polymerization of styrene. Recently Szakacs, Sander et al.[7] have investigated the kinetics of polymerization of styrene initiated by AIBN at 50℃ in the presence of α-aryl-N-phenylnitrones.

In this work, a variety of polycyclic aromatic halogen compounds were tested as polymerization retarders in the AIBN catalyzed polymerization of styrene. The rates were determined vacuum dilatometrically. All experiments were carried out at 45℃ in a dark room in order to avoid the effect of the ultra-violet. The results were analyzed by using a modified a Kice's kinetic scheme[2] and were treated theoretically by the "frontier electron density" method of Fukui.[8,9]

EXPERIMENTAL

Materials

Styrene : Wako company. The styrene was washed several times with a 2 percent sodium hydroxide solution, distilled water, a 2 percent sodium thiosulfate solution, and finally with distilled water until the washings became neutral. This material was then dried over calcium chloride and left to stand overnight in the refrigerator.

The dried styrene was fractionally distilled in a long column-20 inches long and 24mm inside diameter. The distillation was carried out under a reduced pressure and nitrogen atmosphere. The nitrogen was purified with pyrogallol-sodium hydroxide solution, distilled water, concentrated sulfuric acid, and silica gel to remove moisture and oxygen. Only the constantly boiling middle fraction was collected. The typical middle fraction was distilled at 52℃ under the pressure of the system at 25Torr of mercury. The collected styrene was stored in a refrigerator in a round bottle

and used within one week. 2,2′-azobisisobutyronitrile (Aldrich Chemical Co.) was purified by recrystallization several times from methyl alcohol, only the first crop of crystals was collected in each crystallization. They were dried in a vacuum dessicator and stored under refrigeration and recrystallized every three weeks. 1-chloroanthracene (Aldrich Chemical Co.,) was recrystallized twice from methyl alcohol, producing yellow needles (m. p. 83.5℃). 2-chloroanthracene (aldrich Chemical Co.,) was recrystallized twice from carbon tetrachloride. The crystals are yellow needles(m. p. 215-223℃). 9-bromoanthracene(Aldrich Chemical Co.,) was recrystallized twice from methyl alcohol producing yellow needles (m.p. 97-99℃). 9-bromofluorene(Aldrich Chemical Co.) was recrystallized twice from methyl alcohol. The crystals were long yellow needles (m.p. 113-114℃). 9-chloroacenaphthene (Aldrich Chemical Co.,) was recrystallized twice from methyl alcohol. The crystals were yellowish needles (m.p. 64-66℃). 9-bromoacenaphthene (Aldrich Chemical Co.,) was recrystallized twice from methyl alcohol. The crystals were yellow needles. (m.p. 54-56℃). 2-bromonaphthalene (Aldrich Chemical Co.,) was recrystallized twice from benzene, producing yellow plates (m.p.59°). 1-bromonaphthalene (Aldrich Chemical Co.) was recrystallized twice from hot water, producing yellow needles (m. p. 2.0-2.7℃). 5-bromoacenaphthene (Aldrich Chemical Co.) was recrystallized from dilute alcohol twice. The crystals were yellow needles (m.p. 52℃).

Fluorobenzene (Wako Co.,) was distilled twice (b.p. 84.75℃) 9-bromophenanthrene (Aldrich Chemical Co.) was recrystallized from ether twice. The crystals were yellow needles (m.p. 63.8-64.8℃).

Vacuum Dilatometry

Diagrams of the dilatometer are shown Fig. 1. The experimental procedures used in these studies were very similar to those of Bartlett and Kwart,[1] and were calibrated with mercury same the previous study.[6] From Fox and Loshaek's equation,[10] it was computed that one hundred

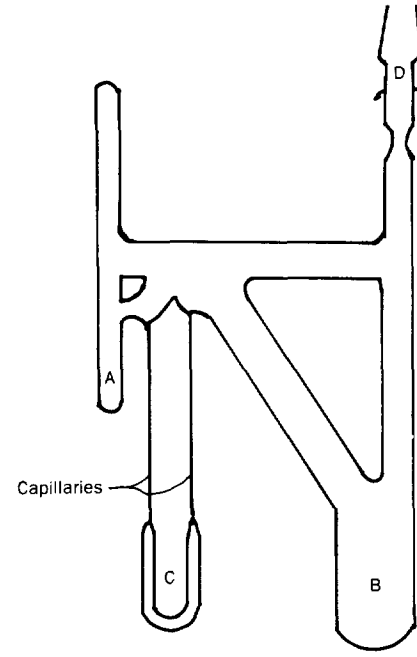


Fig. 1. Vacuum dilatometer.

