

Allylic Polymers IV. The Effect of Alkyl-Substituents on Copolymerization of Allyl Alkyl Ethers with Vinyl Acetate

Yasumasa SHIGETOMI, Naruhito ONO, Hiroshi KATO,
and Michinori ŌKI

*Department of Chemistry, Faculty of Science, Okayama University of Science, 1-1,
Ridai-cho, Okayama 700, Japan*

(Received August 8, 1991)

ABSTRACT: The radical copolymerization of allyl alkyl ethers with vinyl acetate has been studied in the feed range from 10 to 90 mol% allyl alkyl ethers. The following values were obtained by the Kelen–Tüdös method for the reactivity ratios: allyl ethyl ether (M_1)–vinyl acetate (M_2), $r_1 = 0.041 \pm 0.002$, $r_2 = 1.56 \pm 0.08$; allyl propyl ether (M_1)–vinyl acetate (M_2), $r_1 = 0.036 \pm 0.002$, $r_2 = 1.39 \pm 0.07$; allyl butyl ether (M_1)–vinyl acetate (M_2), $r_1 = 0.047 \pm 0.003$, $r_2 = 1.39 \pm 0.07$; allyl isopropyl ether (M_1)–vinyl acetate (M_2), $r_1 = 0.028 \pm 0.002$, $r_2 = 1.56 \pm 0.08$; allyl *t*-butyl ether (M_1)–vinyl acetate (M_2), $r_1 = 0.0057 \pm 0.0003$, $r_2 = 1.51 \pm 0.08$; The Q - e parameters were calculated from the allyl ether (M_1)–vinyl acetate (M_2) reactivity ratios. The e parameters of allylic monomers have been found to be nicely correlated with parameters such as Taft's σ^* constants of the alkyl group for allyl alkyl ether, ^{13}C NMR chemical shift values of the γ carbon in the allylic monomers, and further, f_r^k for the γ carbon of allyl group in the allylic monomers.

KEY WORDS Copolymerization / Allyl Ether / Frontier Molecular Orbital
/ Reactivity Ratio / Q - e Parameter /

Attempts have been made to find the relationship between ease of abstraction of allylic hydrogen and radical addition in allylic monomers^{1,2} and to study the mechanisms of allylic polymerization. The electron-abstracting nature of acyl groups in allyl ester is known to reduce abstraction of allylic hydrogen and enhance radical addition to the double bond to a small extent. One can argue, however, that the electronic effects on these characteristics given by the substituent on the acyl group should be weak because of the substituent is rather remote from the reaction site. It is thus worthwhile to examine the substituent effect on polymerization characteristic in allylic monomers which carry substituents in more proximity than allyl esters.

We chose in this respect allyl alkyl ethers, in which the alkyl group is either straight chain or branched. In ether, there are only

two bonds that intervene between the allylic carbon and the carbon that carry the substituent(s), whereas, in esters, the number of the intervening bonds is three. The weak electron-withdrawing nature of the alkoxy group in allyl alkyl ethers could retard polymerization and enhance hydrogen-abstraction from the allylic position relative to the case of that in the acyloxy group in allyl esters. Nonetheless, we thought they will be an interesting starting point for the investigation on the electronic effects of substituents that are closely located to the allylic position.

In this paper, we report the effects of the alkyl group on copolymerization with vinyl acetate and on the reactivity ratios and the Q - e parameters for a series of allyl ethers. The relationships discussed are; 1) e parameter—Taft's σ^* constant, 2) e parameter— ^{13}C NMR chemical shift, 3) e parameter—molecular

orbital energy.

EXPERIMENTAL

Monomer Synthesis

To 500 ml of an anhydrous alcohol in a 1000 ml flask fitted with a reflux condenser were added gradually 46 g. (2 mol) of sodium in thin slices at such a rate that the mixture boils steadily. When all the sodium had been added, the mixture was heated in a steam bath until the few remaining pieces of sodium disappeared. This was followed by the addition of 2.0 mol of redistilled allyl chloride in small portions, the rather vigorous reaction being allowed to complete itself before each subsequent addition.

