The Copolymerization Characteristics of Ethyl α-Acetoxyacrylate*

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An earlier investigation[1] of the bulk copolymerization characteristics of alkyl α-acyloxyacrylates indicated that ethyl α-acetoxyacrylate (EAA) resembled ethyl acrylate rather than vinyl acetate in this respect. α-Acetoxyacrylic esters may be considered to combine the structural features of acrylic esters and vinyl esters.

$$CH_2{=}\underset{\underset{\displaystyle CO{-}OR_1}{|}}{\overset{\overset{\displaystyle O{=}CO{-}R}{|}}{C}}$$
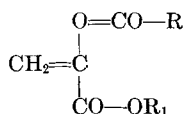
The present study was undertaken to examine these copolymerization characteristics of EAA more closely and to determine in a semiquantitative manner the effect of two substituents of differing polarity upon the ethylenic double bond of vinyl-type monomers.

In general, the study consisted in the determination of the reactivity ratios, r_1 and r_2, of various comonomer pairs involving EAA and therefrom the determination of Q and e values for EAA. Such information should indicate any similarities which may exist between EAA, vinyl acetate and ethyl acrylate. The monomers chosen for copolymerization with EAA were styrene and methyl methacrylate, largely because the considerable amount of data published in regard to their copolymerization characteristics with other monomers makes them valuable reference monomers. Vinyl acetate and ethyl acrylate were also selected so that a direct comparison could be made between the structurally related monomers.

EXPERIMENTAL

Copolymerization

Ethyl α-acetoxyacrylate was prepared as described.[1] The monomer was redistilled before use. Styrene, methyl methacrylate, vinyl acetate, and ethyl acrylate were freshly distilled before use.

In the case of any one comonomer pair, varying proportions of the two monomers were placed in Pyrex glass vials, together with approximately

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0.1% benzoyl peroxide and, after the supernatant atmosphere had been displaced with nitrogen, the vials were sealed. (In the case of copolymers with styrene and vinyl acetate, total monomer weights were about 10 g., whereas in the case of methyl methacrylate and ethyl acrylate, twice this quantity was used.) The vials were rapidly warmed to 60°C. and maintained at this temperature until the visual examination of the increase in viscosity indicated a probable conversion of 5–10%. The vial was opened and the solution poured into approximately 200 ml. of agitated n-

TABLE I

Copolymerization of Styrene (Monomer 1) with Ethyl α-Acetoxyacrylate (Monomer 2)
(Catalyst: Benzoyl Peroxide, 0.1%; Temperature, 60°C.)

Sample no.	Mole fraction of monomer 1 in monomer mix (M_1)	Mole fraction of monomer 2 in monomer mix (M_2)	Conversion, %	Analysis of polymer, % ethoxyl	Mole fraction of monomer 1 in copolymer (m_1)	Mole fraction of monomer 2 in copolymer (m_2)
H549-01A	0.934	0.066	3.7	4.2	0.898	0.102
-01B	0.842	0.158	4.6	7.9	0.798	0.202
-01C	0.769	0.231	5.2	10.2	0.731	0.269
-01D	0.678	0.322	5.2	12.2	0.670	0.330
-01E	0.575	0.425	5.6	14.2	0.604	0.396
-01F	0.481	0.519	4.2	15.9	0.546	0.454
-01G	0.371	0.629	4.0	16.5	0.525	0.475
-01H	0.271	0.729	2.8	18.4	0.454	0.546
-01I	0.143	0.857	2.7	21.0	0.352	0.648
-01J	0.113	0.887	2.4	22.4	0.292	0.708

TABLE II

Copolymerization of Methyl Methacrylate (Monomer 1) with Ethyl α-Acetoxyacrylate
(Monomer 2)
(Catalyst: Benzoyl Peroxide, 0.1%; Temperature, 60°C.)

