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Reactivity Ratios of Vinyl Esters of Aliphatic Acids and Some Common Vinyl Monomers

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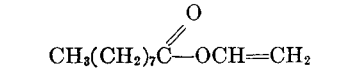
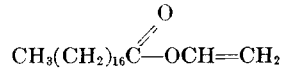
Vinyl acetate has been exhaustively studied as a monomer in vinyl copolymerization reactions but its homologues derived from higher molecular weight acids have received much less attention. The system vinyl stearate–vinyl chloride has been extensively studied by Port, Jordan, Palm, Wittnauer, Hansen, and Swern[1] and that of vinyl palmitate and vinyl acetate has received the attention of Port, Obrien, Hansen, and Swern.[2] Both systems have yielded useful polymeric products.

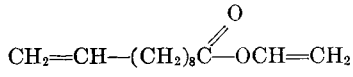
The present investigation has been directed primarily toward determining reactivity ratios in copolymerization reactions for the following vinyl esters with a variety of monomers:



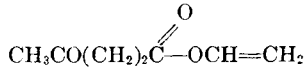
Vinyl pelargonate (I)



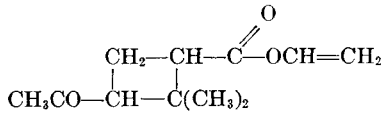
Vinyl stearate (II)



Vinyl undecylenate (III)



Vinyl levulinate (IV)



Vinyl pinonate (V)

The general method of Mayo and Lewis[3] has been employed.

EXPERIMENTAL

Reactivity Ratios

Polymerizations were carried out with benzoyl peroxide as an initiator in four-ounce screw-cap bottles fitted with GR-N rubber gaskets under a nitrogen atmosphere except in cases in which one monomer was a gas. If this was the case, the gaseous monomer was allowed to boil a few moments in order to expel air before the bottle was capped. The polymers were precipitated by pouring the solution into methanol and were purified by reprecipitation from a solvent system into a nonsolvent system. The

purified polymers were dried by the freeze-drying[4] technique where it was applicable, or by storage under high vacuum for prolonged periods if freeze-drying was not applicable. The compositions of the copolymers were determined from the elemental analyses. Tables I–XXII and Figures and Figures 1–44 list the experimental details for the experiments which were used to determine the reactivity ratios.

TABLE I
Reactivity Ratio Data for the Solution Copolymerization of Vinyl Levulinate and Vinyl Chloride at 60°C. (See Figs. 1 and 2)

	Charge[a]				
Number	Vinyl levulinate, g.	Vinyl Chloride, g.	Time, hrs.	Conversion, %	Anal. Cl, %
1	8.02	2.48	26	5	20.08
2	6.53	3.40	26	7	26.30
3	3.48	6.59	10	5	41.89

[a] Solvent, 5 ml. of benzene; initiator, 30 mg. of benzoyl peroxide per charge.

TABLE II
Reactivity Ratio Data for the Bulk Copolymerization of Vinyl Pelargonate and Vinyl Chloride at 60°C. (See Figs. 3 and 4)

	Charge[a]				
Number	Vinyl pelargonate, g.	Vinyl chloride, g.	Time, hrs.	Conversion, %	Anal. Cl, %
1	8.96	1.36	6	2	13.40
2	7.42	2.62	6	4	21.15
3	2.32	7.50	6	8	45.06

[a] Initiator, 15 mg. of benzoyl peroxide per charge.

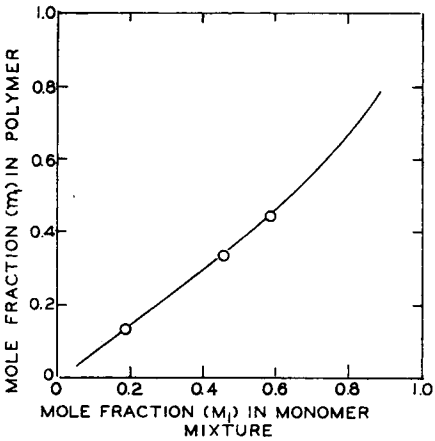


Fig. 1. Copolymer composition curve.

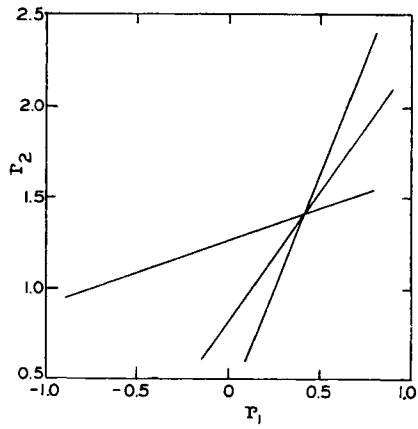


Fig. 2. Reactivity ratio diagram. Copolymerization of vinyl levulinate (M_1) and vinyl chloride (M_2).

TABLE III
Reactivity Ratio Data for the Solution Copolymerization of Vinyl Pinonate and Vinyl Chloride at 60°C. (See Figs. 5 and 6)

Number	Charge[a] Vinyl pinonate, g.	Vinyl chloride, g.	Time, hrs.	Conversion, %	Anal. Cl, %
1	8.91	1.07	48	1	10.70
2	7.64	2.51	48	3	20.15
3	5.02	5.16	27	3	35.00
4	3.04	6.88	24	5	43.58

[a] Solvent, 5 ml. of benzene; initiator, 30 mg. of benzoyl peroxide per change.

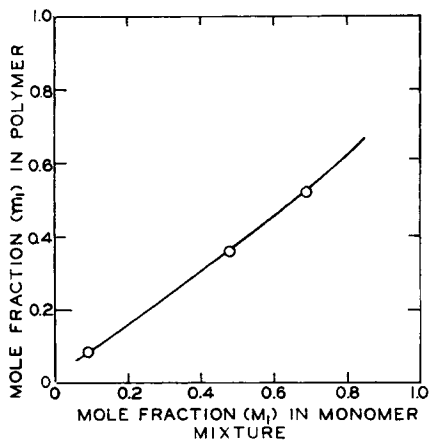


Fig. 3. Copolymer composition curve.

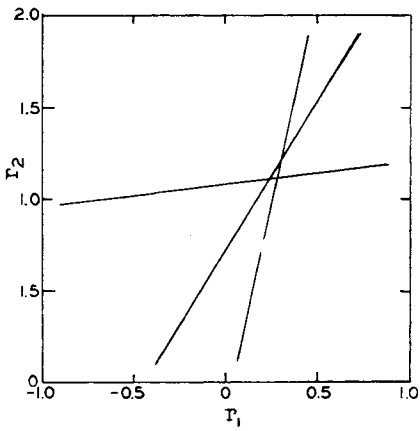


Fig. 4. Reactivity ratio diagram.

Copolymerization of vinyl pelargonate (M_1) and vinyl chloride (M_2).

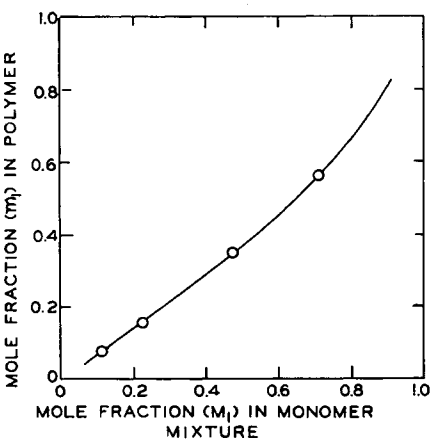


Fig. 5. Copolymer composition curve.

