

Allylic Polymers. I. Copolymerization of Allyl Esters with Vinyl Acetate

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Synopsis

The radical copolymerization of allyl esters with vinyl acetate has been studied in the range from 10 to 90 mol % allyl esters in the feed. The Kelen-Tüdös method was employed to determine the monomer reactivity ratios. The following values were found for the reactivity ratios: allyl propionate (M_1)-vinyl acetate (M_2), $r_1 = 0.42$, $r_2 = 1.29$; allyl butyrate (M_1)-vinyl acetate (M_2), $r_1 = 0.64$, $r_2 = 0.97$; allyl isobutyrate (M_1)-vinyl acetate (M_2), $r_1 = 0.51$, $r_2 = 1.04$; allyl valerate (M_1)-vinyl acetate (M_2), $r_1 = 0.58$, $r_2 = 1.07$; allyl trimethylacetate (M_1)-vinyl acetate (M_2), $r_1 = 0.34$, $r_2 = 1.15$. The $Q-e$ parameters were calculated from the allyl esters (M_1)-vinyl acetate (M_2) reactivity ratios. The e parameters of allyl ester monomers have been found to be nicely correlated with parameters such as dissociation constants of carboxylic acids, which are constituents of allyl ester monomers, and Taft σ^* constants of the alkyl group in the acids. The molecular weights of copolymers were measured by GPC and ranged from $(1.0\text{--}15.0) \times 10^4$.

INTRODUCTION

A great deal of work has been published on the structure-reactivity relationship of vinyl monomers in their radical homo- and copolymerizations.¹⁻⁵ Otsu and co-workers have found that relative reactivities of alkyl methacrylates depend on the polar effect of the alkyl groups but not on the steric effect.¹ Ueda and co-workers have shown that the introduction of a heteroatom into the methyl groups of methyl acrylate increases the reactivity due to polar effects in radical polymerization.⁶⁻¹⁰

It is well known that there is a difference between allyl copolymerizations and ordinary vinyl copolymerizations.¹¹⁻¹³

Chain transfer between an active growing chain and an allylic monomer can not only lead to termination of the growing polymer chain but can also terminate the kinetic chain.^{14,15} Therefore it is necessary to inhibit the termination steps involving abstraction of the allylic hydrogen in copolymerizations to make the molecular weight large. If abstraction of the allylic hydrogen is diminished, degradative chain transfer decreases.¹⁶ In order to retard abstraction of the allylic hydrogen, one can vary the electron density of the alpha carbon atom by introducing electron-attracting groups such as ester groups. The extent of electron-attraction by such groups may be related to the dissociation constants of the corresponding carboxylic acids. Dissociation constants of carboxylic acids decrease, as the extent of electron-donation by the alkyl group increases. Fur-

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ther, this affects the electron density of the double bond of the allylic monomer, through minor in the effect. Thus, the Alfrey-Price e parameters of allyl ester monomers should be correlated with the dissociation constants of the corresponding carboxyl groups.

In this paper, we report the relative reactivity of a series of allyl ester derivatives bearing substituents on the acetyl methyl group of allyl acetate. The reactivity ratios were determined for the monomer pair according to the Kelen-Tüdös method.¹⁷ The Q - e parameters were determined from the reactivity ratios by the Alfrey-Price method.¹⁸ The relationships between the experimentally determined Q - e parameters and various parameters such as Taft's σ^x constants and dissociation constant are also discussed.

EXPERIMENTAL

Monomer Synthesis

In a flask equipped with a reflux condenser, a stirrer, and a dropping funnel were placed 73.5 mL (62.7 g, 1.08 mol) of allyl alcohol, 205 mL (196 g, 1.62 mol) of *N,N*-dimethylaniline, and 200 mL of dry ether. The mixed solution was heated to refluxing, and one hundred mL (107 g, 1.15 mol) of propionyl chloride was added to the stirred solution at such a rate that moderate refluxing continues without the source of heat. When approximately 65 mL of the propionyl chloride was added, *N,N*-dimethylaniline hydrochloride began to crystallize and the mixture refluxed very vigorously. An ice bath was applied immediately, and, after refluxing subsided, the remainder of the propionyl chloride was added. Finally, the flask was dipped into a water bath for 1 h. After the mixture was cooled to room temperature, approximately 200 mL of water was added. Stirring was continued until all the solid material dissolved. The ether layer was separated and extracted several times with 50 mL portions of cold 10% sulfuric acid until the extract did not become turbid on basification with sodium hydroxide. After a final washing with 25 mL of a saturated sodium bicarbonate solution, the ether solution was dried by shaking it with 10 g of anhydrous sodium sulfate. The solution was decanted and allowed to stand over 10 g of Drierite overnight. The solution was filtered, and the ether was removed by distillation. The residue was fractionally distilled, and 75.8–80.8 g (61–65%) of allyl propionate boiling at 122–124°C was obtained (lit.¹⁹ bp 123°C).