percent polymerization of styrene at 45℃ would result in a volume contraction of 16.84 percent. It was found that a fall of one centimeter in the level of styrene in the capillary corresponded to 100/(0.1684×dilatometer constant) percent polymerization. Representative values for the vacuum dilatometer constant were 1579 for #1, 1433 for #2, 1104 for #3, and 2664 for #4 respectively, where #1 refer to dilatometer number 1, etc. The dilatometer was constructed of pyrex glass with precision bored capillary tubing.

RESULTS AND DISCUSSION

Sample plots of data from two typical kinetic runs in a vacuum dilatometer are shown in Fig. 2. It is a simple matter to find the corresponding rate of polymerization by using the appreciate dilatometer constant from the slopes of lines.

Since it is necessary to know the unretarded rate of polymerization, this was determined and found to be dependent on the half power of initiator concentration as follows : $R_0=31.8782\ [AIBN]^{1/2}$,

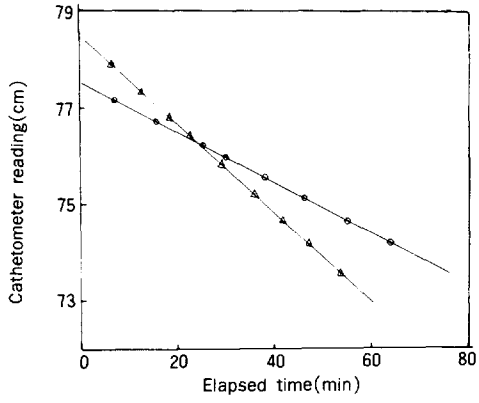


Fig. 2. Sample plots of primitive kinetic data for vacuum dilatometer experiments : unretarded and with anthracene.
⊙–⊙ : anthracene, △–△ : unretarded

where R_0 is the unretarded polymerization in percent per hour, and [AIBN] is the molar concentration of the initiator.

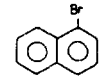
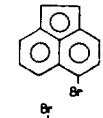
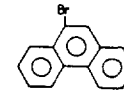
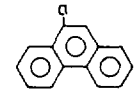
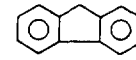
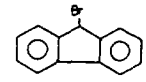
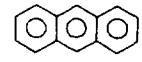
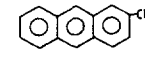
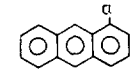
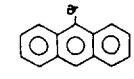
With the unretarded rate available for a given initiator concentration, it is convenient to define the degree of retardation, $\phi = R / R_0$, where R is the observed rate of retarded polymerization and R_0 is the rate of unretarded polymerization calculated for the same initiator concentration used in the retarded run. Thus, $R / R_0 \cong 1$ would mean that added polycyclic aromatic halogen compound has no effect on the rate of polymerization. A ratio of $R / R_0 < 1$ means that the added retarder has some effect, the polymerization has been retarded. A summary of the experimental results is given in Table 1, together with the corresponding values of ϕ.

Basic Kinetic Equation

The kinetics of free radical initiating vinyl polymerization in the presence of materials capable of retarding or inhibiting the reaction is reasonably well understood.[11]

It is generally accepted that any substance which retards the vinyl polymerization does so by reacting with a chain-carrying initiator or polymer radical R ·, yielding a new radical Z ·. These new radicals (Z ·) are relatively unreactive with monomers and are chiefly consumed by

Table 1. Summary of Exerimental Results from vacuum Dilatometer.