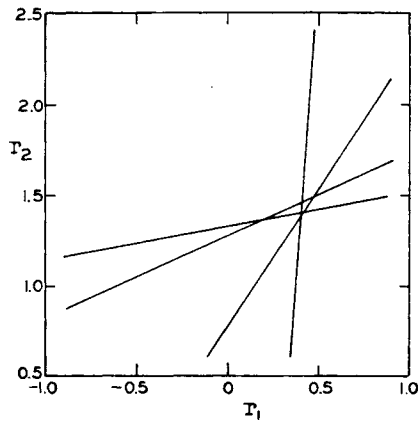


Fig. 6. Reactivity ratio diagram.

Copolymerization of vinyl pinonate (M_1) and vinyl chloride (M_2).

TABLE IV

Reactivity Ratio Data for the Solution Copolymerization of Vinyl Undecylenate and Vinyl Chloride at 60°C. (See Figs. 7 and 8)

	Charge[a]				
Number	Vinyl undecylenate, g.	Vinyl chloride, g.	Time, hrs.	Conversion, %	Anal. Cl, %
1	4.47	5.49	21	8	33.78
2	5.84	3.74	21	6	45.91
3	7.65	2.57	25	5	18.67
4	8.86	1.19	25	4	10.86

[a] Solvent, 5 ml. of benzene; initiator, 15 mg. of benzoyl peroxide per charge.

TABLE V

Reactivity Ratio Data for the Bulk Copolymerization of Vinyl Stearate and Vinyl Chloride at 60°C. (See Figs. 9 and 10)

	Charge[a]				
Number	Vinyl stearate, g.	Vinyl chloride, g.	Time, hrs.	Conversion, %	Anal. Cl, %
1	9.02	1.03	4	2	9.06
2	7.97	1.78	4	4	12.78
3	2.97	6.74	5	5	37.30
4	1.15	9.01	6	8	48.03

[a] Initiator, 15 mg. of benzoyl peroxide per charge.

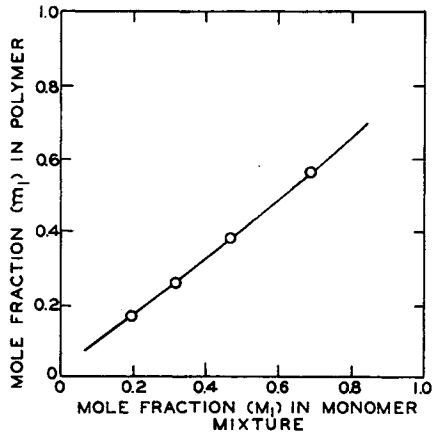


Fig. 7. Copolymer composition curve.

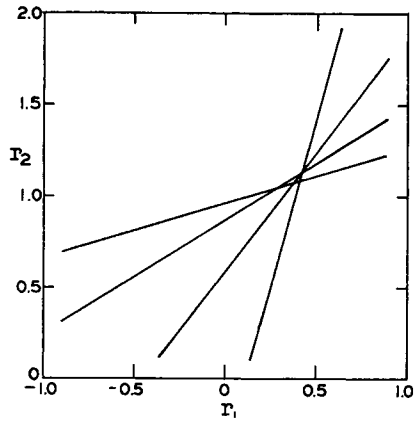


Fig. 8. Reactivity ratio diagram.

Copolymerization of vinyl undecylenate (M_1) and vinyl chloride (M_2).

TABLE VI

Reactivity Ratio Data for the Solution Copolymerization of Vinyl Pelargonate and Vinylidene Chloride at 60°C. (See Figs. 11 and 12)

Number	Charge[a] Vinyl pelargonate, g.	Vinylidene chloride, g.	Time, hrs.	Conversion, %	Anal. Cl, %
1	8.13	1.94	4	4	44.18
2	6.62	3.65	4	5	54.20
3	5.09	5.04	8	5	59.62

[a] Solvent, 5 ml. of benzene; initiator, 15 mg. of benzoyl peroxide per charge.

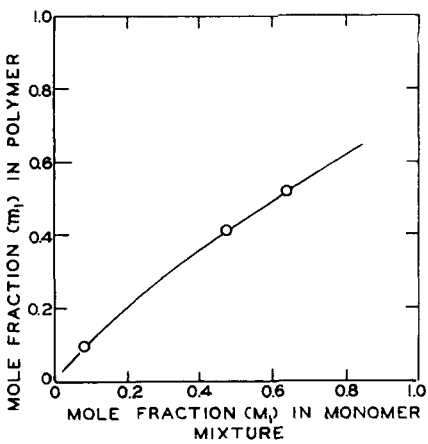


Fig. 9. Copolymer composition curve.

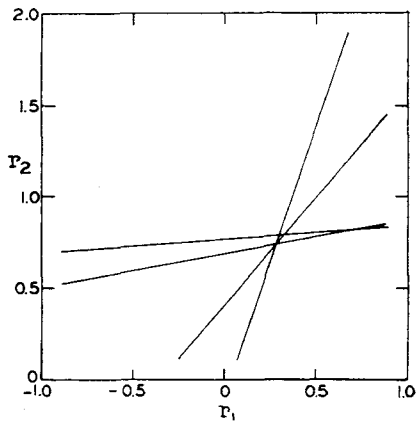


Fig. 10. Reactivity ratio diagram.

Copolymerization of vinyl stearate (M_1) and vinyl chloride (M_2).

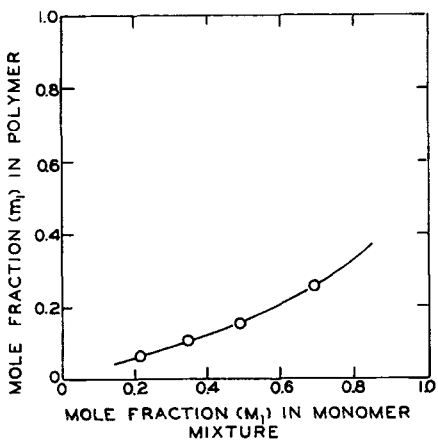


Fig. 11. Copolymer composition curve.

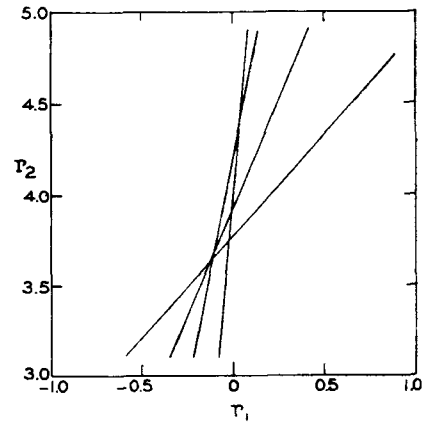


Fig. 12. Reactivity ratio diagram.

Copolymerization of vinyl pelargonate (M_1) and vinylidene chloride (M_2).

