

## Copolymerization of Trialkyl Aconitates with Vinylidene Chloride<sup>1</sup>

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Trialkyl aconitates have been reported to be light stabilizers for polyvinylidene chloride when added either before or after the polymerization process.<sup>3</sup> Since it is known that such esters will copolymerize with many vinyl monomers,<sup>4</sup> this work was undertaken to determine reactivity ratios for trimethyl aconitate and vinylidene chloride and to examine some copolymers of trimethyl, triethyl, and tri-*n*-butyl aconitate with this chloride to see how much of the esters could be introduced into such copolymers. It was hoped that a sufficient amount of the ester might copolymerize to give a plasticized copolymer, but this was not successfully accomplished. The reactivity ratios bear out this finding, for  $r_1$  (trimethyl aconitate) was found to be  $0.01 \pm 0.1$  and  $r_2$  (vinylidene chloride) was found to be  $54 \pm 5$ .

### EXPERIMENTAL

The trimethyl aconitate and triethyl aconitate used in this work were gifts from Dr. L. F. Martin of the Southern Utilization Research and Development Division of the Agricultural Research Service, New Orleans. Tri-*n*-butyl aconitate was made by esterifying commercial aconitic acid with *n*-butyl alcohol in the presence of a little *p*-toluenesulfonic acid.

Trimethyl aconitate	b.p. 95–96° at 0.4 mm., $n_D^{20}$ 1.4635
Triethyl aconitate	b.p. 117–118° at 0.7 to 0.8 mm., $n_D^{20}$ 1.4545
Tri- <i>n</i> -butyl aconitate	b.p. 152–154° at 0.4 to 0.5 mm., $n_D^{20}$ 1.4565

TABLE I  
Reactivity Ratio Data for the Copolymerization of Trimethyl Aconitate and Vinylidene Chloride

Sample No.	Charge		% Cl in copolymer	Mole fraction of trimethyl aconitate in copolymer
	Trimethyl aconitate, g.	Vinylidene chloride, g.		
S <sub>46</sub>	2.05	8.03	72.80	0.002
S <sub>64</sub>	3.00	7.02	72.61	0.003
S <sub>68</sub>	7.03	3.10	70.11	0.019
S <sub>50</sub>	8.07	1.96	68.20	0.032

TABLE II  
 Aconitic Ester-Vinylidene Chloride Copolymers

Polymer No.	Aconitate	Polymerization conditions			Charge		Polymer					Remarks	
					Ester/VCl <sub>2</sub> ratio		Conver- sion, %	Infrared absorption (cm. <sup>-1</sup> )	Cl%	Ester/VCl <sub>2</sub> ratio			Melting point, °C.
		Initiator	Temp., °C.	Time, hr.	Mole	Weight				Mole	Weight		
E <sub>8</sub>	Trimethyl	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	50	20	1:7	1:3	35.7	655	72.25	1:169	1:80	175-180	Snow-white powder
							752						
							1734						
E <sub>88</sub>	Trimethyl	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	50	23	1:5	1:2	30.5	658	71.51	1:91	1:43	175-180	Snow-white powder
							755						
							1740						
E <sub>91</sub>	Trimethyl	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	60	15	1:7	1:3	57.3	659	71.59	1:95	1:45	170-175	Snow-white powder
							756						
							1740						
E <sub>90</sub>	Trimethyl	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	60	15	1:5	1:2	38.7	659	71.60	1:97	1:46	170-175	Snow-white powder
							756						
							1740						
N <sub>85</sub>	Trimethyl	AIBN	60	15	1:7	1:3	49.3	660	71.42	1:85	1:41	175-180	Snow-white powder
							756						
							1740						
R <sub>79</sub>	Trimethyl	Cumene HP	30	16	1:7	1:3	40.1	658	72.54	1:247	1:118	185-190	Snow-white powder
E <sub>71</sub>	Triethyl	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	50	21	1:7	1:2.5	48.9	658	71.76	1:191	1:52	175-180	Slightly beige powder
							754						
							1734						
E <sub>73</sub>	Triethyl	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	50	21	1:5	1:2	38.7	658	70.87	1:189	1:31	175-180	Slightly beige powder
							754						
							1735						

Polymer No.	Polymerization conditions			Charge			Polymer					
	Aconitate	Initiator	Temp., °C.	Time, hr.	Ester/VCl <sub>2</sub> ratio		Conver- sion, %	Infrared absorption (cm. <sup>-1</sup> )	Ester/VCl <sub>2</sub> ratio		Melting point, °C.	Remarks
					Mole	Weight			Mole	Weight		
E <sub>35</sub> <sup>1</sup>	Triethyl	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	60	15	1:7	1:2.5	64.8	656 753	72.17	1:192	1:74	175-180 Slightly beige powder
E <sub>37</sub> <sup>1</sup>	Triethyl	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	60	15	1:5	1:2	56.4	1730 657 754	71.14	1:189	1:35	170-175 Slightly beige powder
N <sub>88</sub>	Triethyl	AIBN	60	15	1:7	1:2.5	43.3	1735 658 755	71.10	1:189	1:35	175-180 Slightly beige powder
R <sub>80</sub>	Triethyl	Cumene HP	30	16	1:7	1:2.5	47.9	1735 659 755	72.06	1:192	1:66	180-185 Snow-white powder
E <sub>172</sub>	Tributyl	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	50	23	1:7	1:2.0	46.0	1735 657 755	70.82	1:250	1:30	175-180 Very slightly beige powder
E <sub>174</sub>	Tributyl	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	50	23	1:5	1:1.4	32.3	1734 656 670	70.73	1:250	1:29	175-180 Very slightly beige powder
E <sub>36</sub> <sup>1</sup>	Tributyl	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	60	15	1:7	1:2.0	49.8	1735 658 754	71.68	1:253	1:49	170-175 Very slightly beige powder
E <sub>33</sub> <sup>1</sup>	Tributyl	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	60	15	1:5	1:1.4	31.6	1735 657 755	71.14	1:251	1:35	170-175 Very slightly beige powder