Retarder	Structure	Retarder conc. (mole/l)	[AIBN]^2 x 10^2 (mole/l)^2	$R_0/[AIBN]$	ϕ
fluoro-benzene		1.46 X 10^{-2}	6.16	1.970	1.003
		2.78 X 10^{-2}	6.16	1.969	1.002
		4.62 X 10^{-2}	6.16	1.981	1.008
1-bromo naphthalene		1.0 X 10^{-2}	6.16	1.963	0.999
		2.0 X 10^{-2}	6.16	1.976	1.006
		4.0 X 10^{-2}	6.16	1.949	0.993
		6.0 X 10^{-2}	6.16	1.957	0.996
2-bromo naphthalene		2.0 X 10^{-2}	6.16	1.977	1.007
		4.0 X 10^{-2}	6.16	1.957	0.996
		6.0 X 10^{-2}	6.16	1.969	1.002
		8.0 X 10^{-2}	6.16	1.989	1.007
5-bromo acenaphthene		1.0 X 10^{-2}	6.16	1.958	0.997
		3.0 X 10^{-2}	6.16	2.004	1.010
9-bromo phenanthrene		1.0 X 10^{-2}	6.16	1.971	1.003
		3.0 X 10^{-2}	6.16	1.959	0.998
		5.0 X 10^{-2}	6.16	1.963	0.999
9-bromo phenanthrene		1.0 X 10^{-2}	6.16	1.981	1.008
		3.0 X 10^{-2}	6.16	1.953	0.994
		5.0 X 10^{-2}	6.16	1.957	0.996
2-bromo fluorene		1.0 X 10^{-2}	6.16	1.979	1.007
		4.0 X 10^{-2}	6.16	1.960	0.998
9-bromo fluorene		1.0 X 10^{-2}	6.16	1.963	0.999
		3.0 X 10^{-2}	6.16	1.971	1.003
		5.0 X 10^{-2}	6.16	1.969	1.001
		6.0 X 10^{-2}	6.16	1.973	1.003
anthracene		1.0 X 10^{-2}	6.16	1.353	0.689
		2.0 X 10^{-2}	6.16	1.054	0.537
		3.0 X 10^{-2}	6.16	0.865	0.441
		4.0 X 10^{-2}	6.16	0.762	0.388
2-chloro anthracene		1.0 X 10^{-4}	6.16	1.442	0.734
		1.13X 10^{-2}	6.16	1.396	0.711
		2.0 X 10^{-2}	6.16	1.000	0.509
		3.0 X 10^{-2}	6.16	0.723	0.368
1-chloro anthracene		0.5 X 10^{-2}	6.16	1.443	0.735
		1.0 X 10^{-2}	6.16	1.270	0.647
		2.0 X 10^{-2}	6.16	0.845	0.430
		3.0 X 10^{-2}	6.16	0.489	0.249
9-bromo anthracene		1.3 X 10^{-2}	6.16	0.918	0.467
		5.3 X 10^{-2}	6.16	0.415	0.213
		8.9 X 10^{-2}	6.16	0.242	0.123

the reaction with other free radicals resulting in chain terminations.

There is, however also another possibility that radical Z · re-initiates a chain by reacting with the monomer and generates another chain carrying radical R ·. Under the conditions of the present research, the following kinetic scheme in assumed:

Reaction	Rate	
I. $\rightarrow 2R.$	$2K_d f[I]$	(1)
$R\cdot + M \rightarrow R\cdot$	$K_p[R\cdot][M]$	(2)
$R\cdot + X \rightarrow Z\cdot$	$K_X[R\cdot][X]$	(3)
$Z\cdot + M \rightarrow R\cdot$	$K_0[Z\cdot][M\cdot]$	(4)
$Z\cdot + R\cdot \rightarrow$ P(inert product)	$K_C[R\cdot][Z\cdot]$	(5)
$Z\cdot + Z\cdot \rightarrow$ P(inert product)	$2K_Z[Z\cdot]$	(6)
$R\cdot + R\cdot \rightarrow$ P(inert product)	$2K_t[R\cdot]$	(7)

In this Scheme, I represent an initiator, R · a chain carrying radical, M a monomer molecule, X a retarder molecule, and Z · a retarder radical.

Other workers have usually found reaction (6) unimportant.[2,5,12] In the present work, this was also the case. Since the rate equations are considerably simplified when this equation is neglected, it is convenient to consider only the simplified kinetic scheme resulting from its omission.

