

Allylic Polymers III. Electronic Effects of Acyloxy Group in Allyl Alkanoates on Polymerization Parameters

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ABSTRACT: The radical polymerization of allyl alkanoates was studied in the temperature range between +60°C and +80°C. The following activation energies were obtained by the Arrhenius plots: allyl acetate, $E_a = 24.3 \text{ kcal mol}^{-1}$; allyl propionate, $E_a = 25.5 \text{ kcal mol}^{-1}$; allyl butyrate, $E_a = 26.0 \text{ kcal mol}^{-1}$; allyl isobutyrate, $E_a = 26.2 \text{ kcal mol}^{-1}$; allyl trimethylacetate, $E_a = 26.8 \text{ kcal mol}^{-1}$. The frontier molecular orbitals (FMO) of the allyl ester were calculated by the AM-1 method. The activation energy for polymerization of the allyl ester has been found to be nicely correlated with parameters such as Taft's σ^* constants of the alkyl group, ^{13}C NMR chemical shift values of the γ carbon, and further, values of frontier electron density (f_r^R) of the γ carbon in the allyl moiety.

KEY WORDS Allyl Alkanoates / Allylic Polymer / Polymerization /

There has been a great deal of work published on the structure–reactivity relationship of vinyl monomers in their radical homo- and copolymerization.^{1–5} Otsu and co-workers studied the reactivity of alkyl methacrylates toward a polystyryl radical and found that their relative reactivities depend on the polar effect of the alkyl groups but not on the steric effect.¹ Ueda and co-workers studied the relationship between radical reactivity and LUMO of methacrylate derivatives and found that the relative addition rate of methacrylate derivatives with styrene depended on the energy of LUMO of them.^{6–8}

The rate of addition of a radical of growing chain to a monomer depends largely on substituent groups of the radical of growing chain or the monomer. In the polymerization, the relative reactivity of a monomer depends on the polar effects of substituent groups but not on steric effects.^{1,6–9} Therefore, the effect of a substituent of a monomer can be conveniently described by the frontier mo-

lecular orbital (FMO) theory: *i.e.*, radicals which have a high energy singly occupying a molecular orbital (SOMO) are nucleophilic and will react with monomers having a low energy lowest unoccupying a molecular orbital (LUMO), while electrophilic radicals characterized by a low energy SOMO will react with monomers with a high energy highest occupying a molecular orbital (HOMO). In each case, polymers of high molecular weight form in good yield.

In this paper, we report the activation energy of polymerization for a series of allyl alkanoates and molecular weights of polymers. The relationships discussed are 1) activation energy–Taft's σ^* constant, 2) activation energy– ^{13}C NMR chemical shift, 3) activation energy–LUMO, 4) activation energy–frontier electron density (f_r^R), and 5) molecular weight–frontier electron density.

EXPERIMENTAL

Monomer Synthesis

Allyl esters were prepared by reacting allyl alcohol with acid chlorides. Allyl acetate from Tokyo Chemical Co. was used after purification by distillation.

*Allyl Acetate*¹⁰: bp 105°C. *Anal.* Calcd for C₅H₈O₂: C, 60.0%; H, 8.1%. Found: C, 60.1%; H, 8.0%. ¹³C NMR (CDCl₃): δ = 117.8 ppm (CH₂=), 132.4 ppm (-CH=), 65.0 ppm (-CH₂-), 170.2 ppm (C=O), and 20.7 ppm (-CH₃).

*Allyl Propionate*¹⁰: Yield 61–65%. bp 122–124°C. *Anal.* Calcd for C₆H₁₀O₂: C, 63.1%; H, 8.8%. Found: C, 63.2%; H, 8.5%. ¹³C NMR (CDCl₃): δ = 117.78 ppm (CH₂=), 132.39 ppm (-CH=), 64.88 ppm (-CH₂-), 173.76 ppm (C=O), 27.53 ppm, and 9.12 ppm (-CH₂-CH₃).