TABLE VII

Reactivity Ratio Date for the Solution Copolymerization of Vinyl Pinonate and Vinylidene Chloride at 60°C. (See Figs. 13 and 14)

Number	Charge[a] Vinyl pinonate, g.	Vinylidene chloride, g.	Time, hrs.	Conversion, %	Anal. Cl, %
1	9.07	1.19	4	1	30.47
2	8.00	1.98	4	1	39.16
3	6.99	3.11	4	1	46.65
4	6.04	3.93	4	2	51.48
5	3.21	7.69	4	2	64.36

[a] Solvent, 3.5 ml. of benzene; initiator, 21 mg. of benzoyl peroxide per charge.

TABLE VIII

Reactivity Ratio Data for the Solution Copolymerization of Vinyl Undecylenate and Vinylidene Chloride at 60°C. (See Figs. 15 and 16)

Number	Charge[a] Vinyl undecylenate, g.	Vinylidene chloride, g.	Time, hrs.	Conversion, %	Anal. Cl, %
1	8.42	1.58	5	5	33.81
2	6.73	3.27	5	8	45.18
3	4.49	5.58	5	10	57.42

[a] Solvent, 5 ml. of benzene; initiator, 15 mg. of benzoyl peroxide per charge.

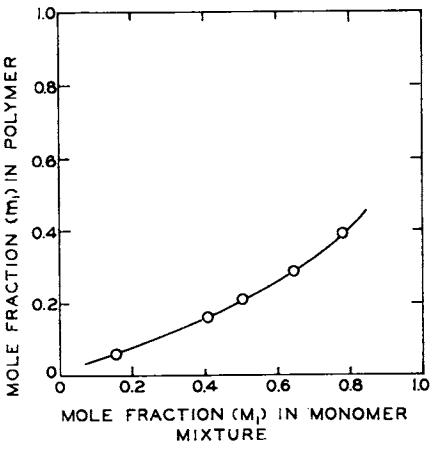


Fig. 13. Copolymer composition curve.

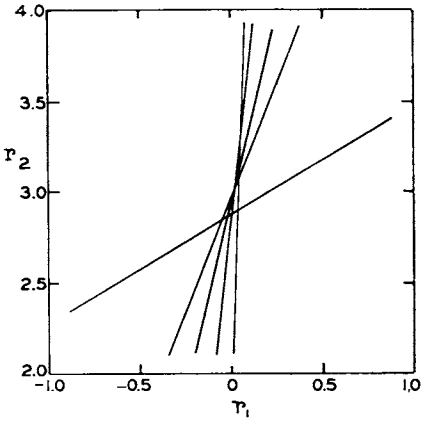


Fig. 14. Reactivity ratio diagram.

Copolymerization of vinyl pinonate (M_1) and vinylidene chloride (M_2).

TABLE IX
Reactivity Ratio Data for the Solution Copolymerization of Vinyl Stearate and Vinylidene Chloride at 60°C. (See Figs. 17 and 18)

Number	Charge[a] Vinyl stearate, g.	Vinylidene chloride, g.	Time, hrs.	Conversion, %	Anal. Cl, %
1	6.96	3.03	4	3	47.76
2	5.73	4.61	4	3	56.10
3	2.96	7.87	4	5	66.73

[a] Solvent, 3.5 ml. of benzene; initiator, 15 mg. of benzoyl peroxide per charge.

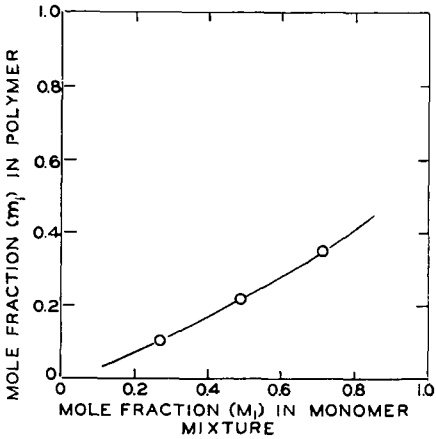


Fig. 15. Copolymer composition curve.

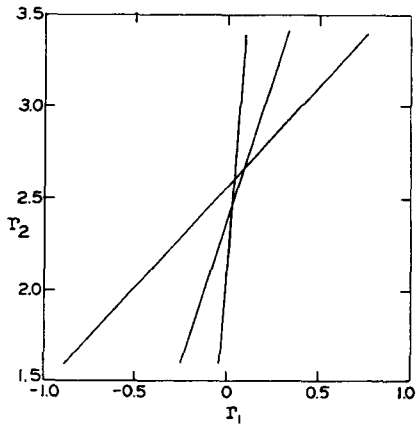


Fig. 16. Reactivity ratio diagram.

Copolymerization of vinyl undecylenate (M_1) and vinylidene chloride (M_2).

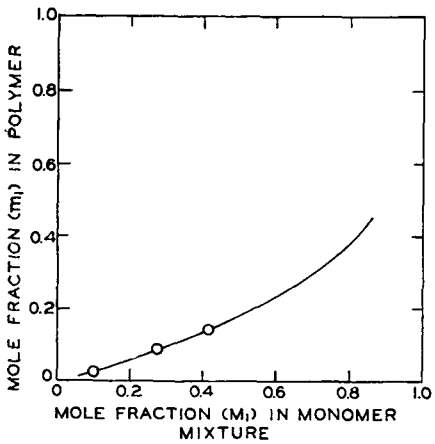


Fig. 17. Copolymer composition curve.

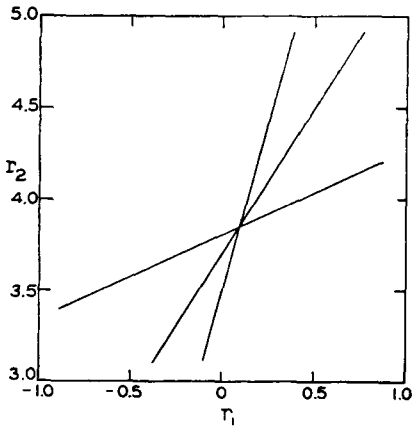


Fig. 18. Reactivity ratio diagram.

Copolymerization of vinyl stearate (M_1) and vinylidene chloride (M_2).

TABLE X

Reactivity Ratio Data for the Solution Copolymerization of Vinyl Pelargonate and Acrylonitrile at 60°C. (See Figs. 19 and 20)

	Charge[a]				
Number	Vinyl pelargonate, g.	Acrylonitrile g.	Time, hrs.	Conversion, %	Anal. N, %
1	9.01	0.99	12	3	8.78
2	8.10	1.93	4	4	14.21
3	4.99	5.17	7	6	21.13
4	3.03	7.08	4	6	23.58

[a] Solvent, 5 ml. of benzene and 5 ml. of *N*,*N*-dimethyl formamide; initiator, 15 mg. of benzoyl peroxide per charge.

TABLE XI

Reactivity Ratio Data for the Solution Copolymerization of Vinyl Pinonate and Acrylonitrile in *N*,*N*-Dimethyl Formamide Solution at 60°C. (See Figs. 21 and 22)

	Charge[a]				
Number	Vinyl pinonate, g.	Acrylonitrile, g.	Time, hrs.	Conversion, %	Anal. N, %
1	8.41	1.52	12	6	11.34
2	8.01	1.94	12	7	12.75
3	7.20	2.82	4	1	15.51
4	5.01	5.02	3	1	20.58
5	2.98	7.05	1	2	23.52

[a] Solvent, 2 ml. of *N*,*N*-dimethyl formamide; initiator, 50 mg. of benzoyl peroxide per charge.

