Allylic Polymers II. Effects of Chloro-Substituents on Copolymerization of Allyl Chloroacetates with Vinyl Acetate

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ABSTRACT: The radical copolymerization of allyl chloroacetates with vinyl acetate has been studied in the feed range from 10 to 90 mol% allyl chloroacetates. The following values were obtained by the Kelen–Tüdös method for the reactivity ratios: allyl acetate (M_1)–vinyl acetate (M_2), $r_1 = 0.43$, $r_2 = 1.8$; allyl chloroacetate (M_1)–vinyl acetate (M_2), $r_1 = 0.69$, $r_2 = 0.77$; allyl dichloroacetate (M_1)–vinyl acetate (M_2), $r_1 = 0.54$, $r_2 = 0.57$; allyl trichloroacetate (M_1)–vinyl acetate (M_2), $r_1 = 0.28$, $r_2 = 0.41$; The Q–e parameters were calculated from the allyl (M_1)–vinyl acetate (M_2) reactivity ratios. The e parameters of allylic monomers have been found to be well correlated with parameters such as Taft's σ^* constants of the chloroalkyl group an acids, ^{13}C NMR chemical shift values of the γ carbon in the allylic monomers, and f_r^R for the γ carbon of allyl group in the allylic monomers. The rate of copolymerization of allyl chloroacetates and conversion to copolymers increased as one goes from allyl alkanoates, such as allyl acetate, allyl butyrate, and allyl trimethylacetate, to allyl chloroacetates, though molecular weights of the copolymers diminished due to the chlorine abstraction by a growing chain.
        KEY WORDS   Allyl Chloraacetate / Allylic Polymer / Copolymerization /

The polymerization of allylic monomers has attracted the interest of many investigators because of the potential utility of allyl polymers as materials for enzyme support, though the polymerization of allylic monomers and the copolymerization of them with other monomers are sluggish and poor in yield.[1−3]

There is a difference between allyl copolymerizations and ordinary vinyl copolymerizations.[4−6] Chain transfer between an active growing chain and an allylic monomer can lead not only to termination of the growing polymer chain but also termination of the kinetic chain.[7,8] Therefore it is necessary to retard the termination steps involving the abstraction of allylic hydrogen in allyl copolymerizations to grow polymers to a large molecular weight. If the abstraction of allylic hydrogen is diminished, the degradative chain transfer decreases.[9]

In order to retard the abstraction of the allylic hydrogen, one could lower the electron density of the allylic carbon by introducing electron-attracting groups such as ester. We selected allyl esters which carry chlorine atom(s) on the acetoxy group of allyl acetate. By introducing chlorine, the sp^3 hybridized orbitals of allylic carbon increase in their s-character to move toward the sp^2 hybridized orbitals to some extent. The bond energy of the C–H with an sp^2 hybridized orbital is higher than in an sp^3 hybridized orbital[10] and so the abstraction of the allylic hydrogen may be decreased.

In this paper, we report the effects of chlorine introduction on copolymerization and on reactivity ratios and Q–e parameters for a series of allyl acetate derivatives bearing chlorine atom(s) on the acetate. 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

Allyl chloroacetate, allyl dichloroacetate, and allyl trichloroacetate were prepared by reacting allyl alcohol with the corresponding acid chlorides.[11] Allyl acetate from Tokyo Chemical Co. was used after purification by distillation.

Vinyl Acetate: bp 72°C. *Anal.* Calcd for $C_4H_6O_2$: C, 55.8%; H, 7.0%. Found: C, 55.7%; H, 7.1%. ^{13}C NMR (CDCl_3): $\delta = 96.4$ ppm ($CH_2 =$), 141.7 ppm ($-CH =$), 167.6 ppm ($C = O$), and 20.2 ppm ($-CH_3$).

Allyl Acetate[12]: bp 105°C. *Anal.* Calcd for $C_5H_8O_2$: C, 60.0%; H, 8.1%. Found: C, 60.1%; H, 8.0%. ^{13}C NMR (CDCl_3): $\delta = 117.8$ ppm ($CH_2 =$), 132.4 ppm ($-CH =$), 65.0 ppm ($-CH_2-$), 170.2 ppm ($C = O$), and 20.7 ppm ($-CH_3$).

Allyl Chloroacetate[13]: Yield 60—67%. bp 164—165°C. *Anal.* Calcd for $C_5H_7O_2Cl$: C, 45.0%; H, 5.3%. Found: C, 44.9%; H, 5.2%. ^{13}C NMR (CDCl_3): $\delta = 119.1$ ppm ($CH_2 =$), 131.3 ppm ($-CH =$), 66.6 ppm ($-CH_2-$), 166.9 ppm ($C = O$), and 40.8 ppm ($-CH_2Cl$).