*Allyl Butyrate*¹⁰: Yield 60–67%. bp 141–143°C. *Anal.* Calcd for C₇H₁₂O₂: C, 65.6%; H, 9.4%. Found: C, 65.6%; H, 9.5%. ¹³C NMR (CDCl₃): δ = 117.72 ppm (CH₂=), 132.48 ppm (-CH=), 64.82 ppm (-CH₂-), 172.88 ppm (C=O), 36.13 ppm, 18.51 ppm, and 13.66 ppm (-CH₂-CH₂-CH₃).

*Allyl Isobutyrate*¹⁰: Yield 59–63%. bp 128–130°C. *Anal.* Calcd for C₇H₁₂O₂: C, 65.6%; H, 9.4%. Found: C, 65.7%; H, 9.2%. ¹³C NMR (CDCl₃): δ = 117.45 ppm (CH₂=), 132.36 ppm (-CH=), 64.67 ppm (-CH₂-), 176.14 ppm (C=O), 33.87 ppm, and 18.84 ppm (-CH(CH₃)₂).

*Allyl Trimethylacetate*¹⁰: Yield 50–55%. bp 134–136°C. *Anal.* Calcd for C₈H₁₄O₂: C, 67.6%; H, 9.9%. Found: C, 67.6%; H, 9.7%. ¹³C NMR (CDCl₃): δ = 117.32 ppm (CH₂=), 132.45 ppm (-CH=), 64.82 ppm (-CH₂-), 177.82 ppm (C=O), 38.75 ppm, and 27.20 ppm (-C(CH₃)₃).

PROCEDURES

Polymerization of Allyl Esters

A mixture of weighed amounts of an allyl

ester (20 ml) and benzene (20 ml), and 1.0 wt% of benzoyl peroxide was placed in a 50 ml heat-resisting glass bottle. The bottle was sealed in a stream of nitrogen and placed in a thermostatted bath in the temperature range of 60°C to 80°C for an appropriate period. Unreacted monomers and solvent were removed by distillation at 25°C in vacuum and the residue was taken as polymers.

MEASUREMENTS

Elemental Analysis

Elemental analyses for carbon, hydrogen and nitrogen of the allyl ester monomers were conducted by a Hitachi Perkin Elmer model 240C.

Determination of Molecular Weight

The determination of molecular weights was carried out using a Shimadzu 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 the standard samples for calibration.

¹³C Nuclear Magnetic Resonance Spectroscopy

¹³C NMR spectra of allyl ester monomers were obtained at 22.5 MHz on a Hitachi R-90 Spectrometer using 25 v/v% chloroform (CDCl₃) 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 acetate was elucidated by the MMP-2 method as described previously. The atomic coordinates were used for the AM-1 method and energy was optimized. LU and the next LU MO's were split by interactions of substituted alkyl group(s), but the energy difference was very small as shown in Table II.

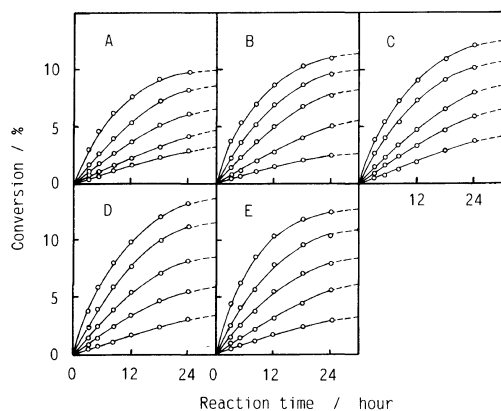


Figure 1. Relationship between conversion and reaction time for polymerization of 50 v/v% allyl esters in benzene by 1.0 wt% BPO at 60, 65, 70, 75, and 80°C. A, allyl acetate; B, allyl propionate; C, allyl butyrate; D, allyl isobutyrate; E, allyl trimethylacetate.