ANAL. Calcd for $C_6H_{10}O_2$: C, 63.1; H, 8.8. Found. C, 63.2; H, 8.5.

The other allyl esters were synthesized in a similar manner. The structural formulas of allyl esters synthesized are shown in Table I.

Allyl butyrate: yield: 60–67%. bp 141–143°C.

ANAL. Calcd for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found. C, 65.6; H, 9.5.

Allyl valerate: yield: 55–60%. bp 160–163°C.

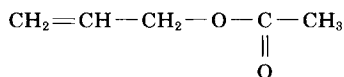
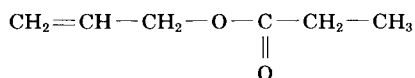
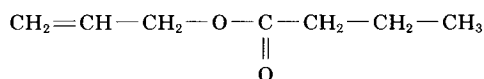
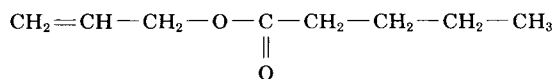
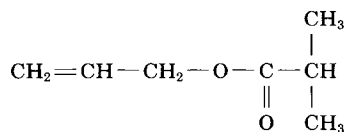
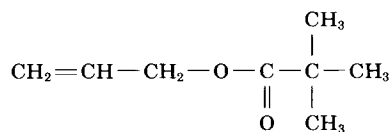
ANAL. Calcd for $C_8H_{14}O_2$: C, 67.6; H, 9.9. Found. C, 67.6; H, 10.1.

Allyl isobutyrate: yield: 59–63%. bp 128–130°C.

ANAL. Calcd for $C_7H_{12}O_2$: C, 65.6; H, 9.4. Found. C, 65.7; H, 9.2.

Allyl trimethylacetate: yield: 50–55%. bp 134–136°C.

ANAL. Calcd for $C_8H_{14}O_2$: C, 67.6; H, 9.9. Found. C, 67.6; H, 9.7.

TABLE I
Allyl Esters**Allyl acetate****Allyl propionate****Allyl butyrate****Allyl valerate****Allyl isobutyrate****Allyl trimethylacetate****Procedures***Copolymerization of Allyl Esters and Vinyl Acetate*

Weighed amounts of allyl esters, and vinyl acetate, and 0.1 wt % of benzoyl peroxide were placed in a 50 mL heat resisting glass bottle and sealed. The bottle was then placed in a thermostatted bath at 60°C for an appropriate period. The feed ratios are shown Tables II and III. The copolymer obtained was isolated and purified by reprecipitation from benzene/petroleum ether.

Measurements*Elemental Analysis*

Elemental analyses for carbon, hydrogen, and nitrogen of the allyl ester-vinyl acetate copolymers were conducted by a Hitachi Perkin-Elmer model

TABLE II
Reactivity Ratios and Q , e Value for the Copolymerization
of Allyl Ester (M_1) with Vinyl Acetate (M_2)^a

Allyl monomer	r_1	r_2	$r_1 r_2$	e	Q
Allyl acetate	0.7	1.0	0.7	-1.48	0.044
Allyl propionate	0.42	1.29	0.54	-1.66	0.040
Allyl butyrate	0.64	0.97	0.62	-1.57	0.049
Allyl valerate	0.58	1.07	0.62	-1.57	0.045
Allyl isobutyrate	0.51	1.04	0.53	-1.68	0.050
Allyl trimethylacetate	0.34	1.15	0.39	-1.85	0.053

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

240C. The copolymer compositions were calculated by using the carbon content of the polymers.

Determination of Molecular Weight

The determination of molecular weights was carried out by using a Simadzu G.P.C., model chromatopac C-R3A. Polystyrene and polyethylene glycol were used as the standard samples.

RESULTS AND DISCUSSION

Reactivity Ratio and Q - e Parameter

The copolymer composition as a function of feed composition for the copolymerization of allyl esters with vinyl acetate is shown in Figure 1. The dashed line represents the ideally random copolymerization conditions. The composition of allylic copolymers is obtained in lower than 5% yield.

