

스티렌 중합에 있어서 방향족 니트로 화합물의 억제 반응 속도에 관한 연구

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Retardation Kinetics of Aromatic Nitro Compounds in Styrene Polymerization

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요 약 : 방향족 니트로 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. 사용된 5개의 니트로 화합물은 모두 억제 효과를 보였다. 스티렌 중합시 얻어진 실험 결과는 Fukui의 frontier electron density법으로 고찰하였다. 그 결과는 다음과 같다. 1) 45°C에서 억제제를 넣지 않고 AIBN과 스티렌 만의 반응 속도는 $-\frac{d\ln[M]}{dt} = R_0 = 8.855 \times 10^{-3} [AIBN]^{1/2}$ percent per sec로 표시할 수 있었다. 2) dinitrotoluene의 K_x 값은 mononitrotoluene 보다 모두 큰 값을 나타내었다. 3) 2,6-, 2,3-, 3,4-dinitrotoluene의 K_x 값은 비슷하지만 2,4-dinitrotoluene 값보다 적었다. 4) 방향족 니트로 화합물의 S_r (또는 S_r') 값은 0.83과 0.86(또는 0.30과 0.39) 사이의 값을 나타내었다.

Abstract : The aromatic nitro 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. All of aromatic nitro 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 : $-\frac{d\ln[M]}{dt} = R_0 = 8.855 \times 10^{-3} [AIBN]^{1/2}$ percent per sec at 45°C. 2) The K_x value of dinitrotoluene is larger than that of mononitrotoluene. 3) The K_x values of 2,6-, 2,3-, 3,4-dinitrotoluene are similar but are smaller than that of 2,4-dinitrotoluene. 4) The S_r (or S_r') values of the aromatic nitrotoluene compounds showed between 0.83 and 0.86(or 0.30 and 0.39).

INTRODUCTION

In 1950, Bartlett and Kwart¹ 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^{2,3} devised for the retarded methyl methacrylate (MMA) polymerization makes this system a priori an ideal one for the present study. Kubin⁴ and Ihrig et al.^{5,6} have studied a variety of retarders including phenols and aromatic amines.

Furthermore, Kim^{7,8} has studied the effects of twenty retarders of various heterocyclic nitrogen compounds on the AIBN catalyzed polymerization of styrene using a dilatometric technique similar to that employed by Bartlett and Kwart. Nobashi and Yokota⁹ and other workers¹⁰ also have investigated the inhibition of radical polymerization under high pressure. Sugiyama, Nakaya and Imoto¹¹ have studied inhibition effect of 1,1,4,4-tetraphenyl-2-tetrazene (TPT) in the radical polymerization of styrene. Recently Szakacs, Sander et al.¹² have investigated the kinetics of polymerization of styrene initiated by AIBN at 50°C in the presence of α -aryl-*N*-phenylnitrones. Tanczos, Ildiko et al.¹³ also studied the effect of monomer concentration on the stoichiometric coefficients of nitroso inhibitors (*p*-nitrosodimethylaniline and *p*-nitrosodiphenylamine) in the AIBN-catalyzed solution polymerization of acrylonitrile, methyl acrylate, and styrene in DMF and benzene.

More recently Park¹⁴ has studied the effects of twelve retarders of polycyclic aromatic halogen compounds on the AIBN catalyzed polymerization of styrene using a dilatometric technique.

In this work, a variety of aromatic nitro compounds were tested as polymerization retarders in the AIBN catalyzed polymerization of styrene. The rate were determined vacuum dilatometrically. All experiments were carried out at 45°C in a dark room in order to avoid the effect of the ultra-violet.

The results were analyzed by using a modified Kice's kinetic scheme² and were treated theoretically by the "frontier electron density" method of Fukui.^{15,16}

EXPERIMENTAL

Materials

Styrene (Waco Company) : The distillation of styrene and recrystallization 2,2'-Azobisisobutyronitrile used the same method in our previous work.¹⁴ 2,6-Dinitrotoluene (Aldrich Chemical Co.) was recrystallized from methyl alcohol twice. The crystals were yellow needles (m.p.66°C). 2,3-Dinitrotoluene (Aldrich Chemical Co.) was recrystallized from methyl alcohol twice. The crystals were yellow needles (m.p.59~61°C). 3,4-Dinitrotoluene (Aldrich Chemical Co.) was recrystallized twice from methyl alcohol, producing yellow needles (m.p.58.3°C). 2,4-Dinitrotoluene (Fulka Co.) was recrystallized from methyl alcohol twice. The crystals were yellow needles (m.p.71°C). Solvents (acetone, methyl alcohol, toluene) and other reagents (sulfuric acid, nitric acid, sodium hydroxide, sodium thiosulfate and pyrogallol) used in this research were the best qualities of chemicals available.