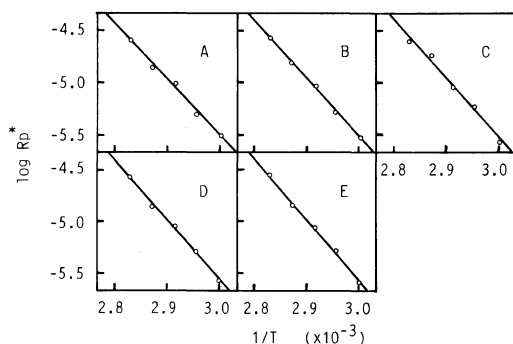


Figure 2. Relationship between logarithm of propagation reaction (R_p) and temperature for polymerization of allyl ester by BPO in benzene at 60, 65, 70, 75, and 80°C. A, allyl acetate; B, allyl propionate; C, allyl butyrate; D, allyl isobutyrate; E, allyl trimethylacetate. * R_p ($\text{mol l}^{-1} \text{s}^{-1}$).

Accordingly, f_r^R is one half the sum of the LU and the next LU frontier densities.

RESULTS AND DISCUSSION

Rates of Polymerization

Conversion versus time plots for the polymerization are shown in Figure 1. At 60°C the curve is closely linear over the conversion range studied. At 80°C, by contrast, there is

Table I. Activation energy and molecular weight in the polymerization of allyl esters

Allyl ester	Activation energy/ kcal mol^{-1}	Molecular weight ^a \bar{M}_w
	E_a	
Allyl acetate	24.3	8100
Allyl propionate	25.5	5100
Allyl butyrate	26.0	4000
Allyl isobutyrate	26.2	3300
Allyl trimethylacetate	26.8	2800

^a Determined by GPC. BPO for initiator is added 0.4 mol%.

slight decrease in the rate after around a 5 wt% conversion to show the tendency of saturation. The polymerization increases with rise of temperature in the range of 60 to 80°C. As the reaction temperature rises, the conversion curve gradually deviates from linearity over the conversion range studied. From the slopes of the approximately linear parts of the curves, which give initial rates, in Figure 1. Arrhenius plots in Figure 2 were constructed and gave an overall energy of activation for the radical polymerization process. Table I shows an apparent activation energy (E_a), and weight-average molecular weight. Apparent activation energy (E_a), an overall energy of activation of the radical polymerization for allyl esters, consists of energy of initiation, propagation, termination, and degradative chain transfer. Because we are treating a series of compounds of similar chemical structures and using the same initiator, we may assume, to the first approximation, that activation energy for initiation is the same throughout the series and propagation is terminated by degradative chain transfer. The rate of propagation (R_p) is then expressed as

$$R_p = R_i \cdot k_p / k_{tr} \quad (1)$$

where R_i is the rate of initiation, k_p the rate of propagation, and k_{tr} the rate of termination. The apparent activation energy is shown by

the following equation

$$E_a = E_i + E_p - E_{tr} \quad (2)$$

where E_i is activation energy of initiation, E_p activation energy of propagation, and E_{tr} activation energy of degradative chain transfer. Therefore, if the activation energy of propagation increases and activation energy of termination (degradative chain transfer) decreases, the activation energy of polymerization increases.

Looking at the data in Table I, we notice that increasing the methyl substitution in the acyl group of the esters results in increase in the activation energies. By taking advantage of this, we conclude that the factors that determine the difference in the amount of activation energy are degradative chain transfer and addition reaction. The reasons for this conclusion follow.

As is well known, the acid dissociation constant of a series of methyl-substituted acetic acids decreases as the number of methyl groups on the acetyl group increases. In other words, the methyl-substitution decreases the electron-withdrawing power of the acyloxy group in the allyl esters. It is also known that by putting an electron-withdrawing substituent on methane, the original true tetrahedral arrangement of the C-H bonds deforms to make the angle larger than 109.5° . This is explained in terms of rehybridization: electron-withdrawing results in changing sp^3 hybridization toward sp^2 . The increase in the s character of the C-H bond should result in increasing the bond energy. These factors imply that substitution of a methyl group for hydrogen in the acetyl of allyl acetate makes the abstraction of the allylic hydrogen facile. Therefore, if abstraction of allylic hydrogen easily occurs, the activation energy of degradative chain transfer decreases. Thus, from eq 2, the apparent activation energy should increase as the number of methyl substituents increases. This is just the observed tendency and suggests that the dominant factor in the apparent activation energy is that for