After the usual steady state assumptions have been made, simple algebraic manipulation leads a straightforward manner to the following equation which gives the functional relationship between the variables involved:[6]

$$\frac{\phi^2[X]}{1-\phi^2} = \frac{K_t \cdot R}{K_p \cdot K_X} - \frac{K_t K_0'[M]}{K_X \cdot K_C} \qquad (8)$$

where $R = -\frac{d\ln[M]}{dt}$, $K_0' = K_0 + K_y / M + K_m$

Kice has noted that the form of the equation derived is not altered if reaction (4) is replaced by the reverse of reaction (3).[13] The inclusion of this reaction allows for the possibility that the intermediate Z · redical is addition complex and their first order breakdown is kinetically significant. It should also be noted that the form of the equation is not altered if reaction (4) is taken to represent the type of reaction postulated by Mayo[14] to account for the action of the halobenzene in transfer reaction. Thus the rate constant in the above scheme must then be interpreted as representing anyone or a combination of the rate constant for the reaction just mentioned.

From equation (8), the experimentally determined parameter, ϕ and R, can be used to make a plot of: $\frac{\phi^2[X]}{1-\phi^2}$ vs R. Its slope will be $\frac{K_t}{K_p K_X}$ and the intercept $\frac{K_0' K_t[M]}{K_X K_C}$

In order to calculate the degree of retardation (ϕ = observed rate / unretarded rate), the unretarded rate of polymerization was determined and found to be: $(\frac{-d\ln[M]}{dt}) = R_0 = 8.855\times10^{-3}[AIBN]^{1/2}$ percent per sec. This value becomes 5.455×10^{-4} percent per sec at $[AIBN]^{1/2} = 0.0616$ $mol^{1/2}/L^{1/2}$. The experimental data were plotted according to equation (8) and these results are shown in Fig. 3 to 6.

From Matheson et al.[15] have calculated the value of the propagation and termination constants:

$K_p = 2.16\times10^7 \exp(-7760/RT)$

and $2K_t = 2.59\times10^9 \exp(-2370/RT)$.

Hence, K_p was 102.28 L / mol-sec and $2K_t = 6.12\times10^7$ L / mol-sec at 45.0℃. From these values, the rate constant K_X and K_0'/K_C were readily obtained from slopes and intercepts of these plots. These results are listed in Table 2.

The Proposed Mechanism in the Retardation of Styrene Polymerization

It is generally accepted that a particular position in a compound is more reactive toward an attacking

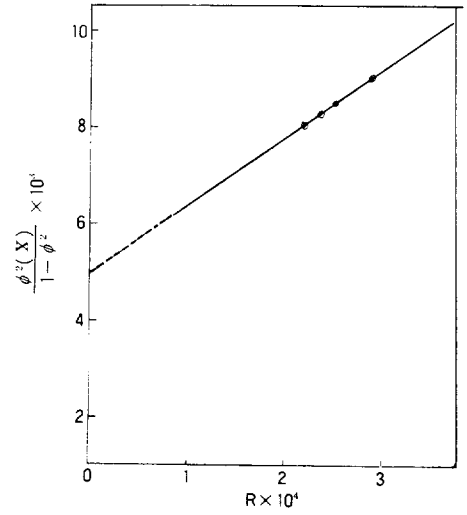


Fig. 3. Plot of equation 8 for anthracene.

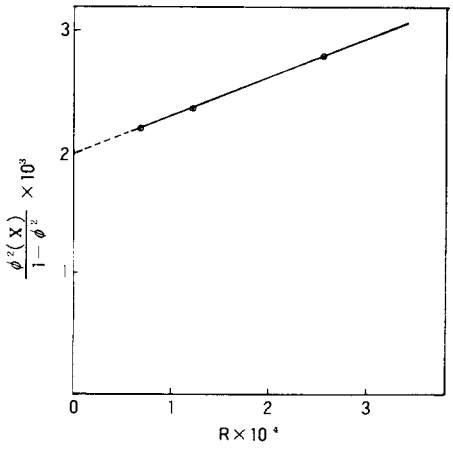


Fig. 4. Plot of equation 8 for 9-bromoanthracene.