The mixture was heated in the steam bath for about five hours. The end of the reaction was determined by withdrawing a sample, filtering it, and heating the filtrate in which little or no precipitate should form. The mixture was cooled, water was added gradually through the condenser until the remainder of the sodium alcoholate reacted with water, and then 300 ml of water were added. The organic portion was washed several times with water, dried over calcium chloride and distilled twice.

Allyl ethyl ether: Yield 65–70%; bp 66–67°C. *Anal.* Calcd for $C_5H_{10}O$: C, 69.7%; H, 11.7%. Found: C, 69.5%; H, 11.8%. ^{13}C NMR ($CDCl_3$): $\delta = 116.2$ ppm ($CH_2=$), 135.4 ppm ($-CH=$), 71.6 ppm ($-CH_2-O-$), 65.6 ppm ($-O-CH_2-$), and 15.2 ppm ($-CH_3$).

Allyl propyl ether³: Yield: 60–67%; bp 92–93°C. *Anal.* Calcd for $C_6H_{12}O$: C, 72.0%; H, 12.1%. Found: C, 71.8%; H, 11.9%. ^{13}C NMR ($CDCl_3$): $\delta = 116.3$ ppm ($CH_2=$), 135.4 ppm ($-CH=$), 71.8 ppm ($-CH_2-O-$), 72.2 ppm ($-O-CH-$), 23.2, and 10.7 ppm ($-CH_2CH_3$).

Allyl isopropyl ether³: Yield: 55–60%. bp 84–85°C. *Anal.* Calcd for $C_6H_{12}O$: C, 72.0%; H, 12.1%. Found: C, 71.9%; H, 12.3%. ^{13}C NMR ($CDCl_3$): $\delta = 116.0$ ppm ($CH_2=$), 135.7 ppm ($-CH=$), 69.1 ppm ($-CH_2-O-$), 70.9 ppm ($-O-CH<$), and 22.1 ppm ($-CH_3$).

Allyl butyl ether³: Yield 60–66%. bp 119–120°C. *Anal.* Calcd for $C_7H_{14}O$: C, 73.6%; H, 12.4%. Found: C, 73.4%; H, 12.1%. ^{13}C NMR ($CDCl_3$): $\delta = 116.3$ ppm ($CH_2=$), 135.3 ppm ($-CH=$), 70.2 ppm ($-CH_2-O-$), 71.9, 37.1, 19.6, and 13.9 ppm ($-OCH_2CH_2CH_2CH_3$).

Allyl *t*-butyl ether³: Yield: 50–56%. bp 100–102°C. *Anal.* Calcd for $C_7H_{14}O$: C, 73.6%; H, 12.4%. Found: C, 73.8%; H, 12.5%. ^{13}C NMR ($CDCl_3$): $\delta = 115.1$ ppm ($CH_2=$), 136.5 ppm ($-CH=$), 63.0 ppm ($-CH_2-O-$), 72.9 ppm ($-O-C-$), and 27.6 ppm ($-CH_3$).

Vinyl acetate from Tokyo Chemical Co. was used after purification by distillation.

Procedures

Copolymerization of Allyl Alkyl Ethers with Vinyl Acetate. A mixture of weighed amounts of an allyl ether and vinyl acetate and 0.1 wt% of benzoyl peroxide was placed in a 50 ml heat-resisting glass bottle. The bottle was sealed and placed in a thermostatted bath at 60°C for an appropriate period. The feed ratios are shown in tables. The copolymer was isolated by precipitation with petroleum ether from the reaction mixture and purified by reprecipitation by petroleum ether from benzene solution.

Measurements

Analysis of Copolymer. Elemental analyses for carbon and hydrogen of the allyl alkyl ether-vinyl acetate copolymers were conducted by a Hitachi Perkin Elmer model 240C. Copolymer compositions were calculated by using the carbon content of the polymers.