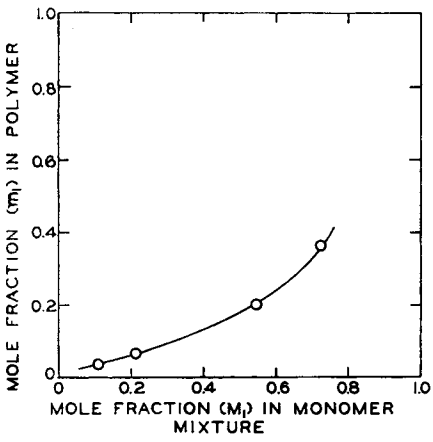


Fig. 19. Copolymer composition curve.

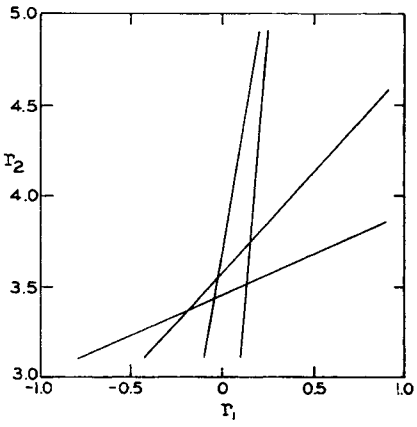


Fig. 20. Reactivity ratio diagram.

Copolymerization of vinyl pelargonate (M_1) and acrylonitrile (M_2).

TABLE XII

Reactivity Ratio Data for the Solution Copolymerization of Vinyl Undecylenate and Acrylonitrile at 60°C. (See Figs. 23 and 24)

Number	Charge[a] Vinyl undecylenate, g.	Charge[a] Acrylonitrile, g.	Time, hrs.	Conversion, %	Anal. N, %
1	7.99	2.36	3	1	11.83
2	6.28	4.29	2	1	15.98
3	4.00	5.96	2	1	19.74

[a] Solvent, 5 ml. of *N*,*N*-dimethyl formamide; initiator, 15 mg. of benzoyl peroxide per charge.

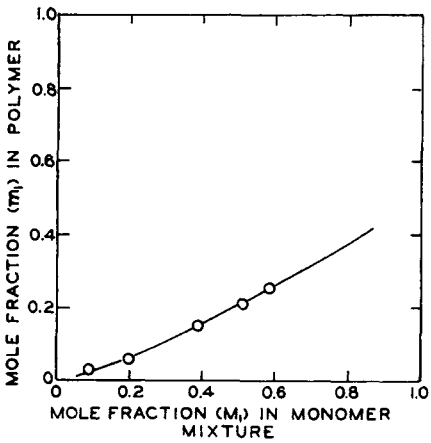


Fig. 21. Copolymer composition curve.

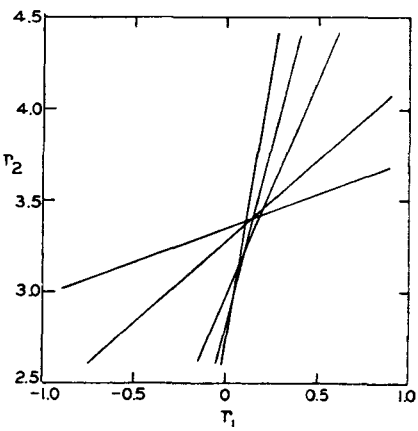


Fig. 22. Reactivity ratio diagram.

Copolymerization of vinyl pinonate (M_1) and acrylonitrile (M_2).

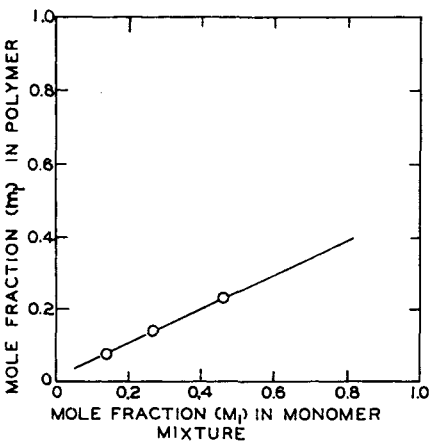


Fig. 23. Copolymer composition curve.

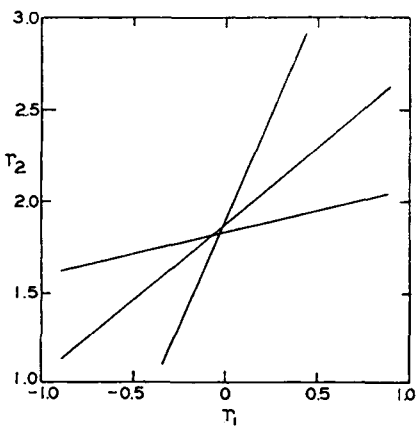


Fig. 24. Reactivity ratio diagram.

Copolymerization of vinyl undecylenate (M_1) and acrylonitrile (M_2).

TABLE XIII

Reactivity Ratio Data for the Solution Copolymerization of Vinyl Stearate and Acrylonitrile at 60°C. (See Figs. 25 and 26)

	Charge[a]				
Number	Vinyl stearate, g.	Acrylonitrile, g.	Time, hrs.	Conversion, %	Anal. N, %
1	8.93	0.98	2	4	9.63
2	7.50	2.43	6	8	15.78
3	6.66	4.02	7	11	19.18

[a] Solvent, 5 ml. of benzene and 5 ml. of N,N-dimethyl formamide; initiator, 15 mg. of benzoyl peroxide per charge.

TABLE XIV

Reactivity Ratio Data for the Solution Copolymerization of Vinyl Undecylenate and Methyl Acrylate at 60°C. (See Figs. 27 and 28)

	Charge[a]				
Number	Vinyl undecylenate, g.	Methyl acrylate, g.	Time, hrs.	Conversion, %	Anal. C, %
1	7.90	2.09	7	4	63.67
2	7.08	2.89	7	6	62.27
3	2.09	8.13	7	2	56.96

[a] Solvent, 5 ml. of benzene; initiator, 20 mg. of benzoyl peroxide per charge.

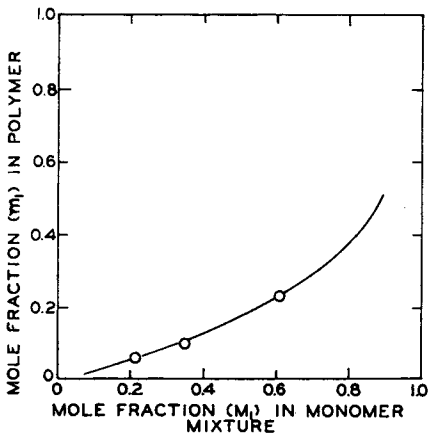


Fig. 25. Copolymer composition curve.

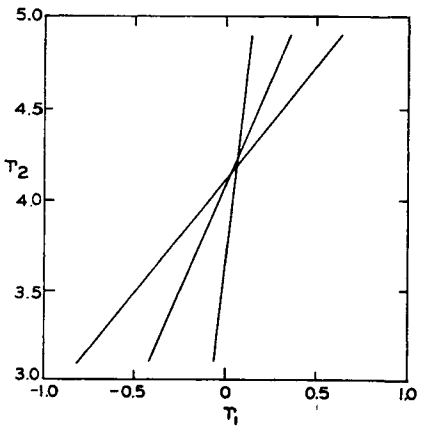


Fig. 26. Reactivity ratio diagram.