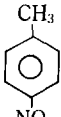
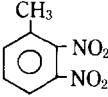
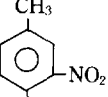
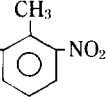
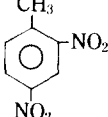
Vacuum Dilatometry

Diagrams of the dilatometer shown in our previous work.¹⁴ 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.⁷ From Fox and Loshaek's equation,¹⁷ it was computed that one hundred percent polymerization of styrene at 45°C 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 are the same values in previous work.¹⁴

Meanwhile 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 : $R_0 = 31.8782$

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Table 1. Summary of Experimental Results from Vacuum Dilatometer

Retarder	Structure	Retarder conc. (mol/L)	$[AIBN]^{1/2} \times 10^2$ (mol ^{1/2} /L ^{1/2})	R %/hr	ϕ
p-nitrotoluene		1.0×10^{-2}	6.16	1.8775	0.956
		1.3×10^{-2}	6.16	1.6923	0.861
		2.66×10^{-2}	6.16	1.4356	0.731
2,3-dinitrotoluene		0.75×10^{-2}	6.16	0.7562	0.385
		1.3×10^{-2}	6.16	0.6054	0.303
		2.0×10^{-2}	6.16	0.4301	0.219
3,4-dinitrotoluene		0.5×10^{-2}	6.16	0.6506	0.332
		0.75×10^{-2}	6.16	0.600	0.306
		1.0×10^{-2}	6.16	0.534	0.273
2,6-dinitrotoluene		0.5×10^{-2}	6.16	0.5904	0.300
		1.0×10^{-2}	6.16	0.4068	0.207
		2.0×10^{-2}	6.16	0.2448	0.124
2,4-dinitrotoluene		0.5×10^{-2}	6.16	0.8052	0.410
		0.75×10^{-2}	6.16	0.6795	0.346
		1.3×10^{-2}	6.16	0.6285	0.320
		2.0×10^{-2}	6.16	0.3594	0.183

$[AIBN]^{1/2}$, 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 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 .

RESULTS AND DISCUSSION

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.¹⁸ The kinetic scheme were represented in our previous work.¹⁴

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 :

$$\frac{\phi^2[X]}{1-\phi^2} = \frac{K_t \cdot R}{K_p \cdot K_x} - \frac{K_t K_0' [M]}{K_x \cdot K_c} \quad (1)$$

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

From equation (1), 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 $\frac{K_t}{K_p \cdot K_x}$ and the intercept $\frac{K_0'K_t[M]}{K_xK_c}$

In order to calculate the degree of retardation (ϕ =observed rate/unretarded rate), the unretarded rate of polymerization was determined and found to be: $[\frac{-d\ln[M]}{dt}] = R_0 = 8.855 \times 10^{-3}$ $[AIBN]^{1/2}$ percent per sec. This value becomes 5.455×10^{-4} percent per sec at $[AIBN]^{1/2} = 0.0616$ $\text{mol}^{1/2}\text{L}^{1/2}$. The experimental data were plotted according to equation (1) and these results are shown in Fig. 1 to 5.

From Matheson et al.¹⁹ have calculated the value of the propagation and termination constants: $K_p = 2.16 \times 10^7 \exp(-7760/RT)$ and $2K_t = 2.59 \times 10^9 \exp(-2370/RT)$.

Hence, K_p was 102.28L/mol-sec and $2K_t = 6.12 \times 10^7$ L/mol-sec at 45.0°C. From these values, the rate constant K_x and K_0'/K_c were readily obtained from slope and intercepts of these plots. These results are listed in Table 2.