Allyl Dichloroacetate: Yield 55—60%. bp 173—175°C. *Anal.* Calcd for $C_5H_6O_2Cl_2$: C, 36.0%; H, 3.6%. Found: C, 35.8%; H, 3.5%. ^{13}C NMR (CDCl_3): $\delta = 119.6$ ppm ($CH_2 =$), 130.5 ppm ($-CH =$), 67.7 ppm ($-CH_2-$), 164.0 ppm ($C = O$), and 64.3 ppm ($-CHCl_2$).

Allyl Trichloroacetate[14]: Yield 50—53%. bp 180—181°C. *Anal.* Calcd for $C_5H_5O_2Cl_3$: C, 30.0%; H, 2.5%. Found: C, 29.9%; H, 2.5%. ^{13}C NMR (CDCl_3): $\delta = 120.2$ ppm ($CH_2 =$), 129.9 ppm ($-CH =$), 69.3 ppm ($-CH_2-$), 161.5 ppm ($C = O$), and 89.7 ppm ($-CCl_3$).

PROCEDURES

Copolymerization of Allyl Esters with Vinyl Acetate

A mixture of weighed amounts of an allyl ester 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 the tables. The copolymer was isolated by precipitation with petroleum ether from the reaction mixture and purified by reprecipitation by petroleum ether from benzene solutions.

MEASUREMENTS

Analysis of Copolymer

Elemental analyses for carbon, hydrogen, and nitrogen of the allyl acetate–vinyl acetate copolymers were conducted by a Hitachi Perkin Elmer model 240°C. The copolymer compositions were calculated by using the carbon content of the polymers.

In the copolymers of allyl mono-, di-, and tri-chloroacetate with vinyl acetate, the copolymer compositions were calculated from the content of chlorine. The content of chlorine was determined as follows.

A sample of about 10—15 mg of the copolymer compound, containing 1—5 mg of chlorine was placed in an L-shaped piece of Whatman No. 40 filter paper, which was folded and placed in a platinum basket of a Heraeus Schoniger combustion flask. An absorption solution, consisting of water (5 ml) and 3.0% aqueous hydrogen peroxide (0.2 ml), was placed in the combustion flask, and the flask was filled with oxygen. When apparatus with a built-in ignition system was used, a sample was placed in the basket in the combustion flask and the flask was inverted to seal the joint with the absorption solution after insertion of a stopper/sample-holder assembly. After ignition, the flask was allowed to cool for 30 min and then was vigorously shaken for complete absorption of the combustion products. The flask was opened and the stopper assembly was washed with a small amount of water. To the solution were added 20 ml of water, 2 ml of 6 N nitric acid, 20 ml of 0.01 N aqueous silver nitrate, 2 ml of nitrobenzene, and 2 ml of saturated aqueous iron(III) ammonium sulfate

(55%), which served as an indicator. The chlorine ion was titrated with 0.01 N aqueous sodium thiocyanate. At the end point, a sharp color change to reddish brown was observed. A blank test was also carried out in the same way.[15,16]

Determination of Molecular Weight

The determination of molecular weight was carried out using a Shimadzu GPC, model chromatopac C-R3A. The column was Shodex AD-804/S and the solvent was N,N-di-methylformanide. 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 ester monomer were obtained at 22.5 MHz on a Hitachi R-90 Spectrometer using 25 v/v% chloroform (CDCl$_3$) monomer 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 esters was elucidated by MMP2 calculation, in which the ester moiety was taken as to assume the Z conformation. The features of the molecular structure, as calculated by the MMP2 method, are that the vinyl group takes 180° conformation with respect to the ether oxygen of the ester and that one of the methyl hydrogens of the acetyl group takes an eclipsing position (0°) with the carbonyl oxygen. The atomic coordinates obtained by MMP2 were used as the starting point for the calculation with AM-1 method and energy was optimized. The LU and the next LU MO's were split by interactions of the substituted alkyl group, but the energy difference was very small, as shown in Table III. Accordingly, f_r^{lu} was one half the sum of the LU and next LU frontier densities. f_r^R was one half the sum of the HO and LU frontier densities. The chlorine atom of allyl chloroacetates was situated as follows. For allyl chloroacetate, the chlorine was placed in the direction of the acetyl-hydrogen in allyl acetate. Two conformations, 0° and 120°, with respect to the C–Cl and C=O bonds are possible. For allyl di-chloroacetate, a similar situation exists: two conformations, 0° and 120°, for the C–H and C=O bonds in the dichloroacetyl group. The energies of these conformations were calculated but they differed little. Therefore the values for one conformation only are given in Table III.