Determination of Molecular Weight. The determination of molecular weight was carried out by using a Simadzu GPC, model chromatopac C-R3A. The column was Shodex AD-804/S and the solvent was *N,N*-dimethylformamide. Polystyrene and poly(ethylene glycol) were used as standard samples for calibration.

^{13}C Nuclear Magnetic Resonance Spectroscopy. ^{13}C NMR spectra of the allyl ether

monomers were obtained at 22.5 MHz on a Hitachi R-90 Spectrometer using 25 v/v% chloroform (CDCl_3) solutions containing 2 v/v% TMS as an internal standard for the chemical shift values. The sample was placed in 5 mm tubes.

Calculation of Molecular Orbital Energy. Molecular electronic structures were calculated as follows; The lowest energy conformation of allyl methyl ether was elucidated by the MMP-2 (MM-2) method as described previously.⁴ Atomic coordinates were used in the AM-1 method and energy was optimized. The frontier electron density, f_r^R , was calculated as one half the sum of the HO and the LU frontier densities.

RESULTS

Copolymer Compositions

The copolymer composition as a function of feed composition for the copolymerization of allyl alkyl ethers with vinyl acetate is shown in

Figure 1. The composition was obtained for allylic copolymers at the stage where the production of the copolymer was less than 5%. The dashed line represents ideally random copolymerization conditions. The curve represents the copolymerization curve, calculated from reactivity ratios according to the Fineman-Ross equation. It can be seen from the copolymer composition plot that the content of an allyl alkyl ethers in a copolymer increases with increasing feed ratios of the allyl alkyl ether. In the copolymerization of allyl alkyl ethers with vinyl acetate, the copolymerization curve showed deviation from the ideally random copolymerization conditions and the gap of allyl *t*-butyl ether was larger than those of the other allyl alkyl ethers.

Rates of Copolymerization and Molecular Weights of Copolymer

The reaction rates for each allyl alkyl ether were measured at various feed ratios. The results are shown in Table I. Since the general

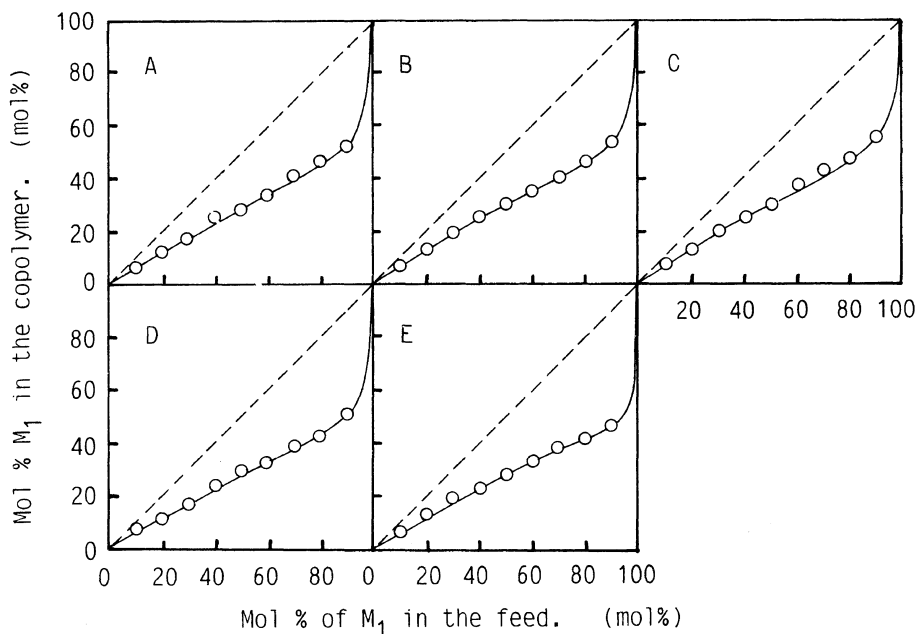


Figure 1. Copolymer composition as a function of feed composition for the copolymerization of allyl ether (M_1) with vinyl acetate (M_2). A, allyl ethyl ether; B, allyl propyl ether; C, allyl butyl ether; D, allyl isobutyl ether; E, allyl *t*-butyl ether.