Sample no.	Mole fraction of monomer 1 in monomer mix (M_1)	Mole fraction of monomer 2 in monomer mix (M_2)	Conversion, %	Analysis of polymer, % acetyl by distillation	Mole fraction of monomer 1 in copolymer (m_1)	Mole fraction of monomer 2 in copolymer (m_2)
H549-03A	0.951	0.049	9.7	1.9	0.955	0.045
-03B	0.844	0.156	9.0	4.0	0.902	0.098
-03C	0.762	0.238	8.9	6.2	0.843	0.157
-03D	0.681	0.319	7.0	8.6	0.774	0.226
-03E	0.583	0.417	8.6	11.6	0.680	0.320
-03F	0.482	0.518	8.4	13.8	0.606	0.394
-03G	0.372	0.628	7.9	17.3	0.475	0.525
-03H	0.264	0.736	8.7	20.3	0.350	0.650
-03I	0.141	0.859	8.3	23.2	0.215	0.785
-03J	0.081	0.919	8.8	24.9	0.128	0.872

hexane. (Addition of a small amount of *n*-hexane to the drained vial, followed by vigorous shaking, enabled one to transfer the last quantities of polymer to the main precipitation.) After standing until the polymer settled, the supernatant hexane was decanted and the precipitate was leached in fresh hexane. Upon decanting again in 2 hours, the polymer in the 250-ml. beaker was dried in vacuum overnight at 50°. The polymer was weighed (to determine the per cent conversion) and redissolved in

TABLE III

Copolymerization of Vinyl Acetate (Monomer 1) with Ethyl α-Acetoxyacrylate (Monomer 2)

(Catalyst: Benzoyl Peroxide, 0.1%; Temperature, 60°C.)

Sample no.	Mole fraction of monomer 1 in monomer mix (M_1)	Mole fraction of monomer 2 in monomer mix (M_2)	Conversion, %	Analysis of polymer, % ethoxyl	Mole fraction of monomer 1 in copolymer (m_1)	Mole fraction of monomer 2 in copolymer (m_2)
H549-21A	0.937	0.063	12.8	16.6	0.568	0.432
-21B	0.865	0.135	10.0	19.5	0.458	0.542
-21C	0.787	0.213	11.9	21.4	0.378	0.622
-21D	0.708	0.292	6.4	23.6	0.276	0.724
-21E	0.614	0.386	4.5	25.0	0.204	0.796
-21F	0.512	0.488	10.6	25.4	0.183	0.817
-21G	0.406	0.594	4.2	26.5	0.121	0.879
-21H	0.293	0.707	5.1	27.4	0.068	0.932
-21I	0.152	0.848	5.8	28.0	0.031	0.969

TABLE IV

Copolymerization of Ethyl Acrylate (Monomer 1) with Ethyl α-Acetoxyacrylate (Monomer 2)

(Catalyst: Benzoyl Peroxide, 0.1%; Temperature, 60°C.)

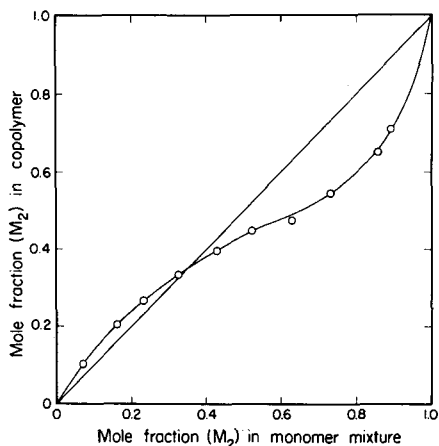| Sample no.	Mole fraction of monomer 1 in monomer mix (M_1)	Mole fraction of monomer 2 in monomer mix (M_2)	Conversion, %	Analysis of polymer, % acetyl by distillation	Mole fraction of monomer 1 in copolymer (m_1)	Mole fraction of monomer 2 in copolymer (m_2)
H549-22A	0.917	0.083	5.9	3.4	0.917	0.083
-22B	0.839	0.161	10.7	6.5	0.835	0.165
-22C	0.756	0.244	17.7	9.7	0.740	0.260
-22D	0.670	0.330	8.2	12.7	0.644	0.356
-22E	0.575	0.425	8.4	14.3	0.588	0.412
-22F	0.468	0.532	8.9	17.3	0.475	0.525
-22G	0.368	0.632	5.4	20.1	0.359	0.641
-22H	0.258	0.742	5.6	22.2	0.263	0.737
-22I	0.135	0.865	7.7	23.1	0.220	0.780
-22J	0.073	0.927	19.4	25.9	0.074	0.926

