NOTE

Radical Reactivities of Vinyl Compounds Bearing Five-Membered Lactone

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Five-membered lactone has a moderate chemical reactivity, and is considered to be one of the chemically functional moieties in functional polymers. In the present paper, radical homopolymerizabilities of 2-vinyl-1,4-butyrolactone (**1**), 3-vinyl-1,4-butyrolactone (**2**), 4-vinyl-1,4-butyrolactone (**3**), and 3-(4-vinylphenoxy)phthalide (**4**), and radical copolymerizabilities of these monomers with acrylonitrile (**5**), a typical radical comonomer, were investigated both experimentally and theoretically. The radical reactivity of 2-vinyl-1,4-butyrolactone (**1**) was estimated only theoretically, since it has not been synthesized as yet.

CALCULATION

All calculations were carried out by the INDO MO method.¹ The radical reactivity index (RRI), the measure of the reactivity of the monomer toward the radical, is defined as,

$$RRI = \sum_i^{\text{occ}} \frac{(C_r^{(i)})^2}{\lambda - \epsilon_i} + \sum_j^{\text{uno}} \frac{(C_r^{(j)})^2}{\epsilon_j - \lambda} \quad (1)$$

where $C_r^{(i)}$, $C_r^{(j)}$ are the coefficients of the $2p\pi$ atomic orbitals in the i th and j th MOs, respectively, and whose energies are ϵ_i and ϵ_j , respectively. λ denotes the energy of the singly-occupied MO of the attacking radical.

The frontier electron density ($f_r^{(R)}$) is defined as,

$$f_r^{(R)} = (C_r^{(\text{HO})})^2 + (C_r^{(\text{LU})})^2 \quad (2)$$

where $C_r^{(\text{HO})}$ and $C_r^{(\text{LU})}$ are the coefficients of the r th $2p\pi$ atomic orbitals in the highest-occupied and

lowest-unoccupied MOs, respectively.

RESULTS AND DISCUSSION

Homopolymerization of both **2** and **3** hardly proceeded.^{2,3} The conversion of **2** was 0.3% after 7 days and that of **3** was even less than that of **2**. These results lead to the conclusion that the homopolymerization of **2** and **3** are difficult. On the other hand, the radical homopolymerization of **4** proceeded in a manner similar to ordinary vinyl monomers.⁴ This means that **4** has a reactivity higher than either **2** or **3** and that **2** is more reactive than **3**. The monomer reactivity ratios (MRR) of the radical copolymerization of **2** and **5**, and that of **3** and **5** are shown in Table I. Of these two copolymerizations, the propagations were influenced only by the terminal monomer unit and are interpreted as a terminal model. Of the radical copolymerization of **4** and **5**, the propagation was influenced not only by the terminal monomer unit but also by the penultimate unit of the growing chain since **4** is very bulky. This propagation is interpreted on the basis of the penultimate model. The monomer reactivity ratios $r_4 = 0.23$, $r_4' = 0.41$, $r_5 = 0.08$, and $r_5' = 0.11$

Table I. Monomer reactivity ratios of the radical copolymerization of **2** and **3** with **5**

Monomer	MRR	
2	$r_2 = 0.058$	$r_5 = 4.6$
3	$r_3 = 0.004$	$r_5 = 4.4$

Table II. Radical reactivity indices (RRI) and frontier electron densities ($f_r^{(R)}$) for 1, 2, 3, 4, and 5

Position	RRI*	$f_r^{(R)}$
a	2.90	—
b	2.98	—
c	2.59	0.360
d	2.78	0.458
e	2.51	0.442
f	2.77	0.597
g	2.51	0.154
h	2.91	0.356
i	2.50	0.525
j	2.82	0.786

* RRI was calculated, taking the value $\lambda = -0.15$ a.u.

were obtained,⁴ on the basis of the chemical composition and triad fraction analysis of the copolymer. Using these results and the published Q and e values of 5,⁵ Q_2 , e_2 , Q_3 , and e_3 were calculated to be $Q_2=0.033$, $e_2=0.053$, $Q_3=0.012$, and $e_3=-0.81$. These values imply that the resonance stabilization of 2 and 3 are low, but the π -electron density of 2 is relatively low and that of 3 is high. The high π -electron density of 3 is considered to be attributable to the ether oxygen atom adjacent to the vinyl group.

In Table II, RRI and $f_r^{(R)}$ are shown. As for $f_r^{(R)}$ of 2, 3, and 4, the coefficients of the vinyl carbon $2p\pi$ atomic orbital in the highest-occupied and lowest-unoccupied MOs are small, but the largest coefficient of the vinyl carbon $2p\pi$ atomic orbital in the occupied MO exists below the highest-occupied MO, and the largest one in the unoccupied MO exists above the lowest-unoccupied MO, respectively. Using the coefficients of these vinyl carbon $2p\pi$ atomic orbitals, $f_r^{(R)}$ was calculated. But, in the case of 1, the coefficients of the vinyl carbon $2p\pi$ atomic orbital are dispersed, and the inability to identify orbitals made evaluation of $f_r^{(R)}$ impossible.

As for RRI, the orbital energy of the radical, λ , which attacks the monomer, is assumed to be -0.15 a.u. Both the RRI and $f_r^{(R)}$ values indicate that the reacting position of these five monomers toward the growing chain radical is situated mostly at the β carbon of the vinyl group. Accordingly, the polymerization proceeds *via* a head-to-tail mechanism and the growing chain terminals are,

The growing chain terminal structures, 6, 7, and 8, are readily converted into allylic radicals by losing 2-hydrogen of 6, 3-hydrogen of 7, and 4-hydrogen of 8, respectively. In addition, there is the possibility of intermolecular hydrogen migration, meaning that these growing chain terminals may also subtract another 2-hydrogen of 1, 3-hydrogen of 2, and 4-hydrogen of 3. Accordingly, in the radical copolymerization of 2 and 5, and 3 and 5, the degrees of polymerization decreased with the content of 2 in the poly(2-co-5) and that of 3 in the poly(3-co-5), respectively.

From RRI, the radical reactivities of these three 1,4-butyrolactone derivatives decreased in the following order; $1 > 2 > 3$. This order coincided with the experimental data, but not the order in $f_r^{(R)}$. RRI predicts that 1 is a highly reactive monomer compared with the other 1,4-butyrolactone derivatives, though 1 has not been synthesized. These trends are not altered by the assumption of λ 's being -0.05 , -0.10 , -0.20 , or -0.25 a.u.

Since RRI is calculated by considering not only the coefficient of the vinyl carbon $2p\pi$ atomic orbital but also its orbital energy, it is possible to assume both the reactivity and reacting position in vinyl compounds, even though coefficients of vinyl car-

bon $2p\pi$ atomic orbitals are dispersed, as in the case of **1** reported in the present paper.

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