Table I. Reaction parameters for copolymerization of allyl alkyl ether (M_1) with vinyl acetate (M_2)

Allyl alkyl ether	Feed ratio [M_1]:[M_2]	Reaction time/day	Yield	Rate	Molecular weight ($\times 10^4$)
			wt%	10^{-4} wt% s $^{-1}$	
Allyl ethyl ether	10:90	0.5	2.9	40	4.0
	30:70	2.0	2.0	6.9	1.5
	50:50	6.0	2.4	2.8	0.5
	70:30	7.0	1.5	1.5	0.3
	90:10	7.0	1.3	1.3	0.2
Allyl propyl ether	10:90	0.5	2.9	40	3.8
	30:70	3.0	2.6	6.0	1.4
	50:50	7.0	2.7	2.7	—
	70:30	7.0	1.5	1.5	0.2
	90:10	7.0	1.2	1.2	0.2
Allyl butyl ether	10:90	0.5	2.8	39	4.0
	30:70	3.0	2.2	5.1	1.5
	50:50	7.0	2.4	2.4	0.6
	70:30	7.0	1.4	1.4	0.3
	90:10	7.0	1.2	1.2	0.1
Allyl isopropyl ether	10:90	0.5	2.6	36	3.9
	30:70	3.0	2.0	4.6	1.3
	50:50	7.0	2.3	2.3	0.6
	70:30	7.0	1.4	1.4	0.3
	90:10	7.0	1.0	0.99	0.2
Allyl <i>t</i> -butyl ether	10:90	0.5	2.4	33	3.9
	30:70	3.0	1.5	3.5	1.3
	50:50	7.0	2.2	2.2	0.5
	70:30	7.0	1.2	1.2	0.3
	90:10	7.0	0.9	0.89	0.2

tendency observed for various feeds is almost the same, we wish to discuss here the rates of copolymerization of allyl alkyl ethers to vinyl acetate and weight-average molecular weights of copolymers in general.

The apparent order of the rates of copolymerization is

allyl ethyl ether \sim allyl propyl ether
 \sim allyl butyl ether
 $>$ allyl isopropyl ether
 $>$ allyl *t*-butyl ether

Thus, the rates of copolymerization become slow, as the number of substitutions of methyl groups increases. The ratio of the rates at 1:9 ($M_1:M_2$) feeds to those of 9:1 ($M_1:M_2$) ranges is about 33. The rate of copolymerization for allyl ethyl ether is 4.0×10^{-3}

wt% min $^{-1}$ at 1:9 feed. The rate of copolymerization for allyl *t*-butyl ether is 3.3×10^{-3} wt% min $^{-1}$ at 1:9 feed. There seems to be little effect of alkyl group of allyl alkyl ethers on the rates of copolymerization.

Weight-average molecular weights of the copolymers are shown in Table I. The weight-average molecular weight (\bar{M}_w) of allyl alkyl ether–vinyl acetate copolymer is small, compared with that of allyl ester–vinyl acetate copolymer. The weight-average molecular weight (\bar{M}_w) decreases a little as the electron-withdrawing nature of the alkoxy group in allyl alkyl ethers decreases.

Effects of Feed Compositions

The feed ratio affects copolymerization in various ways. Figure 1 shows that the reactivity of allyl alkyl ether is lower than that of

vinyl acetate. Table I shows the effect of feed composition on the weight-average molecular weight of copolymers. As the feed of allyl alkyl ethers increases, the weight-average molecular weight of allylic copolymers rapidly decreases. The effect of allylic hydrogen is very large. The weight-average molecular weight of allyl ethyl ether is slightly larger than that of allyl *t*-butyl ether. The alkoxy group of allyl alkyl ether influences the weight-average molecular weight a little.