It can be seen from the copolymer composition plot that the content of allyl esters in copolymers increases with increasing feed ratios of allyl esters, but the azeotropic copolymerization point is not found. Whereas, in the copolymerization of allyl butyrate with vinyl acetate, the composition of copolymers is in accord with the feed ratio as a whole. In the copolymerization of allyl trimethylacetate with vinyl acetate, the copolymerization curve of allyl trimethylacetate show deviation from the ideally random copolymerization condition and its gap is larger than those of the other allyl esters. In the copolymerization of allyl valerate with vinyl acetate, little copolymerization occurred at higher ratios than 75 mol % allyl valerate in the feed.

The feed ratios of monomers and the copolymer compositions were used to calculate the monomer reactivity ratios for allyl ester-vinyl acetate pairs. The Kelen-Tüdös method¹⁷ was employed to determine the monomer reactivity ratios at lower conversion than 5 wt %. The Q - e parameters were determined from the reactivity ratios according to the Alfrey-Price method.¹⁸ The e and Q parameters of vinyl acetate are -0.88 and 0.028 .²⁰ The results are shown in Table II, where the monomer reactivity ratios of allyl acetate-vinyl acetate pairs²¹ are also shown for comparison. The results show that r_1 is smaller than

TABLE III
Reaction Parameters for the Copolymerization of Allyl Ester (M_1) with Vinyl Acetate (M_2)

Allyl ester	Sample number	$[M_1]/[M_2]$	Reaction time (h)	Yield (wt %)	Rate ($\times 10^{-4}$ wt %/min)
Allyl propionate	A-06	1.00	48	3.60	12.5
	A-07	2.00	72	3.49	8.08
	A-08	3.00	120	4.54	6.31
	A-09	4.00	168	4.42	4.38
	A-10	7.00	168	3.65	3.62
	A-11	9.00	168	2.72	2.70
Allyl butyrate	B-06	1.00	48	4.54	15.8
	B-07	2.00	96	3.73	6.48
	B-08	3.00	120	3.73	5.18
	B-09	4.00	168	1.72	1.71
	B-10	9.00	168	1.01	1.00
Allyl valerate	C-06	1.00	48	2.50	8.68
	C-07	1.50	72	1.99	4.61
	C-08	2.33	168	1.39	1.38
	C-09	3.33	240	1.21	0.84
Allyl isobutyrate	D-05	1.00	48	4.17	14.5
	D-06	1.50	72	4.25	9.84
	D-07	2.33	120	3.78	5.25
	D-08	4.00	168	3.22	3.19
	D-09	7.00	168	2.30	2.28
	D-10	9.00	168	1.54	1.53
Allyl trimethylacetate	E-05	1.00	48	3.63	12.6
	E-06	1.50	96	3.58	6.22
	E-07	2.33	120	3.51	4.88
	E-08	4.00	168	1.72	1.71
	E-09	9.00	168	0.99	0.98

unity and, r_2 greater than r_1 in every case. Both radicals formed from M_1 and M_2 on the growing end of the chain prefer to add to M_2 . As the product, r_1r_2 , is smaller than unity in every case, each monomer pair easily copolymerizes. The e parameters range from -1.85 to -1.48 and the Q parameter is around 0.045 . No special relationship between bulkiness of the ester groups and these values is found.

Effect of Feed Composition

The reaction rates for each allyl ester were measured at various feed ratios. The result are shown in Table III. As the mole fraction of allyl esters in the feed increases, the reaction rates of allylic copolymers decrease in each case. The reduction in reaction rates is attributed to degradative chain transfer wherein active radicals in growing chains abstract the allylic hydrogen from an allylic monomer to yield stabilized radicals of lowered reactivity.

The reaction rate of the copolymerization of allyl valerate with vinyl acetate is low, compared to those of other allyl esters. The copolymer is scarcely formed

