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Regional Density Functional Theory for the Initiation Reaction of Anionic Polymerization

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Abstract: The amount of electron transfer from an initiator to a monomer for the initiation reaction of anionic polymerization (ΔN) is calculated by means of the regional density functional theory through *ab initio* quantum chemical calculations, and the correlation of ΔN with reactivity is studied. For each initiator, ΔN increases as the reactivity of the monomer rises. This order of the value of ΔN, moreover, corresponds perfectly to that of the reactivity of the monomer. We reveal the correct order of reactivity of the monomer, which has been hard to account for in terms of the conventional Hammett σ_p parameter.

Introduction

The study of polymerization reactions has long been one of the main trends in both academic and industrial fields of chemical research. In particular, the rate constants of radical polymerization reactions are put in order to detail[1] and the reactivity of polymerization has been elaborated theoretically. In 1947, the Alfrey−Price $Q-e$ scheme for vinyl monomers,[2]

$$k_{12} = P_1 Q_2 \exp(-e_1 e_2) \qquad (1)$$

was suggested to represent the rate constant k_{12} of the chain propagation step of radical polymerization. The parameters are extracted from the experimental data. P_1 and Q_2 denote respectively the measure of reactivity for the monomer radical $M_1{}^{\bullet}$ and the monomer M_2, and e_1 and e_2 are regarded as the characteristic constants proportional to the actual charges on the end group of $M_1{}^{\bullet}$ and on the double bond of M_2, respectively. In terms of the $Q-e$ scheme, the monomer reactivity ratio (MRR) has been estimated for many combinations of monomers. A number of attempts based on the molecular orbital (MO) theory[3−5] have been made to explain the MRR since Evans et al. published the first paper[6] in 1948, where the MO theory was applied to radical polymerization. In this first paper Evans et al. avoided the problem of assigning numerical parameters for particular vinyl monomers, but they discussed general trends of reactivity as a function of the conjugation and electronegativity of the substituents. In 1954, Yonezawa et al.[7] calculated the stabilization energy $(\Delta E)_{r,s}$ of π conjugation, which occurs in the transition state of radical polymerization, and investigated its correlation with reactivity. $(\Delta E)_{r,s}$ was calculated through the second-order perturbation theory as follows:[8]

$$(\Delta E)_{r,s} = 2\Big(\sum_{m}^{\text{occ}}\sum_{n}^{\text{unocc}} - \sum_{m}^{\text{unocc}}\sum_{n}^{\text{occ-N}}\Big)\frac{(a_r^m)^2(b_s^n)^2(\Delta\beta)^2}{F_n - E_m} + 2\Big(\sum_{m}^{\text{occ}} - \sum_{m}^{\text{unocc}}\Big)\frac{(a_r^m)^2(b_s^N)^2(\Delta\beta)^2}{F_N - E_m} \qquad (2)$$

where a and b are the orbital coefficients of carbon atoms r and s in the m and n energy levels of the monomer and the radical having energy eigenvalues of E_m and F_n, respectively. The subscript N refers to the energy level containing the odd electron. They concluded that the larger the value of $(\Delta E)_{r,s}$ the more easily the reaction occurs between position r in the monomer and position s in the radical.[7,9] Moreover, Szwarc[10] and Fueno et al.[11] considered localization energy, that is, the difference between the total π energy of the monomer and that of the radical. The magnitude of the localization energy monitors how much the resonance integral would decrease if a complete electron transfer is attained. Szwarc[10] and Fueno et al.[11] suggested that the localization energy is an excellent index of the radical reactivity of vinyl compounds: the smaller the magnitude of localization energy is the more easily the reaction occurs.