DISCUSSION

Parameters

Q-e Parameters. The feed ratios of monomers and the copolymer compositions were used to calculate reactivity ratios for allyl alkyl ether–vinyl acetate pairs. The Kelen–Tüdös method⁵ was employed to determine reactivity ratios at lower conversion of up to 5 wt%. *Q-e* parameters were determined from reactivity ratios according to the Alfrey-Price method.⁶ The results are shown in Table II.

In every case of copolymerization for allyl alkyl ethers, the results show that r_1 is much smaller than unity and r_2 greater than unity. Both M_1 and M_2 radicals on the growing end of the chain prefer to add to M_2 . Thus, the reactivity of allyl alkyl ether is lesser than that of vinyl acetate. As the product r_1r_2 is smaller than unity, each comonomer pair easily copolymerizes.

The azeotropic point does not occur in the copolymerization. The *e* parameters calculat-

ed range from -3.06 to -2.53 and the *Q* parameters range from 0.072 to 0.117 .

The *e* parameters of allyl alkyl ethers are smaller than that of vinyl acetate, -0.88 . The decrease in electron-withdrawing nature of the alkoxy group of allyl alkyl ether decreases the *e* parameter and the rates of addition to the double bond.

Relationship between *e* Parameters and Various Parameters

It was reported in the previous paper² that the acyloxy group bound to the allylic carbon influences electron density on the double bond of allyl acetate derivatives. The *e* parameter of an allyl ester is a measure of electron density at the double bond, which depends on the nature of substituent groups. That is negative for electron-donating substituents, while positive for electron-withdrawing substituents.

Schwan and co-workers demonstrated a linear relationship between *e* parameters and Hammett σ constants.⁷ We demonstrated a linear relationship between *e* parameters and Taft's σ^* constants. We investigated the relationship between *e* parameters and Taft's σ^* constant² of the alkyl in the alkoxy groups, because the σ^* parameters are a true measure of inductive effects. Figure 2 shows the relationship between *e* and σ^* . It is linear.

The chemical shift in ¹³C NMR depends on the relative electron density. The chemical shift values of the γ carbons are at higher magnetic fields than β carbons. The relationship between δ values for the β and γ carbon

Table II. Reactivity ratios and *Q*, *e* value for the copolymerization of allyl ether (M_1) with vinyl acetate (M_2)^a

Allyl monomer	r_1	r_2	r_1r_2	<i>Q</i>	<i>e</i>
Allyl ethyl ether	0.041 ± 0.002	1.56 ± 0.08	0.064	0.072	-2.54
Allyl propyl ether	0.036 ± 0.002	1.39 ± 0.07	0.050	0.086	-2.61
Allyl butyl ether	0.047 ± 0.003	1.39 ± 0.07	0.065	0.080	-2.53
Allyl isopropyl ether	0.028 ± 0.002	1.56 ± 0.08	0.044	0.079	-2.65
Allyl <i>t</i> -butyl ether	0.0057 ± 0.0003	1.51 ± 0.08	0.0086	0.117	-3.06

^a Vinyl acetate is $Q=0.026$ and $e=-0.88$.

atoms in ^{13}C NMR and e parameters are shown in Figure 3. δ values for γ carbons decrease linearly with decrease in e parameters, while those for β carbons increase