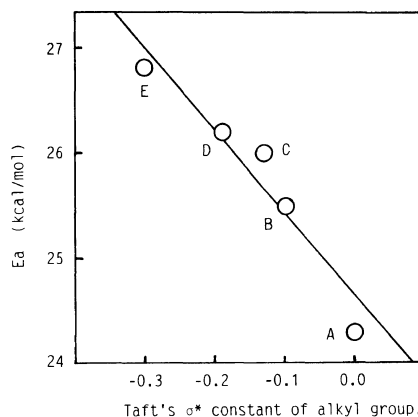


Figure 3. Relationship between Taft's σ^* constant and apparent activation energy (E_a). A, allyl acetate; B, allyl propionate; C, allyl butyrate; D, allyl isobutyrate; E, allyl trimethylacetate.

addition. This conclusion is also verified if one considers the polymerization characteristics. The degradative chain transfer is one of the processes in determining the apparent activation energy (E_a), though its contribution is small.

Effects of Acyloxy Group on Polymerization

By establishing that the main contributor for the observed apparent activation energy is that of propagation, we can now discuss various factors which are affected by methyl substitution.

Electron-withdrawing nature of substituents is known to be reflected by Taft's σ^* constants. The relationship between the activation energy and Taft's σ^* is shown in Figure 3. The correlation coefficient is 0.945. As is expected, it is nicely linear and enrichment of electron-density on the double bond of allyl alkanoates reduces the ease of polymerization.

The Taft's σ^* values do not show, however, which carbon atoms in the double bond takes an important part in polymerization. This information should be obtained by calculating the frontier molecular orbital (FMO) energies. According to the FMO theory, SOMO of the nucleophilic alkyl radical such as formed from

Table II. Frontier electron densities (f_r^R) of radical reaction for allyl ester

CH ₂ =CHCH ₂ -O(CO)-X 1 2 8,9	π^{HO}		π^{LU}		f_r^R		
	E^{ho} (a.u.)	f_r^{ho}	E^{lu} (a.u.)	f_r^{lu}			
X = -CH ₃ allylic hydrogen	-0.37515	C ₁	0.69436	+0.03880 +0.04088 ^a	0.64725	C ₁	0.67081
		C ₂	0.60720		0.62866	C ₂	0.61793
		H ₈	0.12810		0.04858	H ₃	0.08834
		H ₉	0.12810		0.04858	H ₉	0.08834
X = -CH ₂ CH ₃ allylic hydrogen	-0.37466	C ₁	0.69368	+0.03937 +0.04146 ^a	0.64698	C ₁	0.67033
		C ₂	0.60531		0.62895	C ₂	0.61713
		H ₈	0.12863		0.04860	H ₈	0.08862
		H ₉	0.12863		0.04860	H ₉	0.08862
X = -CH(CH ₃) ₂ allylic hydrogen	-0.37458	C ₁	0.69010	+0.03987 +0.04289 ^a	0.64487	C ₁	0.66749
		C ₂	0.60182		0.62708	C ₂	0.61445
		H ₈	0.12914		0.04868	H ₈	0.08891
		H ₉	0.12888		0.04868	H ₉	0.8878
X = -C(CH ₃) ₃ allylic hydrogen	-0.37449	C ₁	0.69142	+0.04009 +0.04450 ^a	0.64705	C ₁	0.66924
		C ₂	0.60247		0.62943	C ₂	0.61595
		H ₈	0.12936		0.04863	H ₈	0.08900
		H ₈	0.12929		0.04843	H ₉	0.08886

^a The next lowest vacant MO's energy.