Copolymerization of vinyl stearate (M_1) and acrylonitrile (M_2).

TABLE XV
Reactivity Ratio Data for the Solution Copolymerization of Vinyl Pelargonate and Butadiene at 60°C. (See Figs. 29 and 30)

Number	Charge[a] Vinyl pelargonate, g.	Butadiene, g.	Time, hrs.	Conversion, %	Anal. C, %
1	9.21	1.00	100	2	83.58
2	8.93	1.05	90	2	85.69
3	8.34	2.01	90	3	86.55
4	6.94	2.90	70	3	87.76
5	6.88	3.06	100	3	87.52
6	5.08	5.01	70	5	88.16

[a] Solvent, 5 ml. of benzene; initiator, 15 mg. of benzoyl peroxide.

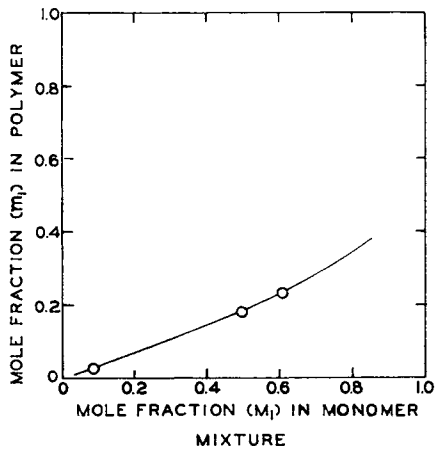


Fig. 27. Copolymer composition curve.

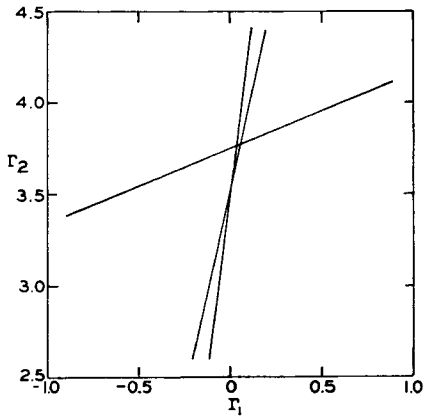


Fig. 28. Reactivity ratio diagram. Copolymerization of vinyl undecylenate (M_1) and methyl acrylate (M_2).

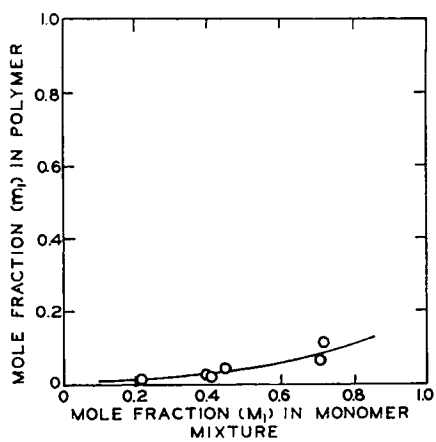


Fig. 29. Copolymer composition curve.

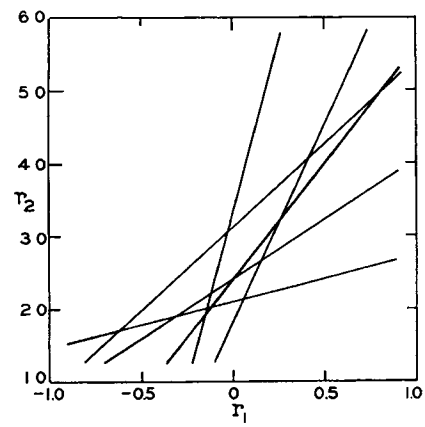


Fig. 30. Reactivity ratio diagram. Copolymerization of vinyl pelargonate (M_1) and butadiene (M_2).

TABLE XVI
Reactivity Ratio Data for the Solution Copolymerization of Vinyl Pinonate and Butadiene at 60°C. (See Figs. 31 and 32)

Number	Charge[a] Vinyl pinonate, g.	Butadiene, g.	Time, hrs.	Conversion, %	Anal. C, %
1	9.02	1.07	90	1	85.77
2	7.92	2.12	90	2	87.22
3	6.95	3.16	90	3	87.61
4	5.33	4.91	90	3	88.38

[a] Solvent, 5 ml. of benzene; initiator, 30 mg. of benzoyl peroxide per charge.

TABLE XVII
Reactivity Ratio Data for the Solution Copolymerization of Vinyl Undecylenate and Butadiene at 60°C. (See Figs. 33 and 34)

Number	Charge[a] Vinyl undecylenate, g.	Butadiene, g.	Time, hrs.	Conversion, %	Anal. C, %
1	9.75	1.00	48	4	86.28
2	8.10	1.93	48	4	87.37
3	6.33	3.82	48	5	88.26
4	3.81	6.06	48	6	88.74

[a] Solvent, 5 ml. of benzene; initiator, 15 mg. of benzoyl peroxide per charge.

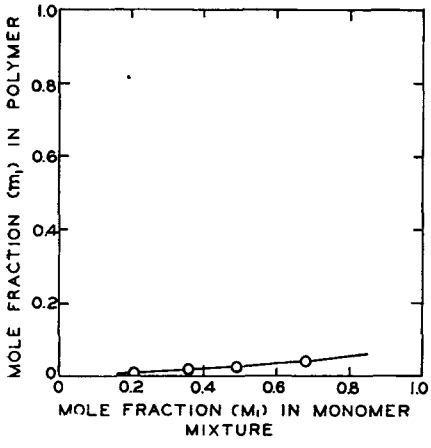


Fig. 31. Copolymer composition curve.

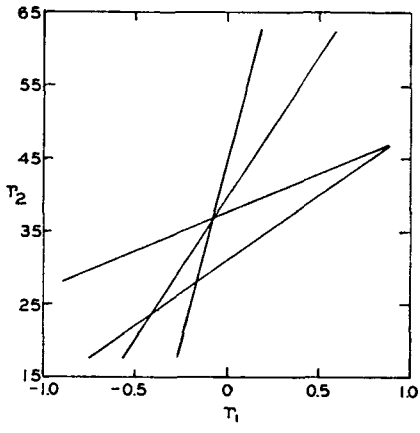


Fig. 32. Reactivity ratio diagram.

Copolymerization of vinyl pinonate (M_1) and butadiene (M_2).

TABLE XVIII
Reactivity Ratio Data for the Solution Copolymerization of Vinyl Stearate and Butadiene at 60°C. (See Figs. 35 and 36)

Number	Charge[a] Vinyl stearate, g.	Butadiene, g.	Time, hrs.	Conversion, %	Anal. C, %
1	9.76	0.75	100	1	85.31
2	9.56	1.02	100	1	86.72
3	8.39	1.55	100	1	87.58
4	7.72	2.26	100	2	88.03
5	7.29	2.85	100	2	88.00
6	5.94	4.06	100	3	88.39

[a] Solvent, 5 ml. of benzene; initiator, 40 mg. of benzoyl peroxide per charge.