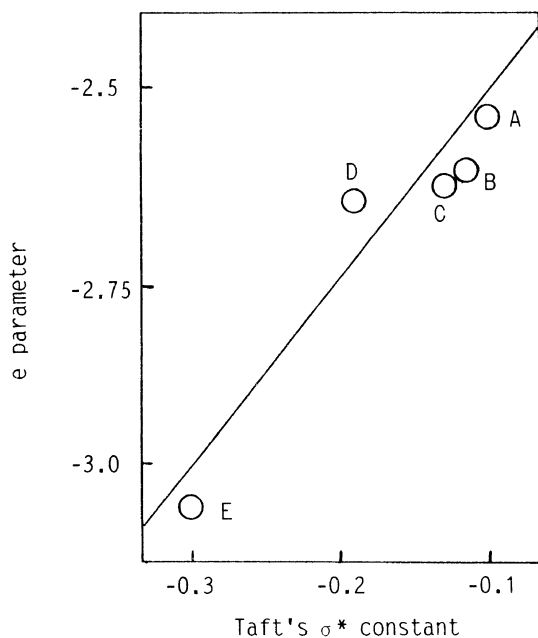


Figure 2. Relationship between Taft's σ^* constant of alkyl group and e parameter of allyl ethers. A, allyl ethyl ether; B, allyl propyl ether; C, allyl butyl ether; D, allyl isopropyl ether; E, allyl *t*-butyl ether.

linearly. In any case, rough values for e parameters can be estimated from ^{13}C NMR chemical shift of allyl alkyl ethers.

Electron densities can be calculated by molecular orbital methods. The results of atomic charge are compiled in Table III. The atomic charge of the γ carbons of the allyl

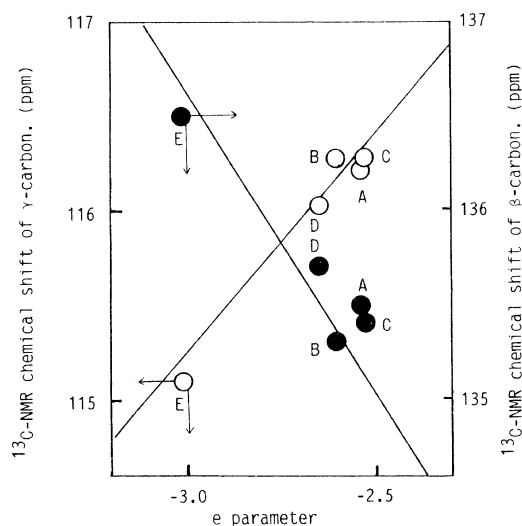


Figure 3. Relationship between e parameter and ^{13}C NMR chemical shift of γ, β -carbon for allyl ether. A, allyl ethyl ether; B, allyl propyl ether; C, allyl butyl ether; D, allyl isopropyl ether; E, allyl *t*-butyl ether.

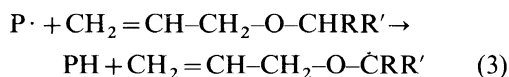
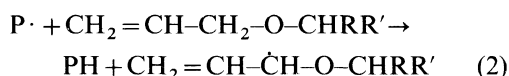
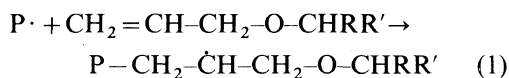
Table III. Frontier electron densities (f_r^R) of radical reactions of allyl ether

CH ₂ =CHCH ₂ -O-X 1 2 8	Atomic charge	π^{HO}		π^{LU}		f_r^R
		E^{ho} (a.u.)	f_r^{ho}	E^{lv} (a.u.)	f_r^{lv}	
X = -CH ₃ 11	C ₁ -0.32898	-0.36783	0.30438	+0.04517	0.63987	C ₁ 0.47213
	C ₂ -0.22966					C ₂ 0.44111
	H ₈ 0.12448					H ₈ 0.06274
	H ₁₁ 0.09676					H ₁₁ 0.00832
X = -CH ₂ CH ₃ 11	C ₁ -0.33044	-0.36619	0.29778	+0.04629	0.63915	C ₁ 0.46847
	C ₂ -0.22955					C ₂ 0.43837
	H ₈ 0.12258					H ₈ 0.06342
	H ₁₁ 0.11168					H ₁₁ 0.00969
X = -CH(CH ₃) ₂ 11	C ₁ -0.33127	-0.36372	0.28316	+0.04730	0.63883	C ₁ 0.46101
	C ₂ -0.22495					C ₂ 0.42872
	H ₈ 0.12306					H ₈ 0.06710
	H ₁₁ 0.16537					H ₁₁ 0.00000
X = -C(CH ₃) ₃	C ₁ -0.33227	-0.36284	0.27705	+0.04773	0.63831	C ₁ 0.45768
	C ₂ -0.22589					C ₂ 0.42651
	H ₈ 0.12348					H ₈ 0.06718