RESULTS

Copolymer Compositions

Thus, chlorine can be introduced into copolymers either by the addition of allyl chloroacetates to a growing polymer chain and/or by the abstraction of chlorine from allyl chloroacetate. As the chlorine-abstraction terminates the copolymerization, this type of chlorine is placed mainly at the end of polymers. On the other hand, the radicals derived from allyl chloroacetates by abstraction of a chlorine atom are introduced into copolymers as kinetic radicals. This introduction should be easy because the radicals, –COCH$_2$·, formed by hydrogen-abstraction from acetate esters, are known to add rapidly to C=C bonds.[7] Therefore, the copolymer composition is little affected by the chain transfer of chlorine in allyl chloroacetates, when polymers of large molecular weight are formed. This confirms that the copolymerization characteristics of the allyl chloroacetates can be discussed by the chlorine content in the copolymers.

The copolymer compositions as a function of feed composition for the copolymerization of allyl esters with vinyl acetate are shown in Figure 1. Composition was obtained for allylic copolymers at the stage where the production of the copolymer was less than 5% yield. The dashed line represents ideally random copolymerization conditions. It can be seen from

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

| Ally ester	Sample number	Reed-ratio $[M_1]:[M_2]$	Reaction time h	Yield wt%	Rate 10^{-5} wt% s^{-1}
Allyl acetate	A-01	10:90	9	4.30	13.3
	A-02	30:70	24	4.54	5.25
	A-03	50:50	48	4.15	2.40
	A-04	70:30	120	5.49	1.27
	A-05	90:10	168	3.82	0.362
Allyl chloroacetate	B-01	10:90	9	5.57	17.2
	B-02	30:70	18	6.41	9.89
	B-03	50:50	24	4.07	4.71
	B-04	70:30	36	3.52	2.72
	B-05	90:10	48	4.32	2.50
Allyl dichloroacetate	C-01	10:90	9	7.26	22.4
	C-02	30:70	18	7.97	12.3
	C-03	50:50	24	5.88	6.81
	C-04	70:30	36	4.57	3.53
	C-05	90:10	48	4.83	2.80
Allyl trichloroacetate	D-01	10:90	9	6.77	20.9
	D-02	30:70	18	7.45	11.5
	D-03	50:50	24	4.57	5.26
	D-04	70:30	36	4.32	3.33
	D-05	90:10	48	4.69	2.71

the copolymer composition plot that the content of allyl esters in copolymers increases with increasing feed ratios of allyl esters to indicate that the relative reactivities of the allyl chloroacetates are not very far from unity relative to vinyl acetate.

Rates of Copolymerization and Molecular Weights and Yields of Copolymers

The parameters related to the ease of copolymerization are shown in Table I. Since the general tendency observed for various feeds is almost the same, we wish to mention here the rates of copolymerization, molecular weights and yields of copolymers only at 50:50 feed ratios of allyl (chloro)acetates to vinyl acetate.

There is a longer induction period in the copolymerization of allyl trichloroacetate than in other allyl acetate derivatives (Figure 2). After the induction period, the rates of

copolymerization are largest for trichloroacetate among the compounds used here. Thus the actual order of the rates of copolymerization is

allyl trichloroacetate > allyl dichloroacetate

> allyl chloroacetate ≫ allyl acetate
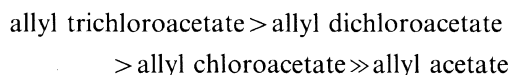
Thus, the rate of polymerization is the faster, when the substitution of more chlorine atoms takes place for the acetyl hydrogens of the allyl acetate.

The relative reactivity of M_1 to the radical of M_2 is shown by $1/r_2$. The $1/r_2$ of allyl acetate, allyl chloroacetate, allyl dichloroacetate, and allyl trichloroacetate is 0.56, 1.30, 1.75, and 2.44, respectively. The value of $1/r_2$ tends to increase as the number of chloro-substituents increases. The order of $1/r_2$ values are roughly in agreement with that of the rate of copolymerization.

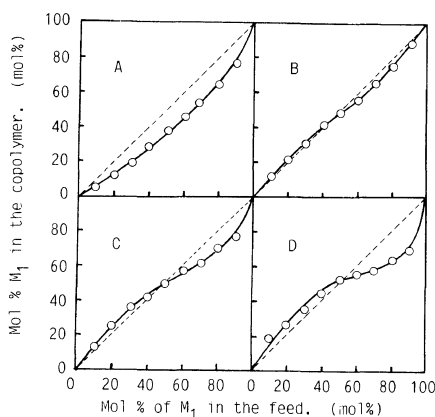Weight-average molecular weights of the

Figure 1. Copolymer composition as a function of feed composition for the copolymerization of allyl ester with vinyl acetate. M_1 monomer is allyl ester. A, allyl acetate; B, allyl chloroacetate; C, allyl dichloroacetate; D, allyl trichloroacetate.