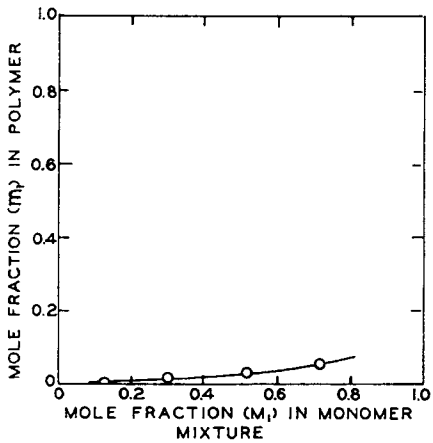


Fig. 33. Copolymer composition curve.

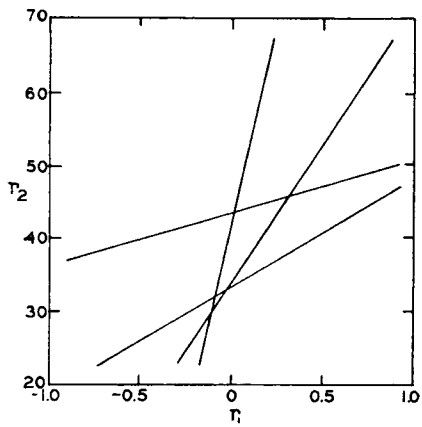


Fig. 34. Reactivity ratio diagram.

Copolymerization of vinyl undecylenate (M_1) and butadiene (M_2).

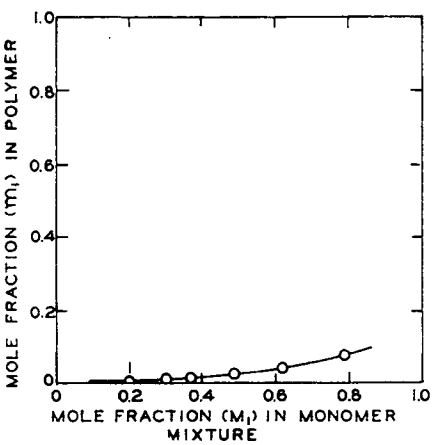


Fig. 35. Copolymer composition curve.

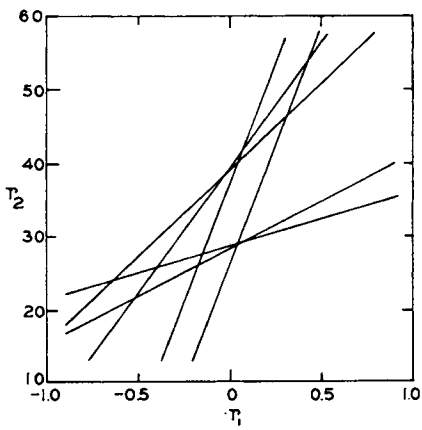


Fig. 36. Reactivity ratio diagram.

Copolymerization of vinyl stearate (M_1) and butadiene (M_2).

TABLE XIX
Reactivity Ratio Data for the Bulk Copolymerization of Vinyl Pelargonate and Styrene at 60°C. (See Figs. 37 and 38)

Number	Charge[a] Vinyl pelargonate, g.	Styrene, g.	Time, hrs.	Conversion, %	Anal. C, %
1	9.10	1.24	9	5	89.42
2	8.08	1.90	6	3	91.08
3	6.00	4.26	5	4	91.87
4	2.45	7.64	5	6	92.10

[a] Initiator, 15 mg. of benzoyl peroxide per charge.

TABLE XX
Reactivity Ratio Data for the Solution Copolymerization of Vinyl Pinonate and Styrene at 60°C. (See Figs. 39 and 40)

Number	Charge[a] Vinyl pinonate, g.	Styrene, g.	Time, hrs.	Conversion, %	Anal. C, %
1	7.91	2.09	19	1	90.66
2	6.60	3.52	12	3	91.51
3	5.50	4.69	12	3	91.85
4	5.09	5.26	19	5	91.98
5	4.06	5.96	6	1	91.96
6	2.02	8.04	6	2	92.19

[a] Solvent, 10 ml. of benzene; initiator, 30 mg. of benzoyl peroxide per charge.

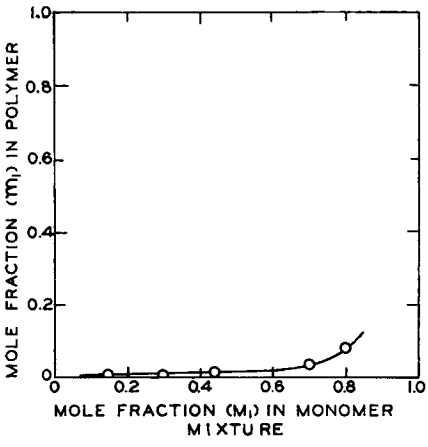


Fig. 37. Copolymer composition curve.

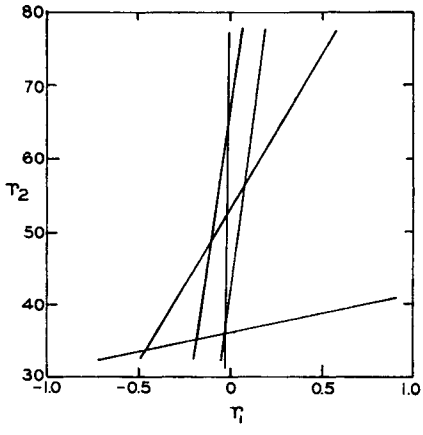


Fig. 38. Reactivity ratio diagram.

Copolymerization of vinyl pelargonate (M_1) and styrene (M_2).

TABLE XXI
Reactivity Ratio Data for the Solution Copolymerization of Vinyl Undecylenate and Styrene at 60°C. (See Figs. 41 and 42)

Number	Charge[a] Vinyl undecylenate, g.	Styrene, g.	Time, hrs.	Conversion, %	Anal. C, %
1	8.34	2.13	10	1	90.59
2	8.02	1.95	19	1	90.63
3	6.63	3.63	10	1	91.10
4	4.39	5.62	8	1	91.72
5	3.01	7.02	6	3	91.98
6	1.22	8.74	6	7	92.14

[a] Solvent, 5 ml. benzene; initiator, 15 mg. of benzoyl peroxide per charge.

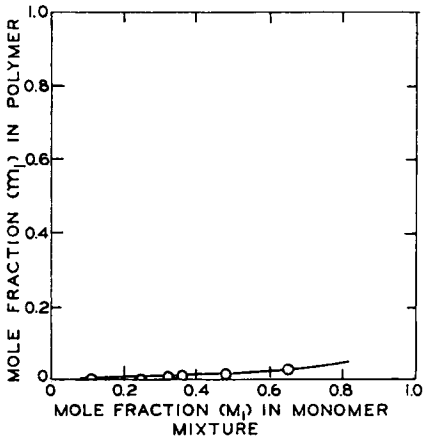


Fig. 39. Copolymer composition curve.