Fig. 1. Copolymer composition curves for the system styrene (M_1), ethyl α-acetoxyacrylate (M_2); temperature, 60°C. benzoyl peroxide, 0.1%.
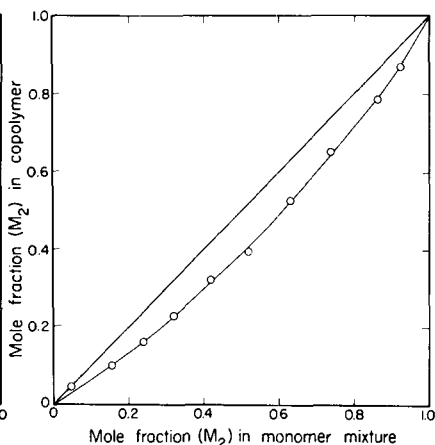

Fig. 2. Copolymer composition curves for the system methyl methacrylate (M_1), ethyl α-acetoxyacrylate (M_2); temperature, 60°C.; benzoyl peroxide, 0.1%.
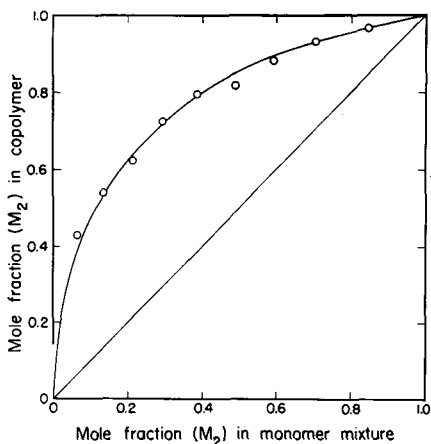

Fig. 3. Copolymer composition curves for the system vinyl acetate (M_1), ethyl α-acetoxyacrylate (M_2); temperature, 60°C.; benzoyl peroxide, 0.1%.
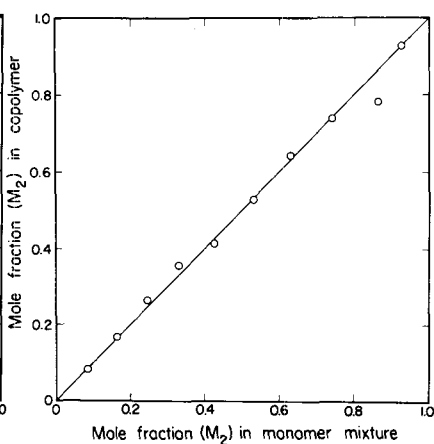

Fig. 4. Copolymer composition curves for the system ethyl acrylate (M_1), ethyl α-acetoxyacrylate (M_2); temperature, 60°C.; benzoyl peroxide, 0.1%.

benzene. This benzene solution was again precipitated into hexane. The operation of reprecipitation was again repeated and the polymer dried overnight in vacuum to a constant weight.

Analysis

The copolymers of ethyl α-acetoxyacrylate with styrene and with vinyl acetate were analyzed for ethoxyl content from which could be calculated the percentage of ethyl α-acetoxyacrylate units in the copolymer.

The copolymers of ethyl α-acetoxyacrylate with methyl methacrylate and with ethyl acrylate were analyzed for acetyl content. The procedure consisted essentially in hydrolyzing a weighed sample of copolymer with excess alcoholic sodium hydroxide, acidifying the hydrolysis mixture with sulfuric acid, and steam-distilling this product. The distillate was then titrated with standard alkali to determine the acetic acid present.

Blanks were run on the homopolymer of ethyl α-acetoxyacrylate in order to determine the effectiveness of both the ethoxyl and the acetyl analysis.