Figure 2. Relation between reaction time and yield in the feed ratio ($M_1 : M_2 = 1 : 1$). A, allyl acetate; B, allyl chloroacetate; C, allyl dichloroacetate; D, allyl trichloroacetate.

copolymers are shown in Figure 3. Clearly, the weight-average molecular weight is smallest for the copolymer of allyl trichloroacetate and decreases as chlorine content in chloroacetate group increases.

Effects of Feed Composition

The feed ratio affects copolymerization in various ways. Figure 1A shows that, for the allyl acetate–vinyl acetate pair, there is no azeotropic point observed and the reactivity of allyl acetate is lower than vinyl acetate. Other graphs in Figure 1 indicate that there are azeotropic points and halogenated allyl acetates exhibit higher reactivity than vinyl acetate at least in the low feed ratios of the allyl esters.

Figure 3 shows the effect of the feed ratio on the weight average molecular weight of copolymers. As the feed ratio of allyl esters increases, the weight-average molecular weight of the allylic copolymers rapidly decreases. The effect is very large for nonsubstituted acetate and decreases to a large extent until the case of the trichloroacetate where the weight average molecular weight of the copolymer is affected only to a small extent by feed composition.
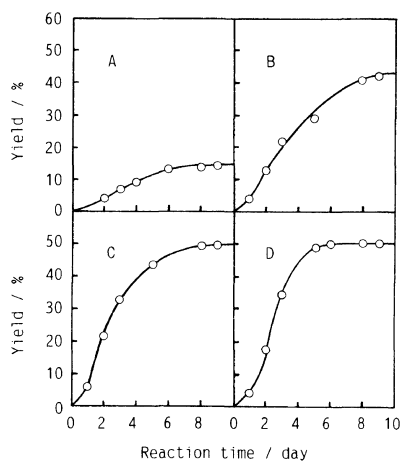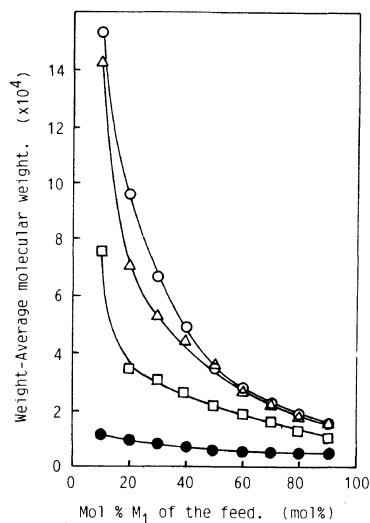

Figure 3. Relation between mol% of ally ester (M_1) in the feed and molecular weight. ○, allyl acetate; △, allyl chloroacetate; □, allyl dichloroacetate; ●, allyl trichloroacetate.

The rates of reaction and yield are also influenced by feed, as are seen in Table I. Close examination reveals, however, the effect of the feed is much larger for the allyl acetate–vinyl acetate pair than the allyl chloroacetate–vinly

Table II. Reactivity ratios and Q, e for the copolymerization of allyl ester (M_1) with vinyl acetate (M_2)[a]

Allyl monomer	r_1	r_2	r_1r_2	Q	e
Allyl acetate	0.43	1.8	0.77	0.023	−1.39
Allyl chloroacetate	0.69	0.77	0.53	0.017	−0.09
Allyl dichloroacetate	0.54	0.57	0.31	0.018	0.21
Allyl trichloroacetate	0.28	0.41	0.11	0.017	0.59

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

Figure 4. Relation between Taft's σ^* of alkyl group and e parameter of allyl ester.
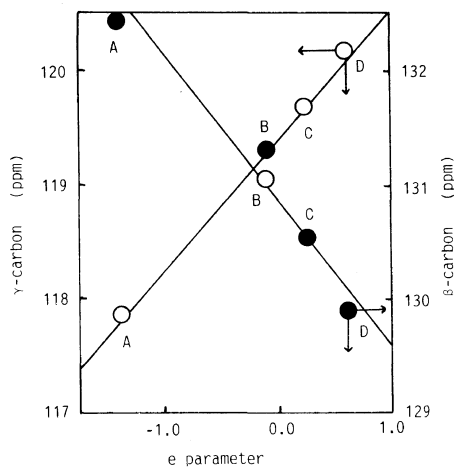
Figure 5. Relationship between e parameter and γ-carbon chemical shift or β-carbon chemical shift of double bond in allyl ester monomer. A, allyl acetate; B, allyl chloroacetate; C, allyl dichloroacetate; D, allyl trichloroacetate.