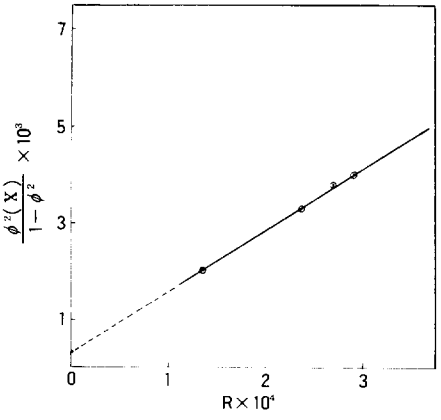


Fig. 5. Plot of equation 8 for 1-chloroanthracene.

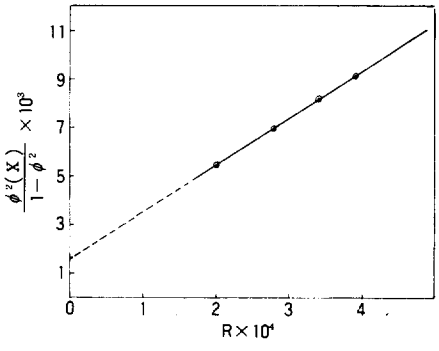


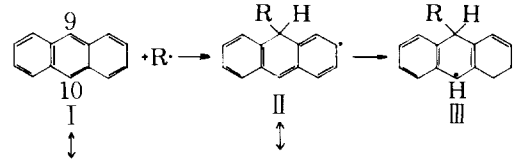
Fig. 6. Plot of equation 8 for 2-chloroanthracene.

Table 2. Rate Constants for Polycyclic Aromatic Halogen Compounds as Retarders in Styrene Polymerization.

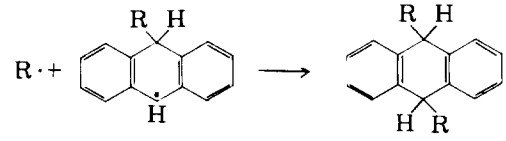
Retarder	Kx(l mol^{-1} · s^{-1})	K_x / K_p	$K_x / K_c \times 10^5$
Anthracene	$2.51 \times 10_4$	2.45×10^5	7.83
9-bromoanthracene	3.96×10^4	3.87×10^5	4.25
2-chloroanthracene	0.81×10^4	0.79×10^5	3.64
1-chloroanthracene	0.85×10^4	0.83×10^5	2.35

free radical. For example in acridine, the reaction with R· takes place only on the carbon hydrogen center of the meso position and not on the nitrogen as Szwarc[16] and Water et al. have noted. The frontier electron density predicts the point.

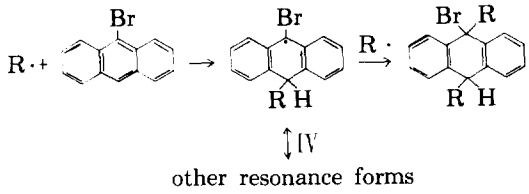
Since the meso position in anthracene is more reactive attacking radical than any other position, the addition may proceed as the following mechanism.

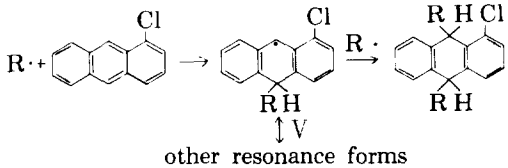


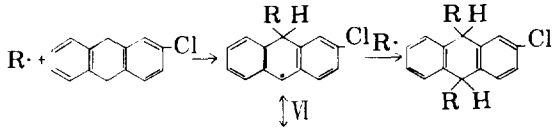
Structure III has two benzoid rings, while in structure II, there is only one benzoid ring. The more benzoid rings the structure has, the more stable structure is. Therefore the structures I and II are relatively unimportant. This means that after an initial free radical attack at the meso position, the subsequent attack in this intermediate radical Z · should take place at the other mesoposition.