On the contrary, the reactivity of anionic polymerization has not been thoroughly investigated theoretically.[3,12] This is because its reaction mechanism is complicated in comparison with that of radical polymerization when the solvent effect[13] or the counterion effect plays an important role. The MO treatments of anionic polymerization reactions have been neither as numerous nor as successful as those of radical reactions. Yonezawa et al.[14] first approached the general problem of

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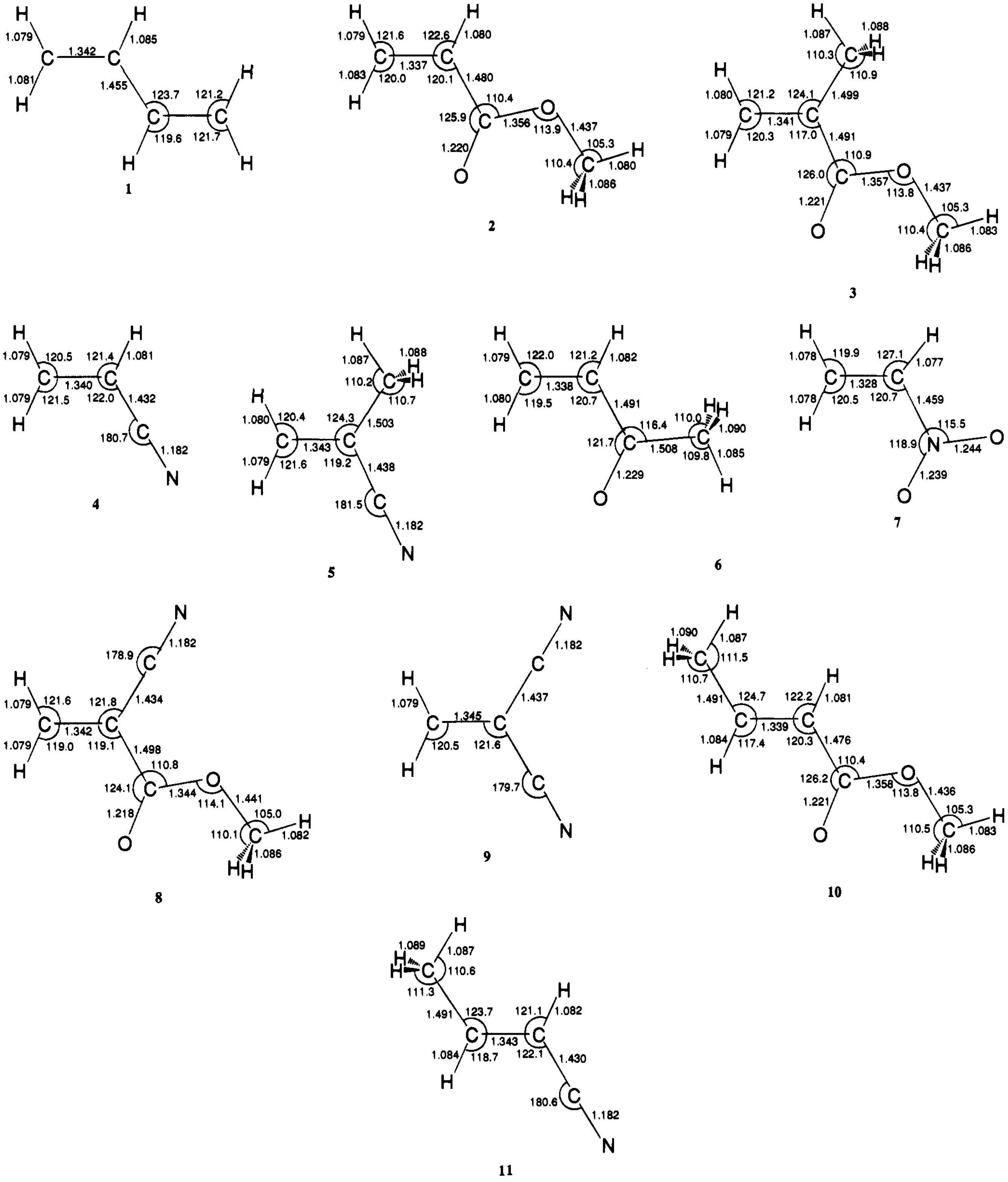

Figure 1. Calculated MP2(full)/6-31G** geometries of monomers **1**–**11**. All bond lengths are in angstroms and angles are in degrees.