acetate pairs. The ratio of the rates at 1 : 9 feed to that of 9 : 1 is about 35 for the allyl acetate–vinyl acetate pair, whereas that for the chloroacetate is close to 7.5. Among the chloroacetates, there seems little effect of the number of chlorine atoms on the rates of copolymerization.
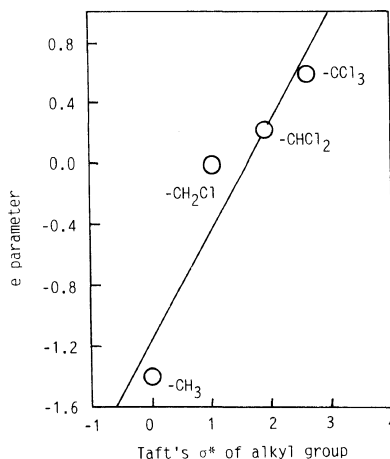
DISCUSSION

Q–e Parameters

The feed ratios of monomers and copolymer compositions were used to calculate reactivity ratios for allyl acetate–vinyl acetate pairs. The Kelen–Tüdos method[17] was employed to determine reactivity ratios at lower conversion than 5 wt%. Q–e parameters were determined from reactivity ratios according to the Alfrey–Price method.[18] The results are shown in Table II.

In the copolymerization of allyl acetate, the results show that r_1 is 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. For the copolymerization of other chlorinated allyl ester monomers, the results show that both r_1 and r_2 are smaller than unity. Thus, the allyl chloroacetate–vinyl acetate, allyl cidhloroacetate–vinyl acetate, and allyl trichloroacetate–vinyl acetate pairs exhibit alternating tendency in copolymerization. As the product r_1r_2 is smaller than unity in every case, each comonomer pair easily copolymerizes.

The azeotropic point can be determined by using the reactivity ratios, r_1 and r_2, and

Finneman–Ross formula. In the copolymerization of allyl acetate with vinyl acetate, the azeotropic point does not occur, whereas in the copolymerization of allyl chloroacetate, allyl dichloroacetate, and allyl trichloroacetate, it occurs at 42.6, 48.3, and 45.0 mol% allyl esters in the feed, respectively. The e parameters calculated range from −1.39 to 0.59 and Q parameters range from 0.017 to 0.023.

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

CH$_2$=CHCH$_2$O(CO)-X 1 2 8,9	Atomic charge	π^{HO} E^{ho} (a.u.)	f_r^{ho}		π^{LU} E^{iu} (a.u.)	f_r^{lu}		f_r^R	
X=–CH$_3$	C$_1$ −0.32056	−0.37515	C$_1$ 0.69436	+0.03880+0.04088[a]		0.64725	C$_1$ 0.67081		
	C$_2$ −0.23920		C$_2$ 0.60720			0.62866	C$_2$ 0.61793		
Allylic hydrogen	H$_8$ 0.15636		H$_8$ 0.12810			0.04858	H$_8$ 0.08834		
	H$_9$ 0.15636		H$_9$ 0.12810			0.04858	H$_9$ 0.08834		
X=–CH$_2$Cl	C$_1$ −0.31644	−0.37974	C$_1$ 0.70038	+0.02870+0.03501		0.64868	C$_1$ 0.67453		
	C$_2$ −0.24269		C$_2$ 0.62523			0.62418	C$_2$ 0.62471		
Allylic hydrogen	H$_8$ 0.15923		H$_8$ 0.12278			0.04847	H$_8$ 0.08563		
	H$_9$ 0.15923		H$_9$ 0.12278			0.04847	H$_9$ 0.08563		
X=–CHCl$_2$	C$_1$ −0.31446	−0.38213	C$_1$ 0.70795	+0.03408+0.04978[a]		0.64948	C$_1$ 0.67872		
	C$_2$ −0.24313		C$_2$ 0.64006			0.62176	C$_2$ 0.63091		
Allylic hydrogen	H$_8$ 0.16185		H$_8$ 0.11709			0.04797	H$_8$ 0.08253		
	H$_9$ 0.16185		H$_9$ 0.11709			0.04797	H$_9$ 0.08253		
X=–CCl$_3$	C$_1$ −0.31197	−0.38521	C$_1$ 0.70860	+0.03109+0.03635[a]		0.65097	C$_1$ 0.67979		
	C$_2$ −0.24505		C$_2$ 0.64780			0.61970	C$_2$ 0.63375		
Allylic hydrogen	H$_8$ 0.16368		H$_8$ 0.11501			0.04866	H$_8$ 0.08184		
	H$_9$ 0.16368		H$_9$ 0.11501			0.04866	H$_9$ 0.08184		

[a] Next lowest vacant MO's energy.

The e parameter of allyl acetate, -1.39, is smaller than other allyl esters and close to the e parameter of vinyl acetate, -0.88, whereas those of the chloroacetates are at more positive side. Increase in the number of chloro substituents increases the e parameter.