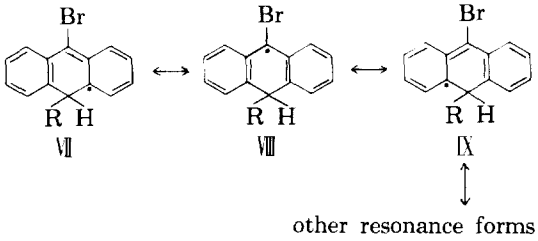
With the same argument, 9-bromoanthracene, 1-chloroanthracene, and 2-chloroanthracene proceed by the following mechanism :





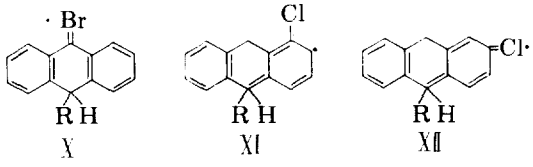


In 9-bromoanthracene, the radical structure is formed from the 10-position attacked by R · . The following radical structures are some of these resonance structures :



The bromine can share more than a pair of electrons. The radical resulting from 10-position attack is a radical from not only of stuctures Ⅶ-Ⅸ, but also of structure Ⅹ in which bromine is joined to the ring by a double bond.

The k_X value of 9-bromoanthracene is larger than that of anthracene (Table 2).



That may be because anthracene and 9-bromoanthracene have two meso positions to be attacked by radical. However, 9-bromoanthracene has larger resonance stability than anthracene. This result makes the structure which the intermediate of 9-bromoanthracene is more stable than that of anthracene. Threrfore, 9-bromoanthracene is more reactive than anthracene.

The k_X values of 1-chloroanthracene and 2-chloroanthracene are observed to be similar. However these values are smaller than that of anthracene (Table 3). This may be because 1-chloroanthracene and 2-chloroanthracene have two meso position just like anthracene, but inductive effect of chlorine makes easily quinoid structures (intermediate structures) such as ⅪⅠ and ⅪⅡ.

This results makes the structure which the intermediate of 1-chloroanthracene and 2-chloroan thracene are less stable than that of anthracene, Therefore, 1-chloroanthracene and 2-chloroan thracene are less reactive than anthracene.

Consideration by Frontier Electron Density Method

The frontier electron theory is based on the assumption that the reaction should occur at the position of the largest electron density in th frontier orbitals, i.e. the HOMO for electro philic reactions, the LUMO for nucleophilic reactions, and both of HOMO and LUMO for radical reactions.

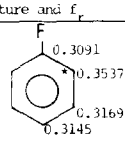
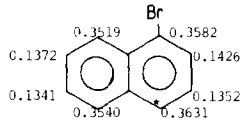
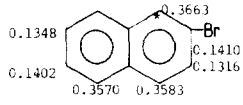
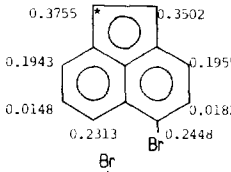
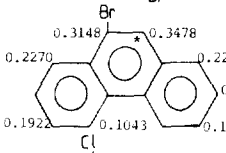
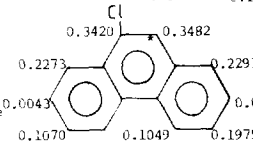
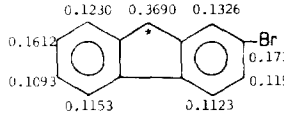
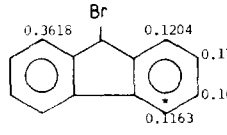
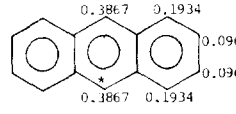
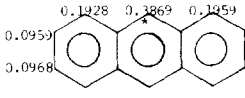
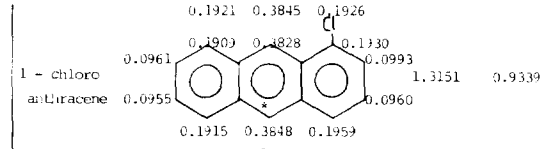
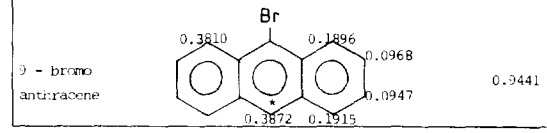
Fuku et al[9,17,18] defined the frontier electron density(f_r) for even-electron systems at rth atom (f_r) as follow[9]:

$$f_r=(2-\nu)(C_r^m)^2+\nu(C_r^{m+1})^2 \qquad (9)$$

where 2 is the number of electrons in the isolated molecules : C_r^m and C_r^{m+1} are the coefficients of aromatic orbitals in the isolated molecule : and which is a number equal to zero for an electrophilic reaction, one for a radical reaction, and two for a nucleophilic reaction.