Calculated ethoxyl content for poly(ethyl α-acetoxyacrylate) = 28.49%; found = 28.7%. Calculated acetyl content for poly(ethyl α-acetoxyacrylate) = 27.21%; found = 27.4%.

DISCUSSION

The data for the copolymerization of ethyl α-acetoxyacrylate with styrene, methyl methacrylate, vinyl acetate, and ethyl acrylate are shown in Tables I–IV.

These data are plotted in Figures 1–4.

The reactivity ratios, r_1 and r_2, were determined in the case of each comonomer pair by the graphical method of intersections.[2] (In each case, r_2 refers to ethyl α-acetoxyacrylate.) Table V lists the values obtained.

TABLE V
Reactivity Ratios for Some Copolymerizations with Ethyl α-Acetoxyacrylate

Monomer 1	r_1	Monomer 2	r_2	$r_1 \cdot r_2$
Styrene	0.57 ± 0.05	Ethyl α-acetoxyacrylate	0.20 ± 0.05	0.114
Methyl methacry-late	1.65 ± 0.07	Ethyl α-acetoxyacrylate	0.65 ± 0.05	1.07
Vinyl acetate	0.08 ± 0.03	Ethyl α-acetoxyacrylate	5.4 ± 0.5	0.432
Ethyl acrylate	1.0 ± 0.1	Ethyl α-acetoxyacrylate	1.0 ± 0.05	1.00

The $r_1 r_2$ value for the system, styrene-EAA, indicates a considerable tendency for the two monomers to alternate in their entry into the copolymer chain. This behavior is very similar to that encountered in the case of the copolymerization of styrene with methyl acrylate.[3] The bulk polymerizations carried to high conversions with 75–95% of EAA in the monomer mixtures gave hazy to opaque polymers, indicating incompatibility of the spectrum of compositions formed.

The bulk copolymerization of methyl methacrylate with EAA carried to 100% conversion gave hard, clear, and colorless polymers throughout the whole range of monomer compositions. The r_1 and r_2 values for this system indicate that the methyl methacrylate monomer has a tendency to enter the copolymer somewhat more readily than EAA monomer.

Monomer mixtures of vinyl acetate and EAA containing 20% or less of the former mass polymerized to hard, clear, and colorless products. Mixtures containing higher ratios of vinyl acetate formed hazy and translucent

polymers. The much greater reactivity of EAA monomer for the radicals of the growing polymer chains results in a broad spectrum of incompatible compositions.

Figure 4 shows that mixtures of ethyl acrylate and EAA in any ratio copolymerize completely randomly at any degree of conversion to produce clear, homogeneous polymers. This is in contrast to the situation encountered in the case of vinyl acetate. The implication is strong that EAA monomer resembles ethyl acrylate very closely and is distinctly different from vinyl acetate in its copolymerization behavior.

This deduction is fully supported by an examination of the Q and e values calculated for EAA from the data just given and compared with the Q and e values for vinyl acetate and ethyl acrylate. The values for EAA (Q_2 and e_2) were calculated from the data given in Table V. The Q and e values for the first monomer (Q_1 and e_1) used in the calculation were those suggested by Price,[4] as shown in Table VI.

TABLE VI
Values of Q_1 and e_1 Used to Calculate Q and e Values for Ethyl α-Acetoxyacrylate

Monomer	Q_1	e_1	Reference monomer used in determining Q_1, e_1
Styrene	1.0	−0.8	—
Methyl methacrylate	0.74	0.4	Styrene
Vinyl acetate	0.028	−0.3	Methyl acrylate
Ethyl acrylate	0.42	0.6	Styrene

Table VII shows the actual values of e and Q which were calculated for EAA from the copolymerization data obtained experimentally in this investigation.