Relationship between e Parameter and Various Parameters

It was reported in the previous paper[11] that the acyloxy group bound to the allylic carbon influenced the electron density of 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 nature of substituent groups. That is negative for electron-donating substituents, while that is positive for electron-withdrawing substituents.

Schwan and coworkers[19] demonstrated a linear relationship between e parameters and Hammett σ constants.[20] We investigated the relationship between e parameters and Taft's σ^* constant[21] of the chloroalkyl in the acyloxy groups, because the σ^* parameters are the true measure of inductive effects. Figure 4 shows the relationship between e and σ^*. It is linear (the correlation coefficient is 0.959).

The chemical shift in ^{13}C NMR for each olefinic carbon, δ values for β and γ carbons in allyl chloroacetates, depends on the relative electron density. The chemical shift values of the γ carbons are at higher magnetic fields than β carbons. The chemical shifts of the γ carbons go to lower magnetic fields on substitution of chlorine for the acetyl hydrogens, whereas those of β carbons go to higher magnetic fields on the same operation. R. A. Vaidya and co-worker[22] studied the relationship between the reactivity of allyl monomer and each carbon in ^{13}C NMR for allyl amine derivatives. The results of allyl amines are similar to that of allyl esters.

The relationship between δ values for the β and γ carbon atoms in ^{13}C NMR and e parameters are shown in Figure 5. δ values for

γ carbons increase linearly with the increase in *e* parameters (the correlation coefficient is 0.992), while those for β carbons decreases linearly (the correlation coefficient is 0.971). As the result of this experiment, it is clarified that *e* parameter means the relative electron density on the γ carbon. It seems that addition of the growing chain to the double bond in homologous monomers mainly occurs at an electron rich site. In any case, rough values for *e* parameters can be estimated from ^{13}C NMR chemical shift of allyl chloroacetates.

Electron densities can be calculated by molecular orbital methods. The results of atomic charge are compiled in Table III. The atomic charges of the γ carbons of the allyl group are in conformity with the ^{13}C NMR data: the larger negative atomic charge on a carbon gives a chemical shift at a higher field. The atomic charge tends to decrease as the number of the chloro substituent increases for γ carbons and the reverse is the case for β carbons. Accordingly, the *e* values are also related linearly with atomic charge.

Effects of Chloro Substituent(s) on Polymerization Characteristics

The chloro substituent on the acyl group of allyl acetate can affect the copolymerization in two ways. The first factor is that the chlorine substituent tends to be abstracted by a growing chain radical. It is reported[23] that the chain transfer constant of vinyl acetateradical to allyl acetate (abstraction of C–H) is 85×10^{-4}, that to dichloroethyl acetate 210×10^{-4}, and to trichloroethyl acetate 4400×10^{-4}. Therefore, it seems that this transfers the chain to make the molecular weight of the copolymer small. The results shown in Figure 3 are interpreted in this way: the molecular weight of copolymers is smallest when trichloroacetate is used and is largest when no chloro substituent is present.

However, the chloro substituent has another effect on copolymerization. It withdraws electrons from the allyl group. This changes the characteristics of the allyl group in two ways. One is, of course, to modify electron densities of the vinyl group as is clearly seen by ^{13}C NMR and the atomic charge of the γ carbons obtained by MO calculations. The other is to enhance the C–H bond energy in the allylic methylene group. This is due to the electron-withdrawing from the sp^3 carbon that tends to shift the hybridization toward sp^2.

The decrease in the electron density of the allylic carbon is demonstrated by the ^{13}C NMR data; 65.0, 66.0, 67.7, and 69.3 ppm from TMS, respectively, for acetate, chloroacetate, dichloroacetate, and trichloroacetate. The decrease in electron density on the allylic hydrogens, as calculated by MO (Table III), as the number of chloro substituent increases, also support the withdrawal of electrons by the acyloxy group.

This strengthening of the allylic C–H bond should result in retardation of the C–H abstraction. However, one may argue that since a hydrogen can be also abstracted from the acetyl group by a radical, distinguishing the two must be made. There is a paper on the kinetic isotope effects on polymerization between allyl acetate and allyl-d_2 acetate. It is reported that deuterium substitution causes increase in the molecular weight of the polymer by a factor of 2.4 and, from these results, deuterium-abstraction by a growing chain must be one third that of hydrogen.[9] This large kinetic isotope effect is not expected if the rates of abstraction of the acetyl C–H are comparable with those of allylic C–H and suggests that the abstraction of the latter C–H is much faster than the former.

Therefore, retardation of the allylic C–H abstraction by introducing chloro substituent(s) to the acetyl group of allyl acetate is expected to enhance the rates of copolymerization, because inactive allylic radicals are formed very slowly and radicals formed by abstraction of the chloro-substituent from the chloroacetyl group adds easily to continue the polymerization, though the formation of the latter is rather easy. The results in Table I

indeed show that the rates of copolymerization are enhanced by chlorine substitution.