Meanwhile, aromatic nitro compounds such as nitrobenzene and dinitrobenzene diminish the rate of polymerization of styrene, i.e., they are typical

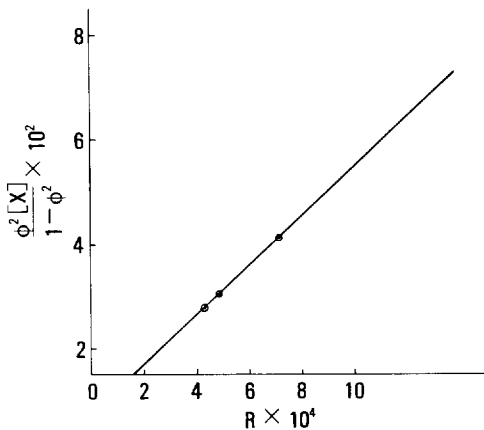


Fig. 1. Results for p-nitrotoluene plotted according to equation 8.

retarders. The nitro compounds act as inhibitors only in a few instances such as in vinyl acetate polymerization. They retard styrene polymerization and have no effect on methacrylate or acrylate polymerization.

The proposed mechanism in the retardation of styrene polymerization about aromatic nitro compounds prefer to function as electron acceptors but styrene radical as an electron donor, which could

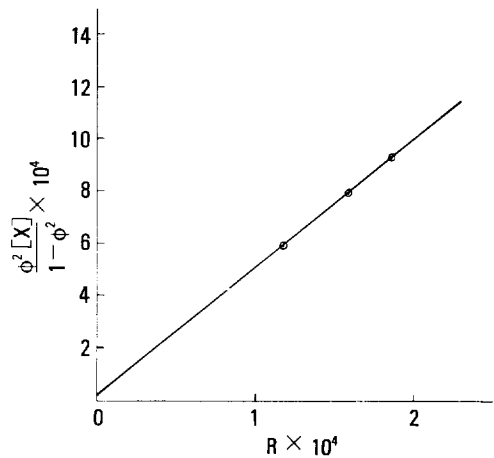


Fig. 2. Results for 2,3-dinitrotoluene plotted according to equation 8.

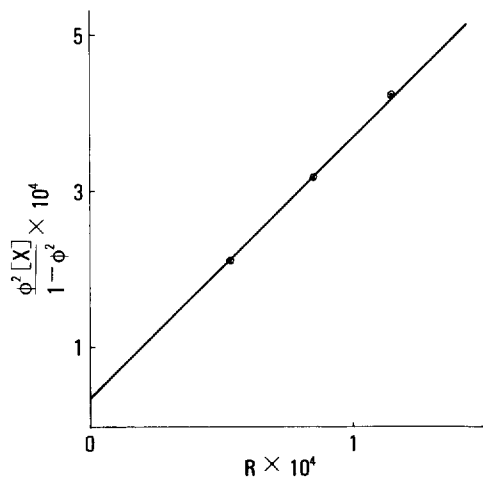


Fig. 3. Results for 3,4-dinitrotoluene plotted according to equation 8.

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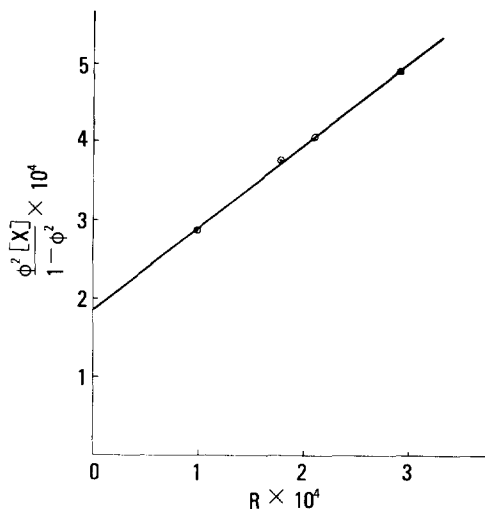


Fig. 4. Results for 2,4-dinitrotoluene plotted according to equation 8.

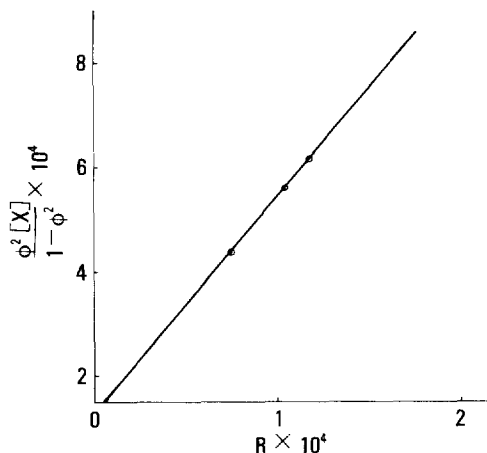


Fig. 5. Results for 2,6-dinitrotoluene plotted according to equation 8.

lead to form structure of type I in the transition state and consequently lower the activation energy.