anionic polymerization using the frontier electron theory.[15] By considering the position of attack in terms of the distribution of electron density in the lowest unoccupied orbital (LUMO) of the monomer, they extended the stabilization energy method to anionic polymerization. For this case, $(\Delta E)_{r,s}$ between a monomer and a polymer anion was calculated as

$$(\Delta E)_{r,s} = 2\left(\sum_{m}^{occ}\sum_{n}^{unocc} - \sum_{m}^{unocc}\sum_{n}^{occ}\right)\frac{(a_r^m)^2(b_s^n)^2(\Delta\beta)^2}{F_n - E_m} \qquad (3)$$

It was concluded that the MRR in anionic copolymerization is able to be interpreted in terms of the value of $(\Delta E)_{r,s}$, but a parallel does not exist between the magnitude of $(\Delta E)_{r,s}$ and the MRR of anionic homopolymerization. The origin of discrepancy is considered to be the determination of the reaction rate of anionic homopolymerization by using the magnitude of

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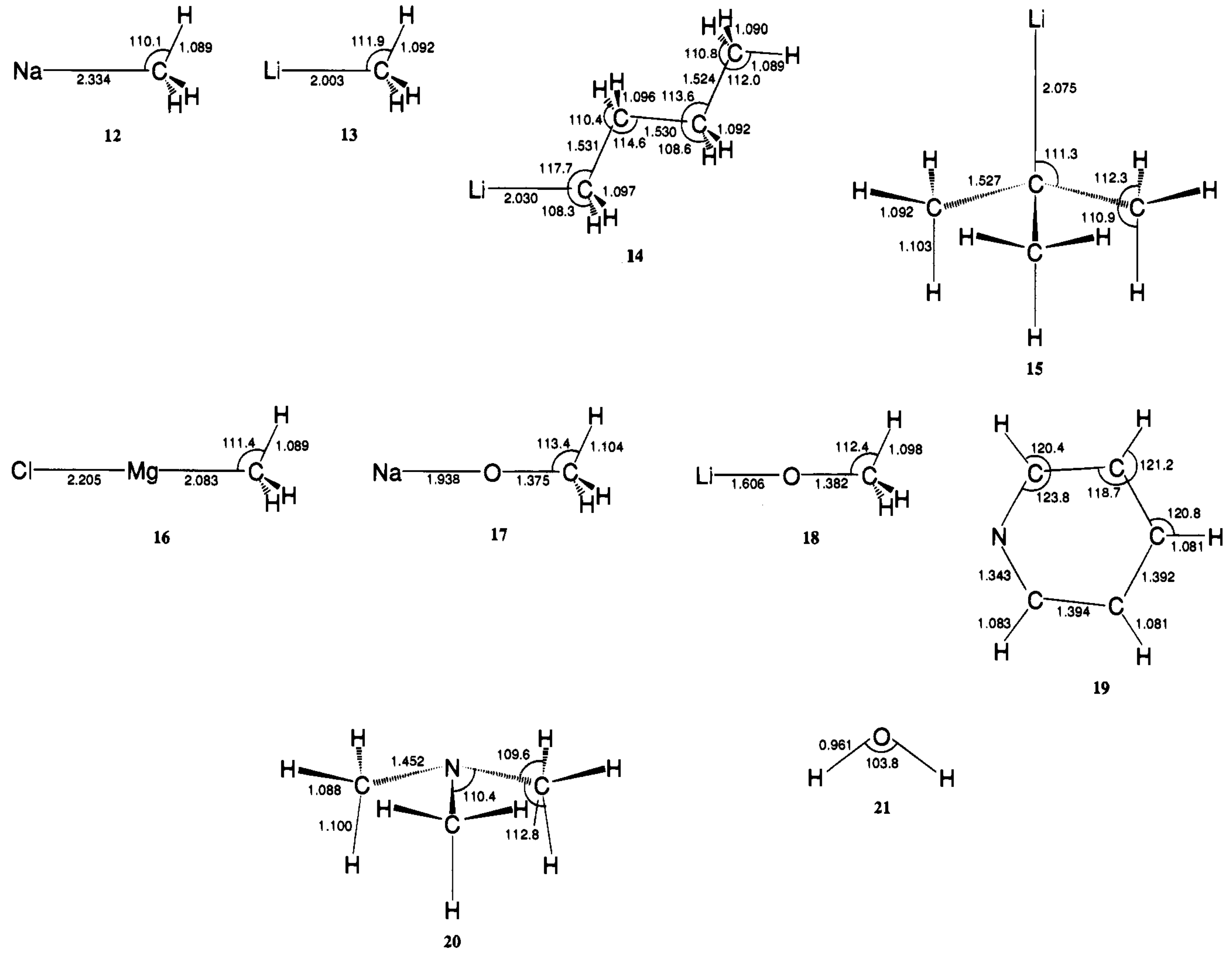