the allyl esters will predominantly interact with LUMO of the allyl esters. On the other hand, it will be difficult for HOMO of allyl esters to interact with SOMO of the nucleophilic alkyl radical such as formed from the allyl esters. Therefore, it seems that the radical propagation occurs by interaction between an alkyl radical SOMO and LUMO of an allyl ester. The energy of molecular orbital and frontier electron density have been calculated to prove the effect of substituent groups. The molecular orbital energy, LU (π) and HO (π), and frontier electron density (f_r^R)^x of the allyl esters are shown in Table II. As can be seen from Figure 4 (the correlation coefficient is 0.960), the value of apparent activation energy for the allyl esters is proportional to the energy of LUMO for allyl esters in polymerization.

The radical reactivity of allyl esters increases with increasing the value of frontier electron density (f_r^R) for γ carbon. The larger the value of f_r^R is, the faster is the rate of the radical addition of allyl esters. The value of f_r^R of the

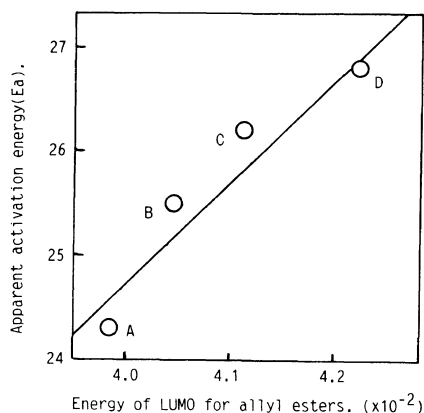
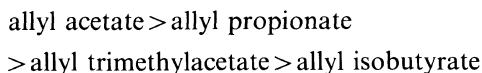


Figure 4. Relationship between energy of LUMO for allyl esters and apparent activation energy (E_a). A, allyl acetate; B, allyl propionate; C, allyl isobutyrate; D, allyl trimethylacetate.

γ carbon for allyl esters decreases in the following order.



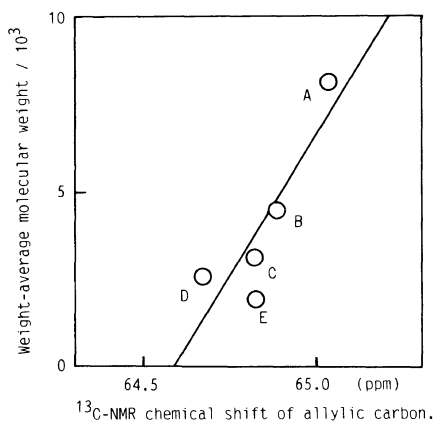


Figure 5. Relationship between ^{13}C NMR chemical shift of allylic carbon and molecular weight. A, allyl acetate; B, allyl propionate; C, allyl butyrate; D, allyl isobutyrate; E, allyl trimethylacetate.

In the radical polymerization of the allylic monomer, the degradative 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.⁸⁻¹⁰ Therefore, the reactivity of active growing chain with the allylic hydrogen of the allylic monomer with respect to the radical addition to the allylic monomer influences the rate of the propagation. Increasing the reactivity of allylic hydrogen is liable to increase the degradative chain transfer. The frontier electron density (f_r^R) of allylic hydrogen is calculated and shown in Table II. f_r^R of allylic hydrogen for allyl esters increases in the following order.

allyl acetate < allyl propionate
< allyl isobutyrate < allyl trimethylacetate

The apparent activation energy of allylic radical polymerization decreases in the following order.

allyl trimethylacetate > allyl isobutyrate >
allyl butyrate > allyl propionate > allyl acetate

The order of apparent activation energy for polymerization is, by and large, the same as