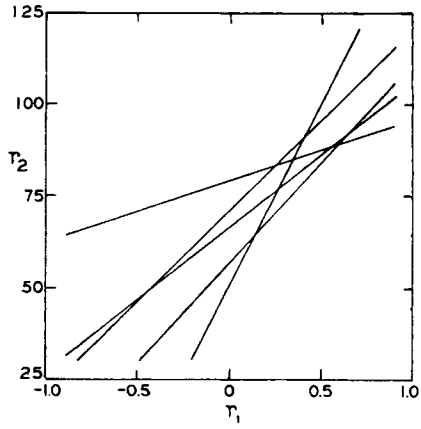


Fig. 40. Reactivity ratio diagram. Copolymerization of vinyl pinonate (M_1) and styrene (M_2).

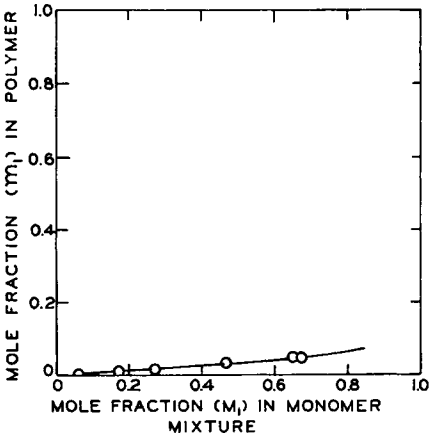


Fig. 41. Copolymer composition curve.

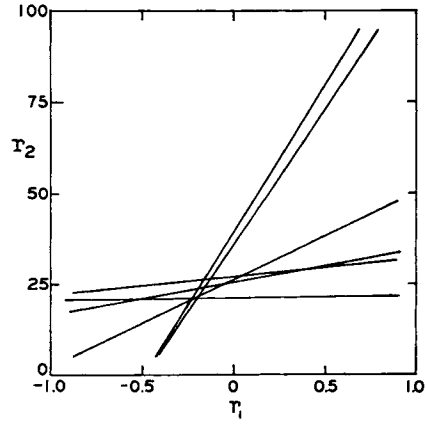


Fig. 42. Reactivity ratio diagram. Copolymerization of vinyl undecylenate (M_1) and styrene (M_2).

TABLE XXII
Reactivity Ratio Data for the Bulk Copolymerization of Vinyl Stearate and Styrene at 60°C. (See Figs. 43 and 44)

Number	Charge[a] Vinyl stearate, g.	Styrene, g.	Time, hrs.	Conversion, %	Anal. C, %
1	8.84	1.41	10	1	91.04
2	8.13	2.08	10	1	91.02
3	6.02	4.08	7	5	92.11
4	3.00	6.94	4	3	91.87

[a] Initiator, 15 mg. of benzoyl peroxide per charge.

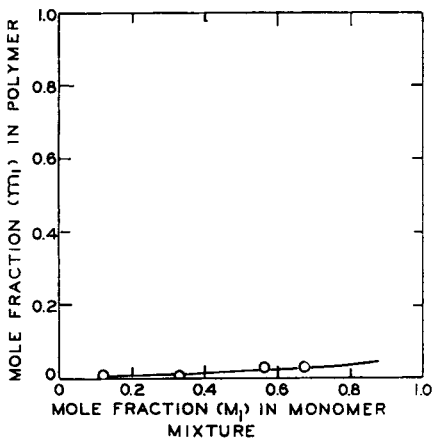


Fig. 43. Copolymer composition curve.

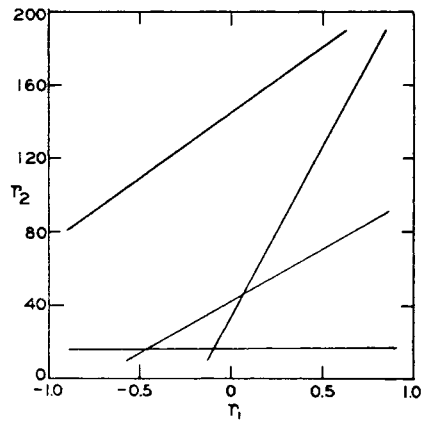


Fig. 44. Reactivity ratio diagram.

Copolymerization of vinyl stearate (M_1) and styrene (M_2).

Polymer Properties

All of the vinyl esters under study were found to copolymerize readily with vinyl chloride to give polymers which ranged from brittle materials to tough, plastic materials with increasing incorporation of vinyl ester component. The polymers were soluble in tetrahydrofuran and dioxane. The products with large amounts of vinyl ester incorporated in the copolymer chain were soluble in benzene.

Vinylidene chloride, when copolymerized with vinyl esters, yielded copolymers which were somewhat plasticized and which were much more soluble in common solvents than polyvinylidene chloride. In order to obtain incorporation of vinyl esters in more than negligible amounts, it was necessary to use high mole fractions of the vinyl esters in the charge.

The copolymers of vinyl esters with acrylonitrile were usually powdery, or hard, brittle materials. Little or no plasticization was noticed as a result of the incorporation of vinyl esters in these copolymers.

Vinyl undecylenate was copolymerized with methyl acrylate to give soft, insoluble polymers having moderate incorporation of vinyl undecylenate. This indicates that the terminal vinyl group of the acid portion probably participates slightly in the copolymerization.

The products resulting from the copolymerization of vinyl esters with butadiene were very sticky, and in some cases were actually viscous liquids, indicating that the molecular weights of these polymers were quite low. The amounts of vinyl ester incorporated in these copolymers were found to be very low, even when large mole fractions of vinyl ester were used in the charge.

Styrene, when copolymerized with vinyl esters, was found to yield copolymers which contained only very small amounts of vinyl ester and which exhibited properties which were essentially similar to those of polystyrene itself.

DISCUSSION

The data obtained in the copolymerizations have been used to calculate the reactivity ratios for the different monomer pairs under consideration, using the intersection method of Mayo and Lewis,[3] in which the mole ratios are substituted into the equation:

$$r_2 = \frac{M_1}{M_2}\left[\frac{m_2}{m_1}\left(1 + \frac{M_1}{M_2}r_1\right) - 1\right]$$

in which M_1 and M_2 are the number of moles, respectively, of monomers 1 and 2 in the charging stock and m_1 and m_2 are the moles, respectively, of monomer 1 and monomer 2 in the copolymer formed. The r_1 and r_2 values listed in Table XXIII are the arithmetic mean of the valid intersections shown on the preceding plots. The error, unless otherwise noted, was determined by multiplying the difference between the maximum and minimum values of the intersection by one half.

For comparison with the reactivity ratios which have been reported above we have listed in Table XXIV the reactivity ratios of some other vinyl esters which have been reported.

The results of the reactivity ratio studies summarized in Tables XXIII and XXIV indicate clearly that the copolymerization behavior of vinyl esters is insensitive to the size and shape of the acyl portion of the ester. All of the vinyl esters thus far studied copolymerize readily with vinyl chloride but not with styrene or butadiene, which produce addition products with the intermediate free radicals with considerable resonance stabilization. Vinylidene chloride, acrylonitrile, and methyl acrylate fall in an intermediate group between the two extremes mentioned.