group are in conformity with the ^{13}C NMR data: the larger negative atomic charge on a carbon gives a chemical shift value at the higher field. The atomic charge tends to increase as the extent of electron-withdrawing power of the alkoxy group increases for the γ carbons and the reverse is the case for β carbons. Accordingly, the e values are also related linearly with atomic charge, indicating that rough values for e parameters can be estimated from atomic charge of allyl alkyl ethers.

Effects of Alkyl Groups on Polymerization Characteristics

The main reactions which could compete in the present investigation are the following three: addition of a growing radical to the allylic double bond (1), abstraction of allylic hydrogen (2) which is degradative chain transfer, and hydrogen abstraction from the α -position of the ether oxygen (3).



The contribution of the reaction 3 should be little for the following reasons. Although abstraction of α -hydrogen of ethers does occur, it should be slower than that of allylic hydrogen because the radicals that are formed by the latter reaction produce stable radicals flanked by a double bond and an ether oxygen. This is also confirmed by the frontier electron densities of the hydrogens shown in Table III. Another point which can be mentioned here is a comparison of polymerization characteristics of the *t*-butyl ether and others. Since the *t*-butyl ether does not carry α -hydrogens, the effect of the α -hydrogen should be eliminated. The effect

of chain transfer must be stronger when the feed ratio of the ether is high. A comparison of the rates and molecular weights of polymers at 1:9 and 9:1 ratios, shown in Table I, suggested that there is no α -hydrogen effect. This indicates that allyl isopropyl ether, which could form the most stable radical by abstraction of hydrogen from the isopropyl group among the compounds investigated here, also has similar tendencies of other ethers.

As discussed already, every parameter, including ^{13}C NMR data for the allylic carbons, shows that, as the substitution of methyl(alkyl) groups takes place for hydrogen of the methyl group in allyl methyl ether, the electron density of γ -carbon increases as does the allylic carbon. Frontier electron densities of γ -carbon and α -hydrogen also increase when substitution occurs.

According to the frontier molecular orbital theory,⁸ SOMO of nucleophilic alkyl radicals such as those formed by addition of a radical to allyl alkyl ethers will predominantly interact with LUMO of the allyl alkyl ethers and vinyl acetate. SOMO of the electrophilic radicals such as formed by addition of a growing radical to vinyl acetate will predominantly interact with HOMO of allyl alkyl ether and vinyl acetate.

The molecular orbital energies, LU (π) and HO (π), and frontier electron density (f_r^R) are shown in Table III. Since the LUMO energy of allyl ethers is lower than that of vinyl acetate, the addition of a nucleophilic radical will be easier to vinyl acetate than to allyl alkyl ethers. However, this radical tends to abstract allylic hydrogens as well, although the rate of the abstraction is smaller than the addition. Thus, relatively speaking, the growing radical which is formed by addition of a radical to vinyl acetate tends to abstract allylic hydrogen to terminate the chain. On the other hand, the growing radical formed by addition of a radical to allyl ethers will not add to the allylic double bond, but will do so to vinyl acetate. These characteristics tend to

make both molecular weights and reaction rates small, as seen in Table I. It is also worthy to note that the tendency makes the composition of vinyl acetate in the copolymer rich.