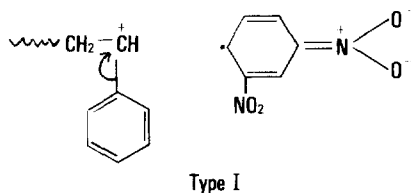


Table 2. Rate Constants for Aromatic Nitro compounds as Retarders in Styrene Polymerization

Retarder	$K_x(\text{L/mol sec}^{-1})$	K_x/K_p	$K_x'/K_c \times 10^7$
p-nitrotoluene	0.31×10^4	0.30×10^2	0.13
2,6-dinitrotoluene	6.01×10^4	5.88×10^2	1.04
2,4-dinitrotoluene	11.99×10^4	11.72×10^2	3.2
2,3-dinitrotoluene	4.91×10^4	4.80×10^2	0.19
3,4-dinitrotoluene	5.31×10^4	5.19×10^2	1.65

The only limitation upon a monoalkyldinitrobenzene as a retarder by this same mechanism would be steric hindrance which decreases resonance between the ring and a nitro group in the ortho position to the alkyl substituent.

The K_x values of 2,6-, 2,3-, 3,4-dinitrotoluene are similar but are smaller than that of 2,4-dinitrotoluene of which the nitro group of the para position lies coplanar with benzene ring in the transition state, while the other dinitrotoluenes having steric hindrances between methyl and nitro groups make the less contribution of resonance during transition.

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 the frontier orbitals, i.e, the HOMO for electrophilic reactions, the LUMO for nucleophilic reaction, and both of HOMO and LUMO for radical reaction.

The values of frontier electron density(f_i), superdelocalizability(S_r), and approximate superdelocalizability(S_r') were calculated by the same method in our previous work.¹⁴ The results shown in Table 3.

In the present work, the difference in electronegativity of carbon and nitro group is considered. It is difficult to estimate accurately h_x and h_{c-x} of aromatic nitro compounds. So many people use different h_x and h_{c-x} values according to their expe-

Table 3. The Frontier Electron Density(f_r), Superdelocalizability (S_r) and Approximate Superdelocalizability(S_r') of Nitro Aromatic Compounds

Compound	Structure and f_r	S_r	S_r'
p-nitrotoluene		0.8343	0.3720
2,3-dinitrotoluene		0.8404	0.3012
3,4-dinitrotoluene		0.8413	0.3470
2,6-dinitrotoluene		0.8457	0.3857
2,4-dinitrotoluene		0.8528	0.3626

rimental results. Also the value of h_x is usually proportional to the difference in electronegativity. The values of h_x and h_{c-x} are estimated as $h_x=2.6$ and $h_{c-x}=0.6$. As shown in Table 3, the values of S_r (or S_r' values) of aromatic nitro compounds tested in the present work are between 0.83 and 0.86 (or 0.30 and 0.39). The value of S_r becomes somewhat correlated with K_x value in comparison with benzene and we showed that the calculated values of S_r and S_r' of polycyclic aromatic halogen compound could be used for the prediction of the retardation effect.¹⁴

The mononitrotoluene and four isomers of dinitrotoluene have all retardation effects. However the values of S_r (or S_r') of the present work can

not be the exact criterion for retarder(or unretarder), since we do not know the S_r values (or S_r' values) of aromatic nitro compounds as an unretarder.

CONCLUSION

All retardation experimentals have been carried out in vacuum with a carefully degassed solution. The reaction rates have been measured dilatometrically. 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) Mononitrotoluene and five isomers of dinitrotoluene show all retardation effects. (2) The K_x values of dinitrotoluene show larger than that of mononitrotoluene. The K_x values of 2,6-, 2,3-, 3,4- dinitrotoluene are similar but are smaller than that of 2,4-dinitrotoluene. It is concluded that nitro group contribute a resonance effect because nitro group of the para position, in case of 2,4-dinitrotoluene, lies coplanar with benzene ring. (3) The S_r (or S_r') values of the retarder, generally, explained reasonably the reactivities of the retarders. The S_r (or S_r') values of the aromatic nitrotoluene compounds show between 0.83 and 0.86(or 0.30 and 0.39).

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