Frontier Molecular Orbital theory (FMO)[24] are often used for explanation of organic reactions including polymerization. FMO explains that radicals which have a high energy singly occupied molecular orbital (SOMO) are nucleophilic and will react with molecules having a low energy lowest unoccupied molecular orbital (LUMO), while electrophilic radicals characterized by a low energy SOMO will react with molecules with a high energy highest occupied molecular orbital (HOMO). Thus, the SOMO of the nucleophilic alkyl radical such as those formed by addition of a radical to allyl acetates will predominantly interact with LUMO of the allyl acetates and vinyl acetate. The SOMO of the electrophilic radical such as formed by the addition of a radical to vinyl acetate[25] will predominantly interact with the HOMO of the allyl acetate and vinyl acetate. Therefore, in radical copolymerization, radical addition to monomers can be described by frontier electron density (f_r^R).

The molecular orbital energies, LU (π) and HO (π), and frontier electron density (f_v^R) are shown in Table III. It may be argued that there is a too small difference among the values of frontier electron density for allyl esters, but the difference is significant.[26] The values of f_r^R for the γ carbon of allyl acetates increases as chlorine substitution increases and are in agreement with the observed order of ease of copolymerization. Table III also shows that the frontier electron density of the allylic hydrogen decreases as the chlorine substitution increases. This tendency is in accord with our assumption that the hydrogen-abstraction from the allylic position becomes difficult when the substituent becomes electronegative.

The yields and saturation yields (Fig. 2) are also affected by chlorine substitution. It seems that Fig. 2 shows the tendency of saturation because of dead-end polymerization. The more chlorine substitution seems to increase the
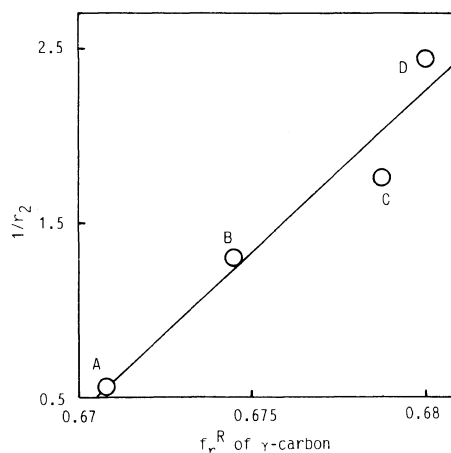

Figure 6. Relationship between f_r^R of γ-carbon and $1/r_2$ in the allyl chloroacetate(s)–vinyl acetate copolymerization. A, allyl acetate; B, allyl chloroacetate; C, allyl dichloroacetate; D, allyl trichloroacetate.

yields of copolymers. We should like to attribute this to competition between the allylic hydrogen abstraction and chlorine abstraction. The allylic hydrogen abstraction practically terminates the polymerization, while that of the chlorine in the acyloxy group produces active radicals. The former reaction is more facile in allyl acetate but is retarded in chloroacetates, though the latter occurs in chloroacetates. The f_r^R of each atom for a compound shows the relative reactivity in the radical reaction. The relative reactivity of allyl acetates to the radical produced from vinyl acetate is shown by $1/r_2$. The relationship between $1/r_2$ and f_r^R of γ-carbon of allyl acetates is shown in Fig. 6. The $1/r_2$ increases linearly with increase in f_r^R (the correlation coefficient is 0.966). The reactivity of allyl acetates toward radicals increases as the number of chloro substituent increases.

Effects of Feed Compositions on Copolymerization Characteristics

The feed ratio should affect the molecular weight. The molecular weights of copolymers, as measured at various feed ratios, are shown in Figure 3. As the feed of allyl esters increases,

the molecular weight of allylic copolymers rapidly decreases, while the rates of copolymerization is larger for the halogenated acetates than the nonhalogenated acetate.

In discussing the effects of feed ratios on the molecular weights of copolymers, there are several points we must take into account. The reactivities of olefins toward radical additions in vinyl acetate and in chloroacetates are different. While the former is constant if a given radical adds to vinyl acetate, it changes to a certain extent when the number of species chlorine atom vary. Chain transfer by allylic hydrogen abstraction is influenced by the chlorine substituent on the acyl group, whereas increasing the number of chlorine substituents increases the chance of chlorine abstraction as well as increasing the ease of chlorine abstraction.[23] In addition to these factors, increasing the feed ratio of allyl chloroacetates increases the chance of radical addition to the allylic double bonds, at the expense of that to vinyl acetate, abstraction of allylic hydrogen, and that of chlorine. The results shown in Figure 3 reflect all these factors.