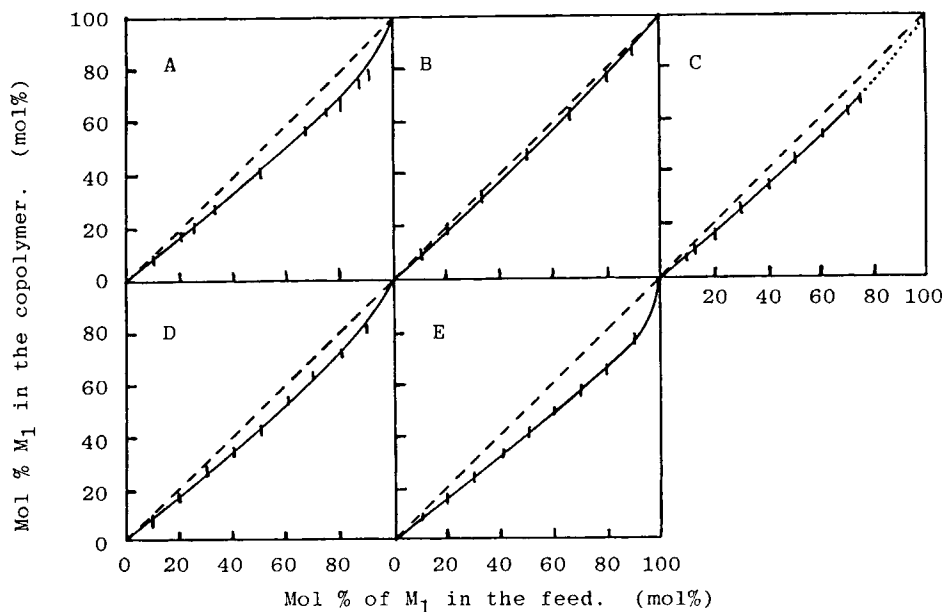


Fig. 1. Copolymer composition as a function of feed composition for the copolymerization of allyl ester (M_1) with vinyl acetate (M_2): (A) allyl propionate, (B) allyl butyrate, (C) allyl valerate, (D) allyl isobutyrate, (E) allyl trimethylacetate.

at more than 75 mol % allyl valerate in the feed. It seems that the long alkyl chain of allyl valerate interferes with the copolymerization.

The feed ratio naturally affects the molecular weight. The molecular weight of the copolymers was measured at various feed ratios. The result is shown in Figure 2. As the mole fraction of allyl esters in the feed increases, the molecular weights of allylic copolymers rapidly decrease.

The feed ratio of an allyl ester evidently affects the degradative chain transfer, i.e., the termination. The molecular weights of the copolymers of allyl trimethylacetate are higher than those of other copolymers such as allyl propionate and allyl isobutyrate. The results might imply that termination by abstraction of a hydrogen atom from the α -position of the acyl group in the allyl ester is significant.

Effect of Acyloxy Group on e Parameter

The interpretation of effect of alkyl groups on the ionization of carboxylic acids is the first recognition of what is now known as the inductive effect. Similarly, it is expected that the inductive withdrawing of electron from the carbon in the allyl groups laid the acyloxy group retards the elimination of the hydrogen on the alpha carbon atom in allyl esters. Therefore, the dissociation constant of a carboxylic acid moiety which is a constituent of the allyl ester should be related to the abstraction of the hydrogen on the methylene carbon atom in the allyl group. That is, as the dissociation constants of carboxylic acids decreases, the electron-attraction of the acyloxy group decreases so that the electron density on the alpha carbon atom in the allyl group relatively

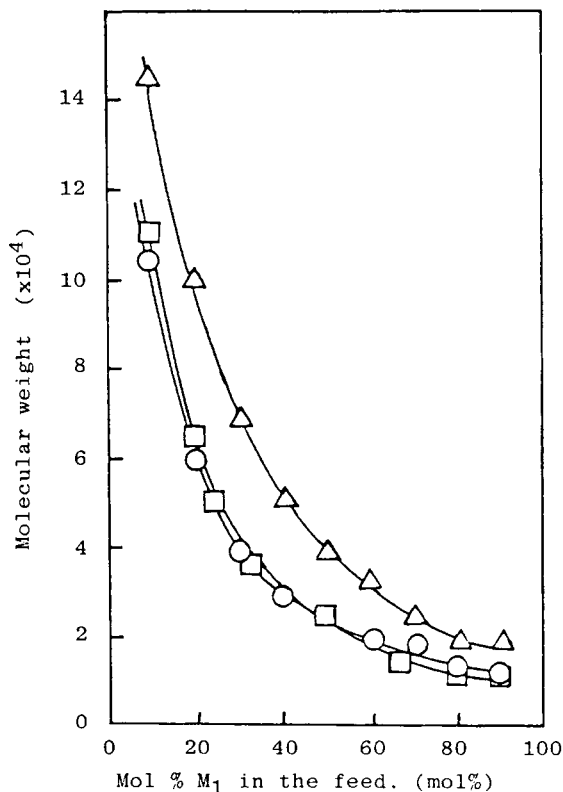


Fig. 2. Relation between mol % of allyl esters (M_1) in the feed and molecular weight: (\square) allyl propionate, (\circ) allyl isobutyrate, (\triangle) allyl trimethylacetate.