Fukui and his workers[19,20] have also derived a reactivity index called the superdelocalizability (S_r) by the application of the perturbation theory to a model in which the incoming group forms a weak bond to atom r of an otherwise unmodified

Table 3. The Frontier Electron Density(f_r), Superdelocalizability and Approximate Superdelocalizabilities of Polycyclic Aromatic Halogen Compound.

Compound	Structure and f_r	S_r	S_r'
Fluoro - benzene		0.8930	0.5129
1 - bromo naphthalene		0.9999	0.5931
2 - bromo naphthalene		1.0017	0.5951
5 - bromo naphthalene		1.2577	0.6915
9 - bromo phenanthrene		1.0071	0.5801
9 - chloro phenanthrene		1.0082	0.5810
2 - bromo fluorene		0.9760	0.5476
9 - bromo fluorene		0.9549	0.5376
anthracene		1.3132	0.9441
2 - chloro anthracene		1.3156	0.9335
1 - chloro anthracene		1.3151	0.9339
9 - bromo anthracene			0.9441

system.

$$S_r=(2-\nu)\sum_{j}^{m}\frac{C_{rj}^2}{\lambda_j}+\nu\sum_{j=m+1}^{n}\frac{C_{rj}^2}{-\lambda_j} \qquad (10)$$

where n is the number of the atomic orbital in an isolated molecule : $E_j(=\alpha+\lambda_j\beta)$ is the energy of the jth molecular orbital in the isolated molecule : and h is the coulomb integral for the pseudo atom. The S_r is positive for most of the usual compounds. The greater the value of S_r, the more reactive is the rth position in the compound. Fukui et al[19]. have also noted that the superlo calizability serves as a reactivity index for comparing the reactivity of different molecules, while the frontier electron density becomes the reactivity index in comparing reactivity of different positions in a given molecules.

Fukui et al.[21] have noted that S_r' serves not only as a one-term approximation but also as index of properties which are intermadiate between S_r and the frontier electron density. The S_r' can be expressed as :

$$S_r'=(2-\nu)\frac{(C_r^m)^2}{\lambda_m}+\nu\frac{(C_r^{(m+1)})^2}{-\lambda_{m+1}} \qquad (11)$$

In the present research work, Fukui's frontier electron densities were calculated from the HMO calculations. For the position of the highest frontier electron density in each retarder molecule, the S_r and S_r' were calculated by the equation (10) and (11). The results and shown in Table 3.

For comparative purposes, frontier electron densities, superdelocalizabilities, and approximate superdelocalizabilities of the aromatic hydrocar

bons were also calculated. The results are shown in Table 4.

As shown in Table 3 and 4, the values of S_r and S_r' for most of the polycyclic aromatic halogen compounds are higher than those of the corresponding aromatic hydrocarbons. The S_r values of the polycyclic aromatic halogen compounds which have the retarding effects are larger than 1.31, while the S_r' values of those compounds which do not have any retarding effects are less than 1.26 (Table 3). The S_r values of compounds which exihibit retarding effects are larger than 0.94, while the S_r' values of compounds which exihibit no effects are less than 0.69. In case of polycyclic aromatic halogen compounds, 9-bromoanthracene which is the strongest retarder in the present work has the largest S_r and S_r' values. The k_X values of 1-chloroanthracene and 2-chloroanthracene are similar, and the S_r values of these compounds are also similar (Table 3). The k_X values of anthracene is larger than of 1-chloroanthracene and 2-chloroanthracene : however, the S_r or S_r' value of anthracene is less than those of 1-chloroanthracene and 2-chloroan thracene. This may be because the energy levels difference between the HOMO and LUMO is relatively small in 1-chloroanthracene and 2-chloroanthracene.

Table 4. The Frontier Electron Densities, Superdelocalizabilities and Approximate Superdelocalizabilities of Aromatic Hydrocarbons.