Coming back to the effect of the alkyl groups in the ethers, we notice that both the rates and molecular weights become small, as substitution in the methyl group of allyl methyl ether increases. This tendency is consistent with the above discussion, because the increase of the methyl substitution increases electron densities on the double bond as well as allylic hydrogen. These are also reflected in the f_r^R of the respective atoms. The largest deviation of the composition curve in Figure 1 for the *t*-butyl case from the ideal copolymerization must be ascribed to the largest substituent effects of the *t*-butyl group among the compounds investigated.

Effects of Feed Compositions on Copolymerization Characteristics

The feed ratio should affect the rate and molecular weight. The rate and weight-average molecular weight of copolymers, as measured at various feed ratios, are shown in Table I. As the feed of allyl alkyl ethers increases, the weight-average molecular weight and rate of allylic copolymers rapidly decrease. This may be interpreted in terms of easy abstraction of allylic hydrogen. Thus, by increasing the molar fraction of allyl alkyl ethers, chain transfer between active growing chain by abstraction of the allylic hydrogen easily takes place and leads to termination of the growing polymer chain.

When one compares the molecular weights and rates of copolymerization at the feed ratios of 1:9 and 9:1, they are seen to be remarkably constant among the compounds examined. The rate ratios are 30, 31, 31, 32, and 37, whereas the molecular weight ratios are 20, 19, 40, 19, and 19, for ethyl, propyl, butyl, isopropyl, and *t*-butyl ethers, respectively. These indicate that the chance of

encounter is the predominant factor in determining the fate of radicals involved in the study. This is difference a point of the cases of copolymerization of allyl chloroacetates and vinyl acetate.⁹

In summary, the abstraction of allylic hydrogen is enhanced by the introduction of electron donating alkyl groups to the methyl in allyl methyl ether. The copolymerization of allyl alkyl ethers, having weak electron-withdrawing groups, takes place more sluggishly, compared with allyl esters, having a relatively strong electron-withdrawing acyloxy group.

The rates of copolymerization of an allyl ether with vinyl acetate are slow, compared to that of an allyl ester with vinyl acetate. The molecular weights of the copolymer for an allyl ether are smaller than that of an allyl ester at the same feed ratio. The rate of copolymerization for an allyl ether decreases with decreasing extent of electron withdrawing power of alkoxy group for allyl ethers. In frontier molecular orbital calculations, f_r^R of γ -carbon of allyl ethers is smaller than that of allyl ester and f_r^R of γ -carbon decreases with decrease of the extent of electron withdrawing power of the alkoxy group for allyl ethers. Therefore, it is concluded that the reactivity of allyl ethers is poorer than that of allyl esters and the reactivity of double bonds for allyl ethers decreases with decreasing extent of electron withdrawing power of the alkoxy group for allyl ethers. The effect of the alkyl group on the f_r^R of γ -carbon for allyl ethers is smaller than that for allyl esters.

REFERENCES

1. C. E. Schildknecht, "Allyl Compounds and Their Polymers," John Wiley & Sons, New York, 1973, p 258.
2. Y. Shigetomi, T. Kojima, and N. Ono, *J. Polym. Sci., A*, **28**, 3317 (1990).
3. C. E. Schildknecht, "Allyl Compounds and Their Polymers," John Wiley & Sons, New York, 1973, p 400.

Effect of Alkyl Group on Allylic Copolymerization

4. E. Ōsawa, K. Watanabe, M. Mizuno, and M. Sugie, "Keisankagaku Gaido Bukku" (Japaneses), 3rd ed, Maruzen, 1989, pp 13—88.
5. T. Kelen and F. Tüdös, *J. Macromol. Sci-Chem.*, **A9**, 1, (1975).
6. R. Z. Greenley, *J. Macromol. Sci. Chem.*, **A14**, 427 (1980).
7. T. C. Schwan and C. C. Price, *J. Polym. Sci.*, **40**, 457 (1959).
8. I. Fleming, "Frontier Orbitals and Organic Chemical Reactions," John Wiley & Sons, New York, 1976.
9. Y. Shigetomi, N. Ono, H. Kato, and M. Ōki, *Polymer J.*, in press.