Figure 2. Calculated MP2(full)/6-31G** geometries of initiators **12**–**21**. All bond lengths are in angstroms and angles are in degrees.

the activation energy of the initiating step, in which the monomer and the initiator do not conjugate with each other in the transition state. The anionic localization energy L_A was also calculated according to the simple LCAO MO method as follows:[4,14,16]

$$L_A = \epsilon_I^- - \epsilon_M = 2\left(\sum_j^{occ} F_j - \sum_j^{occ} E_j\right) \qquad (4)$$

where ϵ_M and ϵ_I^- are the total π energy of a monomer and an anionic complex, respectively. The relative reactivities of monomers in anionic homopolymerization explain why the smaller the value of $L_A/(-\beta)$, the more easily the initiation reaction takes place.[14,16] However, the initiation reaction itself, under consideration to the interaction between monomer and initiator, has not been treated by the MO theory.[3]

The anionic polymerization is initiated by a nucleophilic attack of an anion B:$^-$ generated from an initiator AB to the double bond of a monomer $CH_2{=}CHR$,

$$A^+\cdots B:^- + CH_2{=}CHR \rightarrow B{:}CH_2C^-HR\cdots A^+ \qquad (5)$$

and the succeeding nucleophilic addition of the carbanion formed by reaction 5 to a new monomer leads to the propagation reaction.

However, the initiation reaction of anionic polymerization does not necessarily occur in every combination of monomer and initiator. Monomers have been classified into several groups by their reactivity.[17] Table 1 lists the reactivity of monomers and initiators in the initiation reaction of anionic polymerization arranged by Tsuruta in 1961.[18] The monomers are classified into four groups (A–D), as are the initiators (a–d). The former are located in order of reactivity and the latter in order of unreactivity, and only in the combinations indicated by an arrow from the upper left to the lower right does anionic polymerization occur.

Table 1, moreover, shows the Hammett substituent constant σ_p of the p-substituted compound[19] for the substituent added to the α-carbon. A good correlation is observed between the Hammett constant and the reactivity of monomers, but in fact, this correlation could not always stand up, or some exceptions exist: for example, methyl vinyl ketone may be polymerized by NaOR or NaCN.[20] In 1971, Tsuruta moved methyl vinyl ketone to the D group from the B group,[21] and the old D group was revised to the new E group. Furthermore, for unsaturated esters and nitriles respectively belonging to the B and C groups, it is well-known that the order of reactivity is easily changed according to solvent,[21,22] so these two groups have been considered to have a similar reactivity.

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Table 1. Reactivity of Monomers and Initiators for Anionic Polymerization Arranged by Tsuruta