Structure	Position	f_r for radical attack	S_r for radical attack	S_r' for radical attack
benzene	- -	0.3333	0.8333	0.6666
naphthalene	1	0.3618	0.9344	0.5854
anthracene	9,10	0.3868	1.3132	0.9335
pyrenanthrene	9,10	0.3445	0.9975	0.5632

CONCLUSION

All retardation experimentals have been carried out in vacuum with a carefully degassed solution. The reaction rates have been measured dilatome trically. The data obtained were examined in light of Fukui's frontier electron density methods for correlating mechanism and reactivity. The results were as follows :

(1) The K_X value of 9-bromoanthracene is larger than that of anthracene. It is concluded that bromine is jointed to the ring by a double bond so that 9-bromoanthracene has larger resonance stability than anthracene.

(2) The compounds not possessing the mesomeric position do not show any retarding effect in styrene polymerization.

(3) The K_X values of 1-chloroanthracene and 2-chloroanthracene are observed to be similar, however, these values are smaller than that of anthracene. It is concluded that inductive effect of chlorine makes easily quinoid structures that the intermediate of 1-chloroanthracene and 2-chloroanthracene are less stable tan that of anthracene. (4) The S_r(or S_r') value of the retarder, generally, explained reasonably the reactivities of the retarders. The S_r and S_r' values of the polycyclic aromatic halogen compounds which show retardation effect are larger than about 1.31 and 0.94, respectively.

REFERENCES

1. P. D. Bartlett and H. Kwart, *J. Am. Chem. Soc.*, **72**, 1051(1950).
2. J. L. Kice, *J. Am. Chem. Soc.*, **76**, 6274(1954).
3. K. Kubin and L. Zirkmund, *Coll. Czec. Chem. Comm.*, **32**, 535(1956).

4. W. R. Yates and J. L. Ihrig, *J. Am. Chem. Soc.*, **87**, 710(1960).
W. R. Yates, The Reactivity of Aromatic Amines Toward Free Radicals. Ph. D. dissertation. University of Hawaii, 1964.
5. J. L. Ihrig and S. P. Sood, *J. Polym. Sci.*, **A3**, 1573(1965).
6. K. Yang, *J. of Science (Pusan National Univ., 16*, 63(1973).
7. Szakacs, Sandor : Bereznich, Tamara, Ferenc : Jokay, Laszlo, *Magy. Kem. Foly.*, **84(12)**, 557(Hung) (1978).
8. K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **27**, 1247(1957).
9. K. Fukui, T. Yonezawa and C. Nagata, *J. Chem. Phys.*, **22**, 1433(1954).
10. Y. G. Fox and S. Loshaek, *J. Polym. Sci.*, **15(A3)**, 371(1955).
11. C. H. Bamford, W. G. Barb, A. D. Jenkins and P. F. Onyon, The Kinetics of Vinyl Polymerization by Radical Mechanism, Academic Press Inc., New York, 1958, chapter 6 ; K. H. S. Bagdasar, The Thory of Free Radical Polymerization, Isarel Program for Scientific Translaton Jerusalem, 1968, chapter V.
12. R. G. Caldwell and J. L. Ihrig *J. Polym. Sci.*, **46(A3)**, 507(1960).
13. J. L. Kice, *J. Polym. Sci.*, **19(A3)**, 123(1956).
14. F. R. Mayo, *J. Am. Chem. Soc.*, **75**, 6133 (1953).
15. M. S. Matheson, E. B. Bevilacoya and E. J. Hart, *J. Am. Chem. Soc.* **73**, 1700(1951).
16. M. Szwarc and J. H. Bink, Theoretical Organic Chemistry, Batterworths Scientific Publication, London, 1958, p.262.
17. G. W. Wheland, *J. Am. Chem. Soc.*, **64**, 900 (1942).
18. K. Fukui, T. Yonezawa, and C. Nagata, *J. Chem. Phys.*, **26**, 831(1957).
19. K. Fukui, T. Yonezawa, and C. Nagata, *Bull. Chem. Soc. Japan*, **27**, 423(1954).
20. R. D. Brown, *J. Chem. Soc.*, 2232(1959).
21. K. Fukui, C. Nagata, T. Yonezawa, T. Inamoto, and A. Imamura, *Gann*, **51**, 67(1960).