TABLE VII
Values of e and Q Calculated for Ethyl α-Acetoxyacrylate from Copolymerization Data Involving Various Monomers

Monomer 1	Ethyl α-Acetoxyacrylate	
	e	Q
Styrene	0.67	0.54
Methyl methacrylate	0.66	0.53
Vinyl acetate	0.62	0.27
Ethyl acrylate	0.60	0.42
	0.57[a]	0.42[a]

[a] Calculated from e_1 and Q_1 values obtained for ethyl acrylate from Vanderhoff's data in copolymerizing ethyl acrylate and styrene (J. W. Vanderhoff, Thesis, Univ. of Buffalo, 1951).

The agreement in the values is fairly good, considering that the $Q = e$ scheme is considered to be merely a semiquantitative device for characteriz-

ing various monomers in their copolymerization reactivities and behavior. The Q value obtained from copolymerization data for vinyl acetate is low, but it should be pointed out the value of 0.028 used for Q_1 in calculating the Q value for ethyl α-acetoxyacrylate is only one of several which have been reported.   These vary from 0.022 to 0.047, depending upon the comonomer used.   The value of 0.028 was selected because it was obtained from a copolymerization of vinyl acetate with methyl acrylate and hence was considered to be a more appropriate value than the Q_1 values obtained when using other monomers, such as vinylidene chloride, allyl chloride, and vinyl chloride.

The reported[4] values of e for ethyl acrylate and methyl methacrylate of 0.6 and 0.4, respectively, are significant as detected by this study (cf. Figs. 2 and 4).   There is less tendency toward randomness in the case of methyl methacrylate than in ethyl acrylate, as shown by our r_1 and r_2 values, even though the r_1, r_2 products are both close to unity.

CONCLUSIONS

The copolymerization behavior of ethyl α-acetoxyacrylate is almost identical with that of ethyl acrylate.   It shows little resemblance to the copolymerization characteristics of vinyl acetate.   Consequently, if ethyl α-acetoxyacrylate is considered to be a 1,1-disubstituted ethylene, the effect of the acetoxyl substituent on the polarity of the ethylenic double bond is very small, being swamped by the much larger effect of the electron-acceptor characteristics of the carbethoxyl substituent.

References

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3. F. M. Lewis, C. Walling, W. Cummings, E. R. Briggs, and F. R. Mayo, *J. Am. Chem. Soc.*, **70**, 1519 (1948).

4. C. C. Price, *J. Polymer Sci.*, **3**, 772 (1948).

Synopsis

The copolymerization characteristics of ethyl α-acetoxyacrylate with four different monomers have been investigated, and the reactivity ratios r_1 and r_2 determined in the case of each comonomer pair.   The monomers used were styrene, methyl methacrylate, vinyl acetate, and ethyl acrylate.   From these data were calculated the Q and e values for ethyl α-acetoxyacrylate.   It is apparent that this monomer resembles ethyl acrylate very closely in its copolymerization characteristics.

Résumé

Les caractéristiques de la copolymérisation de l'α-acétoxyacrylate d'éthyle avec quatre monomères différents ont été étudiées et les rapports de réactivité, r_1 et r_2, ont été déterminés dans le cas de chaque paire de comonomères.   Les monomères utilisés sont le styrène, le méthacrylate de méthyle, l'acétate de vinyle et l'acrylate d'éthyle. Les valeurs de Q et de e pour l'α-acétoxyacrylate d'éthyle ont été calculées au dépens de

ces données. Il en ressort que ce monomère ressemble très fort à l'acrylate d'éthyle quant à ses caractéristiques de copolymérisation.

Zusammenfassung

Das Verhalten von Äthyl-α-acetoxyacrylat bei der Copolymerisation mit vier verschiedenen Monomeren wurde untersucht und die Reaktivitätsverhältnisse r_1 und r_2 für jedes Monomerenpaar bestimmt. Als Monomere wurden Styrol, Methylmethacrylat, Vinylacetat und Äthylacrylat verwendet. Aus diesen Zahlen wurden die Q und e-Werte für Äthyl-α-acetoxyacrylat berechnet. Offenbar ist dieses Monomere in seinem Verhalten bei der Copolymerisation dem Äthylacrylat sehr ähnlich.