initiator	monomer		
	name	structure	σ_P
group a[a]	group A		
SrR_2	α-methylstylene	$CH_2{=}C(CH_3)_3C_6H_5$	−0.161
CaR_2	butadiene	$CH_2{=}CHCH{=}CH_2$	
K;KR	styrene	$CH_2{=}CHC_6H_5$	0.009
Na;NaR			
Li;LiR			
group b[b]	group B		
ketyls	ethyl methacrylate	$CH_2{=}C(CH_3)CO_2C_2H_5$	0.352
RMgX	methyl vinyl ketone	$CH_2{=}CHCOCH_3$	0.516
	ethyl acrylate	$CH_2{=}CHCO_2C_2H_5$	0.522
group c[c]	group C		
ROK	acrylonitrile	$CH_2{=}CHCN$	0.628
RONa			
ROLi			
strong alkalis			
group d[d]	group D		
pyridine	nitroethylene	$CH_2{=}CHNO_2$	0.778
NR_3	ethyl methylenemalonate	$CH_2{=}C(CO_2C_2H_5)_2$	1.004
weak alkalis	ethyl α-cyanoacrylate	$CH_2{=}C(CN)CO_2C_2H_5$	1.150
ROR	ethyl α-cyanosorbate	$CH_3CH{=}CHCH{=}C(CN)CO_2C_2H_5$	1.150
H_2O	vinylidene cyanide	$CH_2{=}C(CN)_2$	1.256

[a] a → A, B, C, D. [b] b → B, C, D. [c] c → C, D. [d] d → D.

In this context, we shall calculate ΔN,[23,24] the electron transfer from an initiator to a monomer, in the initiation reaction of anionic polymerization by the regional density functional theory,[25] and investigate the relationship between reactivity and ΔN.

Method of Calculation

In terms of the density functional theory, two new properties of a chemical system were defined by Parr and his co-workers.[26] They are the electronic chemical potential, μ,[27] and the chemical hardness, η.[28] The exact definition of these quantities follows

$$\mu = \left(\frac{\partial E}{\partial N}\right)_{\nu(\mathbf{r})}, \quad \eta = \frac{1}{2}\left(\frac{\partial^2 E}{\partial N^2}\right)_{\nu(\mathbf{r})} = \frac{1}{2}\left(\frac{\partial \mu}{\partial N}\right)_{\nu(\mathbf{r})} \tag{6}$$

where E is the electronic energy, N is the number of electrons, and $\nu(\mathbf{r})$ is the "external" potential, the potential due to fixed nuclei.

Finite-difference expressions of μ and η are

$$\mu = -\frac{I+A}{2} = -\chi, \quad \eta = \frac{I-A}{2} \tag{7}$$

where I is the ionization potential and A is the electron affinity of the system. χ is called the absolute electronegativity.[27] It is well-known that the expression $\mu = -(I + A)/2$ has been proved to be exact for a grand canonical ensemble,[29] and recently the expression $\eta = (I - A)/2$ was also proved to be exact for the grand canonical ensemble.[30] Other manipulation gives other formula for the chemical potential[26,31] and the chemical hardness.[26]

In the bimolecular chemical reaction of the type in eq 5, the electron density $\varrho(\mathbf{r})$ of the supermolecule is given as the sum of regional electron densities,

$$\varrho(\mathbf{r}) = \varrho(\mathbf{r})_{\text{mono}} + \varrho(\mathbf{r})_{\text{init}} \tag{8}$$

where $\varrho_{\text{mono}}(\mathbf{r})$ and $\varrho_{\text{init}}(\mathbf{r})$ are the regional electron densities of monomer and initiator, respectively. The electron number N is accordingly given as follows:

$$N = N_{\text{mono}} + N_{\text{init}} \tag{9}$$

where

$$N_{\text{mono}} = \int \varrho(\mathbf{r})_{\text{mono}}\, \mathrm{d}\mathbf{r}, \quad N_{\text{init}} = \int \varrho(\mathbf{r})_{\text{init}}\, \mathrm{d}\mathbf{r} \tag{10}$$

The N is an integral number, while the regional electron numbers $N_{\text{mono,init}}$ are allowed to change continuously from their initial integral numbers as reaction proceeds. In the early stage of the chemical reaction, the regional electron densities are deformed to result in a monotone change of the regional electron numbers,

$$\mathrm{d}N_{\text{mono}} > 0, \quad \mathrm{d}N_{\text{init}} = -\mathrm{d}N_{\text{mono}} < 0 \tag{11}$$

where d means infinitesimal change along the reaction coordinate.