The addition of growing radicals to the C=C bond in the trichloroacetate is fast with respect to hydrogen abstraction from the allylic position. Since the chlorine-abstraction in the trichloroacetate is fast, which is termination of a chain though it produces another active radical, the molecular weight of the copolymer is rather small. This ease must be responsible for the smaller molecular weight of the copolymer from the vinyl acetate-allyl trichloroacetate even at a high vinyl acetate ratio.

When the number of chlorine atoms on allyl chloroacetates decreases, at high feed ratios of vinyl acetate, the chances of radical addition to the vinyl double bond rapidly increase due to decrease in the chances of encounter with the allylic double bond as well as decrease in the reactivity of the allylic double bond toward radicals and in the ease of abstraction of the chlorine atom. Although the decrease in the number of chlorine atoms increases the ease of

allylic hydrogen abstraction, this factor is rather minor, because polymerization should not take place in allyl acetate. Thus, the molecular weight of the copolymer increases rapidly as the number of chlorine atoms in allyl chloroacetate decreases.

In the simple polymerization of allyl chloroacetates, differences in molecular weight become small, when one goes from allyl acetate to allyl trichloroacetate. This may again be explained by taking account of the factors discussed earlier. When the number of chlorine atoms decreases, allylic hydrogen abstraction becomes easy, whereas addition to the double bond is slow. When the number of chlorine atoms increases, the addition to the double bond becomes easy as well as chlorine abstraction. These factors tend to make differences in molecular weights of the polymers small, the effects being observed in the case of 1 : 9 feed ratios of vinyl acetate to allyl chloroacetates.

The factors cited above also explain the enhancement of the rates of polymerization in the case of halogenated acetates. When an allyl mono-, di-, or tri-chloroacetate is used, the rates of formation of inactive allylic radicals are diminished and radicals formed by abstraction of chlorine do not terminate the copolymerization.

As result, the higher feed ratios of allyl chloroacetate in the copolymerization increase the rate of copolymerization while the weight-average molecular weight of the copolymer decreases with respect to allyl acetate which lacks chlorine atoms. The effect of the dichloroacetoxy moiety is not well understood at the present but it may well be the case where the factors mentioned above all cancel out to make the results very similar to the trichloroacetate case.

The results in Table I also indicate that, as the feed ratio of the allyl acetate increases, the rates of copolymerization decrease. However, the ratio of the rate constants, the rate at 1 : 9 ratio to that of 9 : 1, is much larger for allyl

acetate than those of allyl chloroacetates.

The first should result from the chance of hydrogen abstraction from the allylic position being more abundant in larger M_1/M_2 ratio and/or the addition of the growing chain to the $C = C$ bond of vinyl acetate is a much easier reaction than that of allyl (chloro)acetates. However, if one takes into consideration the fact that the copolymer composition is analogous to the feed ratio at $1:1$ allyl (chloro)acetate and vinyl acetate, as is seen in Figure 1, it should be concluded that the chain transfer by the hydrogen-abstraction at the allylic position is the main factor that lowers the rate of polymerization at the larger allyl ester feed.

The second point indicates that the effect of the feed ratio of allyl acetates is much larger for nonsubstituted allyl acetate than allyl chloroacetate. This is again reflection of the factors cited above: reactivities of vinyl acetate and allyl (chloro)acetates including addition to double bonds, abstraction of allylic hydrogen, and abstraction of chlorine. When allyl acetate carries no chlorine atom, radical addition is rather slow and hydrogen abstraction becomes significant at a high feed ratio of the ester, rendering the rates of polymerization slow, although overall polymerization was relatively fast due to the addition to vinyl acetate when the feed ratio of vinyl acetate was high. On the other hand, in the case of the trichloroacetate, radical addition to the double bond is relatively fast to allyl acetate and the allylic hydrogen abstraction is slow, rendering the observed rate of polymerization large with respect to allyl acetate.

In summary, abstraction of allylic hydrogen is diminished by introducing chlorine atom(s) on the methyl group of allyl acetate and the radical addition of an active growing chain to a double bond of comonomer takes place more easily, but the chain transfer reaction between the chlorine of allyl chloroacetates and active growing chain takes place. The copolymerization of allyl chloroacetates consequently takes

place more rapidly, compared with that of allyl alkanoate esters. The copolymer is obtained in satisfactory yields but weight average molecular weight of the copolymer decreases when chlorine is introduced on the methyl group of allyl acetate.

It is shown that there is an excellent correlation between e parameters and Taft's σ^* constants, δ values of ^{13}C NMR, and molecular orbital energies. While we can obtain the values of ^{13}C NMR of substituted allyl acetate and of Taft's σ^* constant of alkyl group of allyl acetate only by experimental measurement, it is possible to obtain theoretically f_r^R of substituted allyl acetates by the Molecular Orbital method. f_r^R can be a potentially convenient parameter in predicting reactivity in radical polymerization.

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