Alfrey and Price[12] have attempted to calculate quantitatively the contributions of resonance effects and polar effects in copolymerization reactions. By means of the equations which they derived, the Q and e values for the vinyl esters which have been studied and reported in Table XXIII

TABLE XXIII
Reactivity Ratios of High Molecular Weight Vinyl Esters

M_1	M_2	r_1	r_2
Vinyl levulinate	Vinyl chloride	0.419 ± 0.002	1.40 ± 0.004
Vinyl pelargonate	Vinyl chloride	0.282 ± 0.035	1.16 ± 0.06
Vinyl pinonate	Vinyl chloride	0.446 ± 0.028	1.458 ± 0.04
Vinyl undecylenate	Vinyl chloride	0.358 ± 0.065	1.06 ± 0.05
Vinyl stearate	Vinyl chloride	0.290 ± 0.025	0.745 ± 0.025
Vinyl pelargonate	Vinylidene chloride	0.0 ± 0.01	4.08 ± 0.20
Vinyl pinonate	Vinylidene chloride	0.030 ± 0.028	3.00 ± 0.18
Vinyl undecylenate	Vinylidene chloride	0.054 ± 0.030	2.58 ± 0.09
Vinyl stearate	Vinylidene chloride	0.075 ± 0.025	3.80 ± 0.05
Vinyl pelargonate	Acrylonitrile	0.059 ± 0.095	3.57 ± 0.16
Vinyl pinonate	Acrylonitrile	0.143 ± 0.046	3.40 ± 0.04
Vinyl undecylenate	Acrylonitrile	0.0 ± 0.010	1.82 ± 0.04
Vinyl stearate	Acrylonitrile	0.064 ± 0.005	4.20 ± 0.02
Vinyl pelargonate	Butadiene[a]	0.02 ± 0.02	26.3 ± 10.0
Vinyl pinonate	Butadiene	0.015 ± 0.015	37.8 ± 6.5
Vinyl undecylenate	Butadiene	0.015 ± 0.015	37.9 ± 4.0
Vinyl stearate	Butadiene	0.034 ± 0.034	34.5 ± 6.6
Vinyl pelargonate	Styrene[a]	0.01 ± 0.01	49.5 ± 15
Vinyl pinonate	Styrene	0.01 ± 0.01	65 ± 17
Vinyl undecylenate	Styrene	0.02 ± 0.02	29 ± 9
Vinyl stearate	Styrene	0.01 ± 0.01	68 ± 30
Vinyl undecylenate	Methyl acrylate	0.031 ± 0.026	369 ± 0.12

[a] The values listed for r_1 in the determination with butadiene and styrene are equal to $(1/2r_2) \pm (1/2r_2)$ and were determined by assuming the maximum value of $r_1 = 1/r_2$ and the minimum value of $r_1 = 0$.

TABLE XXIV
Literature Values for Vinyl Ester Reactivity Ratios

M_1	M_2	r_1	r_2	Ref.
Vinyl acetate	Vinyl chloride	0.23 ± 0.02	1.68 ± 0.08	5
Vinyl acetate	Vinylidene chloride	0. ± 0.03	3.6 ± 0.5	6
Vinyl formate	Acrylonitrile	0.04 ± 0.005	3.0 ± 0.6	7
Vinyl acetate	Acrylonitrile	0.061 ± 0.013	4.05 ± 0.3	5
Vinyl acetate	Acrylonitrile	0.02 ± 0.02	6 ± 2	8
Vinyl stearate	Acrylonitrile	0.03	4.3	9
Vinyl acetate	Styrene	0.01 ± 0.01	55 ± 10	5
Vinyl acetate	Methyl acrylate	0.1 ± 0.1	9 ± 2.5	5
Vinyl stearate	Methyl acrylate	0.03	5.8	9
Vinyl trifluoroacetate	Vinyl acetate	0.32	0.6	10
Vinyl palmitate	Vinyl acetate	0.78 ± 0.10	1.15 ± 0.13	11
Vinyl palmitate	Vinyl acetate	0.66 ± 0.07	0.84 ± 0.10	11

have been calculated and plotted on a Q–e map in Figure 45 in relation to the position of the reference monomers which are based on Q–e values previously calculated.[13] The very small range of values obtained for Q and e for the vinyl esters studied strengthens the view that the copolymerization behavior of such esters is virtually independent of the acyl group.

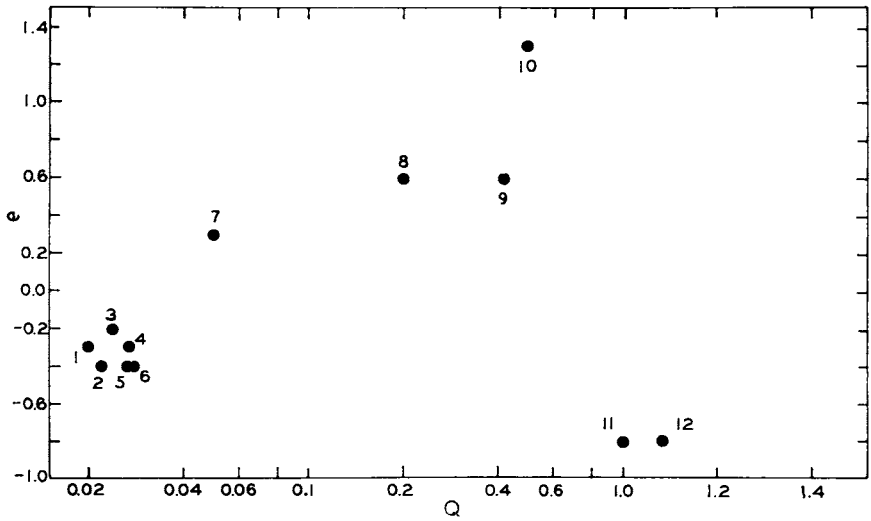


Fig. 45. *Q–e* map for a number of monomers: (1) vinyl acetate, (2) vinyl pelargonate, (3) vinyl pinonate, (4) vinyl undecylenate, (5) vinyl levulinate, (6) vinyl stearate, (7) vinyl chloride, (8) vinylidene chloride, (9) methyl acrylate, (10) acrylonitrile, (11) styrene, (12) butadiene.

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Synopsis

The copolymerization reaction of five vinyl esters of aliphatic acids with vinyl chloride, vinylidene chloride, acrylonitrile, butadiene, styrene, and methyl acrylate have been studied. The reactivity ratios have been determined and the Q and e values for the esters have been calculated. The results clearly show that the nature of the acyl residue in a vinyl ester has little influence on its reactivity ratio in a copolymerization reaction or on the Q or e value.

Résumé

On a étudié la copolymérisation de cinq esters vinyliques d'acides aliphatiques avec le chlorure de vinyle, le chlorure de vinylidène, l'acrylonitrile, le butadiène, le styrène et l'acrylate de méthyle. Les rapports de réactivité ont été déterminés et les valeurs Q et e de ces différents esters ont été calculées. Les résultats indiquent clairement que la nature du résidu acyle dans un ester vinylique n'exerce qu'une faible influence sur les rapports de réactivité dans les réactions de copolymérisation ou sur les valeurs de Q et de e.

Zusammenfassung

Die Copolymerisationsreaktion von fünf Vinylestern von aliphatischen Säuren mit Vinylchlorid, Vinylidenchlorid, Acrylnitril, Butadien, Styrol und Methylacrylat wurden untersucht. Die Reaktivitätsverhältnisse wurden bestimmt und die Q- und e-Werte für die Ester wurden berechnet. Die Resultate zeigen bestimmt, dass die Natur des Acylrückstandes in einem Vinylester wenig Einfluss auf sein Reaktivitätsverhältnis in einer Copolymerisationsreaktion oder auf die Q- und e-Werte hat.

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