increases to make the hydrogen abstraction facile. Therefore, it is expected that the copolymer of higher molecular weight will be formed from allyl esters which carry a carboxylic residue of a low dissociation constant. Propionic acid and isobutyric acid are known to exhibit almost the same dissociation constants. And in deed the molecular weight of a copolymer of allyl propionate is approximately the same with that of a copolymer of allyl isobutyrate. The dissociation constant of trimethylacetic acid is smaller than those of other carboxylic acids. And the molecular weight curve of the copolymer of allyl trimethylacetate is significantly higher than those of other allyl esters.

The acyloxy group bonded to the alpha carbon atom may influence the electron density of the double bond of allylic monomer. The e parameter of a monomer is a measure of the electron density at the double bond of a monomer, which depends on the nature of the substituent groups. It is negative for electron-donating substituents, but it is positive for electron-withdrawing substituents. Schwan and co-workers²² demonstrated a linear relationship between e parameters and Hammett σ constants.²³ We explored the relationship between e parameters and Taft σ^* constants which are the measure of the true inductive effects and should be a better substituent constant than the Hammett σ in this case.²⁴ Figure 3 shows the relationship between e parameters and Taft σ^* constants, which is linear. Since the dissociation constant is related

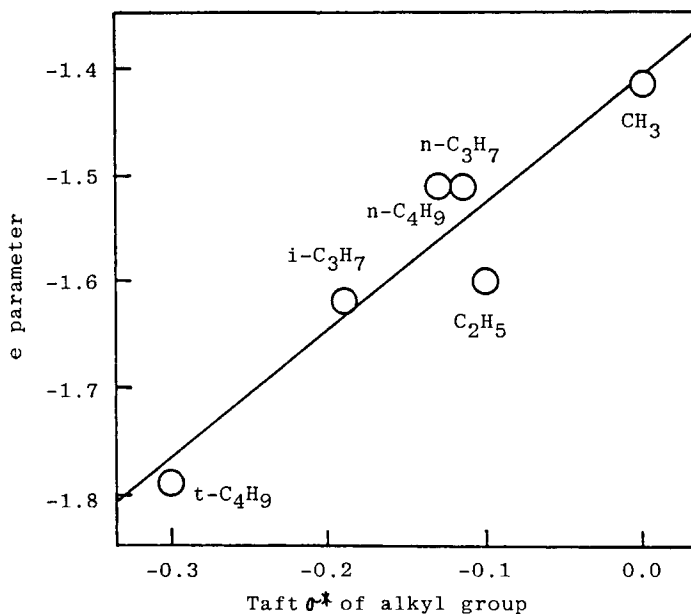


Fig. 3. Relation between Taft σ^* of alkyl group and e parameter of allyl ester.

to the Taft σ^* constant, a linear relationship between e parameters and pK_a is also obtained as shown in Figure 4.²⁵ The correlation coefficient is 0.980. The linear relationship between the electron density of a double bond and the e parameters hold, as well in this case.

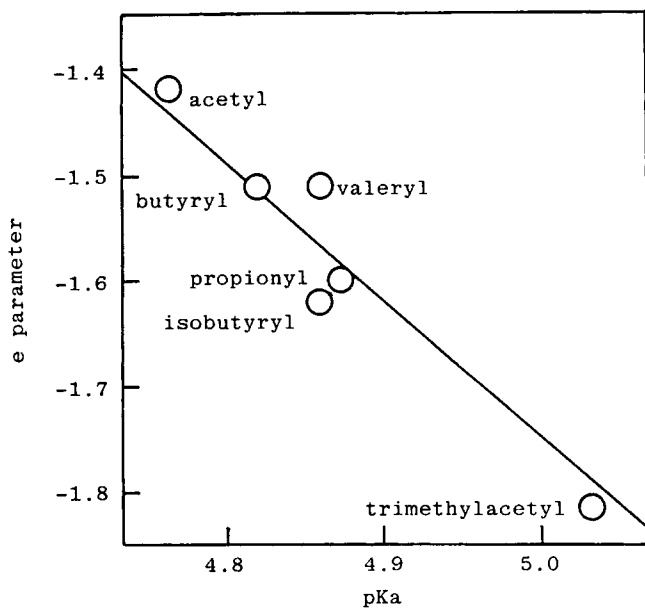


Fig. 4. Relation between dissociation constant and e parameter of allyl esters.

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