The infinitesimal change of N_{mono} is represented as,[25,30]

$$\mathrm{d}N_{\text{mono}} = [\mathrm{d}\mu_{\text{mono}} - \mathrm{d}\mu_{\text{init}} - \int (f_{\text{mono}}(\mathbf{r}) - f_{\text{init}}(\mathbf{r}))\, \mathrm{d}\nu(\mathbf{r})\, \mathrm{d}\mathbf{r} - \int (\Delta f^{\text{init}}_{\text{mono}}(\mathbf{r}) - \Delta f^{\text{mono}}_{\text{init}}(\mathbf{r}))\, \mathrm{d}\nu(\mathbf{r})\, \mathrm{d}\mathbf{r}]/[2(\eta_{\text{mono}} + \eta_{\text{init}})] \tag{12}$$

where $\mu_{\text{mono,init}}$, $\eta_{\text{mono,init}}$, $f_{\text{mono,init}}$, and $\Delta f_{\text{mono,init}}$ denote respectively the standard regional chemical potentials, the standardized hardnesses, the standard regional fukui functions, and the corrections of the standard regional fukui functions. This is an exact formula in the regional density functional theory.

In the present paper, we calculate ΔN by integrating eq 12 from the reactant isolated species, denoted by superscript 0, to the point $*$ where the standard regional chemical potentials are equal to each other:

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$$\begin{aligned}\Delta N &= \int_0^* \mathrm{d}N_{\mathrm{mono}} \\ &\approx \frac{1}{2(\eta^0_{\mathrm{mono}} + \eta^0_{\mathrm{init}})}\left(\int_0^* \mathrm{d}\mu_{\mathrm{mono}} - \int_0^* \mathrm{d}\mu_{\mathrm{init}}\right) \\ &= \frac{1}{2(\eta^0_{\mathrm{mono}} + \eta^0_{\mathrm{init}})}(\mu^*_{\mathrm{mono}} - \mu^0_{\mathrm{mono}} - \mu^*_{\mathrm{init}} + \mu^0_{\mathrm{init}}) \\ &= \frac{\mu^0_{\mathrm{init}} - \mu^0_{\mathrm{mono}}}{2(\eta^0_{\mathrm{mono}} + \eta^0_{\mathrm{init}})} \end{aligned} \qquad (13)$$

where the condition

$$\mu^*_{\mathrm{mono}} = \mu^*_{\mathrm{init}}$$

is a mandate of the electronic equilibrium state due to Sanderson.[32] The terms of the integral with respect to $\mathrm{d}\nu(\mathbf{r})$ are ignored but should be significant as the overlap of the reactant orbitals becomes large. Moreover, the standardized hardnesses are regarded as constant in the path of the integral. In the very early stage of the chemical reaction, these simplifications are considered valid.

The *ab initio* molecular orbital calculations were carried out with the Gaussian 92 program[33] at the MP2(full)/6-31G** level. We optimized the structure and calculated the energy E_{neutral} of neutral monomers and initiators in Tables 2 and 3. For the monomers and initiators, we calculated the energy of the cation, E_{cation}, and that of the anion, E_{anion}, using the same nuclear configuration as the neutral molecule. The ionization potential and the electronic affinity were then calculated as

$$I = E_{\mathrm{cation}} - E_{\mathrm{neutral}}, \qquad A = E_{\mathrm{neutral}} - E_{\mathrm{anion}} \qquad (14)$$

Furthermore, the absolute electronegativities and the absolute hardnesses were calculated with eq 7. Substituting these quantities for χ^0 and η^0 in eq 11, we get $2\Delta N$ for each combination of the monomer and the initiator as follows

$$2\Delta N = \frac{\chi^0_{\mathrm{mono}} - \chi^0_{\mathrm{init}}}{\eta^0_{\mathrm{mono}} + \eta^0_{\mathrm{init}}} \qquad (15)$$

It should be noted that eq 15 is first derived through integration of the exact differential form (eq 12) that allows a well-defined precise correction if desired. Also, it leads to the conventional formula[26] that is useful as a handy index of chemical reactivity. In fact, the values of calculated ΔN for a large number of reactant pairs (both inorganic and organic) have been correlated with the experimental rate constants and equilibrium constants.[24]

Results and Discussion

Table 4 shows results of calculations for monomers and the Hammett constant σ_p of p-substituted compounds with substituents added only to the α-carbon. The σ_p parameter of bisubstituted olefins is represented by the sum of the σ_p parameters of each substituent. Table 5 shows the results for initiators. The values of $2\Delta N$ from eq 15 are listed in Table 6.