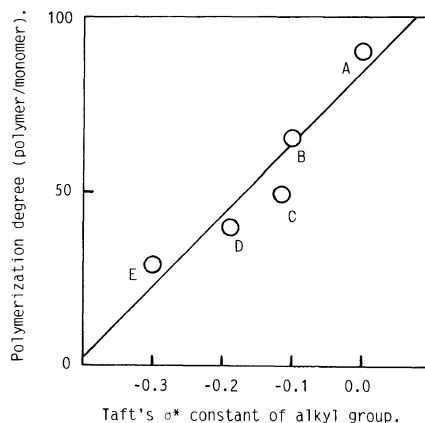


Figure 6. Relationship between Taft's σ^* constant of alkyl group for allyl esters and polymerization degree of allyl ester. A, allyl acetate; B, allyl propionate; C, allyl butyrate; D, allyl isobutyrate; E, allyl trimethylacetate.

the order of f_r^R of γ carbon for allyl esters. Thus, relatively speaking, the reactivity of a γ carbon increases with decreasing reactivity of the allylic hydrogen in allyl esters. As a result, the order of apparent activation energies of the allylic polymerization is consistent with that of the frontier electron density for allyl esters.

The influence of the electron donating nature of alkyl groups on the electron density of each carbon atoms was investigated by measurement of ^{13}C NMR spectrum. The actual electron density of allylic carbon is indicated by the δ value of ^{13}C NMR chemical shift. δ for allylic carbon of allyl esters in ^{13}C NMR chemical shift are consistent with atomic change obtained by the MO calculation. A linear relationship between the δ value and molecular weight was obtained as shown in Figure 5 (correlation coefficient is 0.864).

The Molecular Weight

With increasing extent of electron withdrawing power of acyloxy groups, the rate of addition increases and degradative chain transfer by the abstraction of allylic hydrogen decreases. Therefore, the molecular weight increases as the acyl group carries less methyl groups.

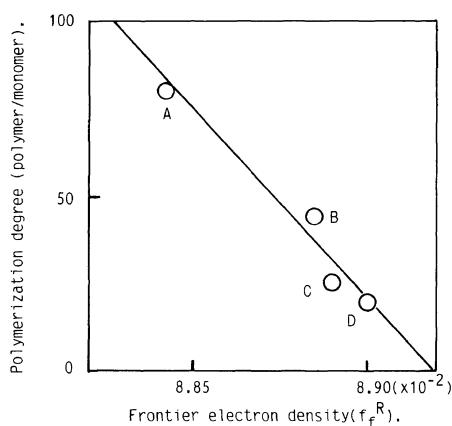


Figure 7. Relationship between f_r^R of allylic hydrogen for allyl ester and polymerization degree of poly allyl ester. A, allyl acetate; B, allyl propionate; C, allyl isobutyrate; D, allyl trimethylacetate.

The weight-average molecular weight (\bar{M}_w) of allylic polymers was measured. The result is shown in Table I. The weight-average molecular weight (\bar{M}_w) of allylic polymer decreases in the following order.

allyl acetate > allyl propionate > allyl butyrate
> allyl isobutyrate > allyl trimethylacetate

Figure 6 shows the relationship between Taft's σ^* constant and polymerization degree as indicated by the average number of allylic monomers in the polymer, which is linear. The correlation coefficient is 0.946. As the extent of electron-donating power of an alkyl group in the allyl esters increases, the molecular weight of allylic polymers decreases, because by increasing the extent of electron-donating power of the alkyl group, the chain transfer between active growing chains and allylic hydrogens takes place easily to terminate the growing polymer chains. The frontier electron density has been calculated to prove the effect of alkyl groups. The extent of the reactivity of allylic hydrogen is indicated by f_r^R of allylic hydrogen. An inversely linear relationship between f_r^R value of allylic hydrogen and the

polymerization degree was obtained as shown in Figure 7 (the correlation coefficient is 0.980).

In summary, it is shown that there is excellent correlation between the apparent activation energy or molecular weight of a polymer and Taft's σ^* constant, chemical shift of ^{13}C NMR, and frontier molecular orbital energy. While we can obtain δ values of ^{13}C NMR and those of Taft's σ^* constants of acyl group of allyl ester only by experimental measurement, we can theoretically obtain LU (π), HO (π), and f_r^R of allyl ester by the Molecular Orbital method. The molecular orbital parameters are shown to be highly useful and convenient in predicting radical polymerization.

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