For all initiators, the order of $2\Delta N$ completely corresponds to that of the reactivity of monomer, except for monomers of B and C groups which are easily affected by the solvent effect. It is determined that the more reactive monomer generally has the larger value of χ, and that the interrelation between the σ_p parameter and the reactivity of monomer is not perfect.

Table 2. List of Monomers for Calculation

group	monomer	structure
A	butadiene (**1**)	CH_2=CHCH=CH_2
B	methyl acrylate (**2**)	CH_2=$CHCO_2CH_3$
	methyl methacrylate (**3**)	CH_2=$C(CH_3)CO_2CH_3$
C	acrylonitrile (**4**)	CH_2=CHCN
	methacrylonitrile (**5**)	CH_2=$C(CH_3)CN$
D	methyl vinyl ketone (**6**)	CH_2=$CHCOCH_3$
E	nitroethylene (**7**)	CH_2=$CHNO_2$
	methyl α-cyanoacrylate (**8**)	CH_2=$C(CN)CO_2CH_3$
	vinylidene cyanide (**9**)	CH_2=$C(CN)_2$
?	methyl crotonate (**10**)	$CH(CH_3)$=$CHCO_2CH_3$
	crotononitrile (**11**)	$CH(CH_3)$=CHCN

Table 3. List of Initiators for Calculation

group	initiator	structure
a	methyl sodium (**12**)	CH_3Na
	methyl lithium (**13**)	CH_3Li
	n-butyl lithium (**14**)	*n*-C_4H_9Li
	tert-butyl lithium (**15**)	*t*-C_4H_9Li
b	methylmagnesium chloride (**16**)	CH_3MgCl
c	sodium methoxide (**17**)	CH_3ONa
	lithium methoxide (**18**)	CH_3OLi
d	pyridine (**19**)	C_5H_5N
	trimethylamine (**20**)	$(CH_3)_3N$
	water (**21**)	H_2O

Table 4. Theoretical parameters and the Hammett Constant for Monomers

monomer	I/eV	A/eV	χ/eV	η/eV	σ_p
butadiene	8.6636	−2.2124	3.211	5.423	
methyl crotonate	9.8441	−1.7801	4.032	5.812	
methyl methacrylate	9.8195	−1.7580	4.031	5.789	+0.14
crotononitrile	10.2479	−1.7384	4.255	5.993	
methacrylonitrile	10.3425	−1.7539	4.294	6.048	+0.49
methyl acrylate	10.4263	−1.6784	4.374	6.052	+0.31
acrylonitrile	10.8251	−1.5899	4.618	6.207	+0.660
methyl vinyl ketone	10.5925	−1.3488	4.622	5.971	+0.502
methyl α-cyanoacrylate	10.7972	−0.4992	5.149	5.648	+0.97
nitroethylene	11.3624	−0.7676	5.297	6.065	+0.778
vinylidene cyanide	11.4165	−0.1131	5.652	5.765	+1.320

Table 5. Theoretical Parameters for Initiators

initiator	I/eV	A/eV	χ/eV	η/eV
CH_3Na	5.9894	−0.0789	2.955	3.034
CH_3Li	6.9370	−0.2291	3.354	3.583
n-BuLi	6.4169	−0.0854	3.166	3.251
t-BuLi	5.9689	0.0496	2.960	2.910
CH_3MgCl	9.6188	−0.8712	4.374	5.245
CH_3ONa	6.9662	0.2024	3.584	3.382
CH_3OLi	8.0738	−0.1952	3.939	4.134
C_5H_5N	9.5359	−2.5559	3.490	6.046
$(CH_3)_3N$	8.3075	−5.0019	1.653	6.655
H_2O	12.1855	−5.1224	3.532	8.654

To conclude, ΔN increases in the following order of the five groups: A, (B and C), D, and E. In other words, ΔN has a good correlation with the reactivity of a monomer arranged by Tsuruta. Particularly, even for methyl vinyl ketone whose reactivity cannot be explained by the σ_p parameter, the reactivity can be expressed by ΔN. Moreover, for methyl crotonate and crotononitrile, which have not been classified into one of the five groups defined by Tsuruta, the estimated reactivity using ΔN predicts the correct order of the real experimental reactivity.

Table 7 shows the localization energy L_A and the stabilization energy $(\Delta E)_{r,s}$ which have been used to explain the MRR of vinyl monomers. The former has been regarded as one of the parameters which have a good correlation with the MRR for anionic polymerization, but like the Hammett σ_p parameter, it

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Table 6. Values of $2\Delta N$ Calculated for Initiation Reaction

	initiator									
monomer	CH_3Na	CH_3Li	*n*-BuLi	*t*-BuLi	CH_3MgCl	CH_3ONa	CH_3OLi	C_5H_5N	$(CH_3)_3N$	H_2O
butadiene	0.030	−0.016	0.005	0.030	−0.109	−0.042	−0.076	−0.024	0.129	−0.023
methyl crotonate	0.122	0.072	0.096	0.123	−0.031	0.049	0.009	0.046	0.191	0.035
methyl methacrylate	0.122	0.072	0.096	0.123	−0.031	0.049	0.009	0.046	0.191	0.035
crotononitrile	0.144	0.094	0.118	0.145	−0.011	0.072	0.031	0.064	0.206	0.049
methacrylonitrile	0.147	0.098	0.121	0.149	−0.007	0.075	0.035	0.066	0.208	0.052
methyl acrylate	0.156	0.106	0.130	0.158	0.000	0.084	0.043	0.073	0.214	0.057
acrylonitrile	0.180	0.129	0.154	0.182	0.021	0.108	0.066	0.092	0.231	0.073
methyl vinyl ketone	0.185	0.133	0.158	0.187	0.022	0.111	0.068	0.094	0.235	0.075
methyl α-cyanoacrylate	0.253	0.194	0.223	0.256	0.071	0.173	0.124	0.142	0.284	0.113
nitroethylene	0.257	0.201	0.229	0.260	0.082	0.181	0.133	0.149	0.286	0.120
vinylidene cyanide	0.307	0.246	0.276	0.310	0.116	0.226	0.173	0.183	0.322	0.147

Table 7. Anionic Localization Energies and Stabilization Energies

group	monomer	L_A[a]	$(\Delta E)_{r,s}$[a]
A	butadiene	1.644	0.8994
B	methyl acrylate	1.511	
	methyl methacrylate	1.428	
C	acrylonitrile	1.283	0.9122
	methacrylonitrile	1.240	0.8820
D	methyl vinyl ketone	1.299	
E	nitroethylene	0.940	
	vinylidene cyanide	0.970	0.7586

[a] From ref 16 in units of $-\beta$. [b] From ref 14 in units of $-(\Delta\beta)^2/\beta$.

cannot interpret the order of reactivity of methyl vinyl ketone. The most serious defect of L_A is that it is the quantity which represents the instability by a complete electron transfer without any consideration of the electron donor. The latter is not seen to have any correlation with the MRR for anionic homopolymerization though the interaction with the electron donor is explicitly considered. On the other hand, the ΔN calculated in this paper adopts the interaction with the initiator but also has a perfect correlation with reactivity. It covers the weak points that L_A and $(\Delta E)_{r,s}$ each carry.

As the foundation of our theory, ΔN is the amount of electron transfer in the initial stage of the chemical reaction where the monomer and the initiator are far apart from each other, so we argue that each of them independently accepts or donates the electron, that is, the change in the number of electrons in one species does not affect the other. It is very interesting that such ΔN has a good correlation with the reactivity of the initiation reaction of anionic polymerization which occurs as the monomer and initiator come close.

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