(continued)

TABLE II (continued)

Polymer No.	Polymerization conditions			Charge		Polymer					Remarks	
	Aconitate	Initiator	Temp., °C.	Time, hr.	Ester/VCl <sub>2</sub> ratio		Conver- sion, %	Infrared absorption (cm. <sup>-1</sup> )	Ester/VCl <sub>2</sub> ratio			Melting point, °C.
					Mole	Weight			Mole	Weight		
N <sub>87</sub>	Tributyl	AIBN	60	15	1:7	1:2.0	38.7	660 756 1738	70.11	1:248	1:23	175-180 Snow-white powder
R <sub>81</sub>	Tributyl	Cumene HP	30	16	1:7	1:2.0	43.2	658 755 1734	71.91	1:254	1:58	185-190 Very slightly beige powder
E <sub>29</sub>	VCl <sub>2</sub> homo- polymer	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	50	20	—	—	85.9	656 753	72.33	—	—	185-190 Beige powder
E <sub>29</sub> <sup>1</sup>	VCl <sub>2</sub> homo- polymer	K <sub>2</sub> S <sub>2</sub> O <sub>8</sub>	60	15	—	—	92.9	—	—	—	—	185-190 Dark beige powder
N <sub>88</sub>	VCl <sub>2</sub> homo- polymer	AIBN	60	15	—	—	86.1	658 755	70.86	—	—	185-190 Very slightly beige powder; looks like the most sensitive to heat decomposition
R <sub>82</sub>	VCl <sub>2</sub> homo- polymer	Cumene HP	30	12	—	—	96.3	658 754	72.88	—	—	185-190 Beige powder

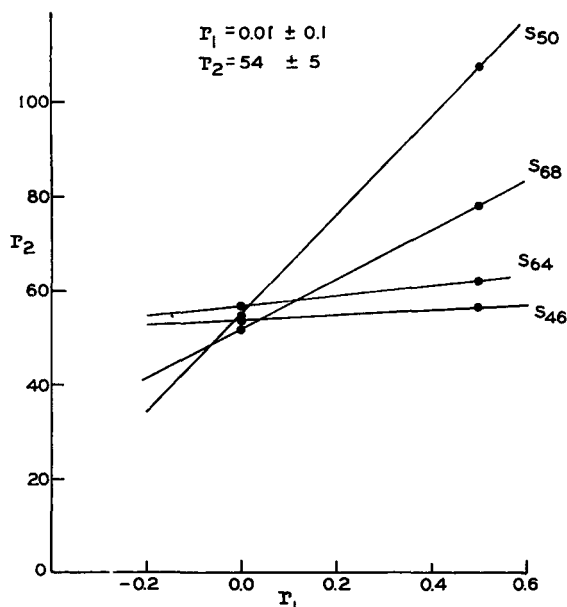


Fig. 1. Reactivity ratio diagram: *trans*-trimethyl aconitate-vinylidene chloride.

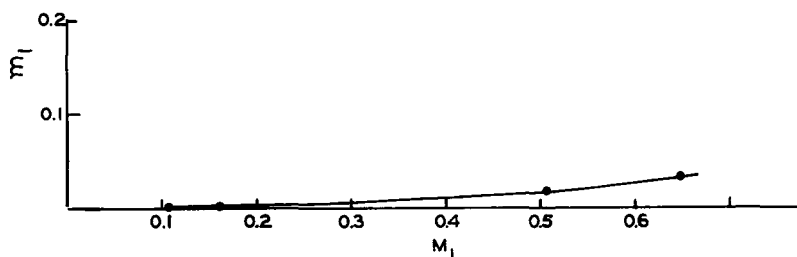


Fig. 2. Copolymer composition curve: *trans*-trimethyl aconitate-vinylidene chloride.

The vinylidene chloride was a gift from the Dow Chemical Company. It was washed with aqueous 10% potassium hydroxide solution to remove inhibitor and then with water until the water washings were neutral to litmus.

### Reactivity Ratios

Reactivity ratios were determined by the procedure of Mayo and Lewis.<sup>5</sup>

The copolymerizations were carried out in benzene solution with benzoyl peroxide as the initiator at 60°. Conversions were less than 10%. The copolymers were purified by boiling the powdered material with methanol followed by centrifuging the mixture. This was repeated five times. The powder was then dried for 2 days under 0.01 mm. pressure at room temperature. All samples showed an absorption band at 1735–1740  $\text{cm}^{-1}$

which indicates the presence of the ester component. The experimental data are given in Table I.

Figure 1 shows the reactivity ratio diagram and Figure 2 shows the copolymer composition curve.

### Aconitic Ester-Vinylidene Chloride Copolymers

The copolymerizations were carried out in three different recipes: the Mutual GR-S recipe<sup>6</sup> with potassium persulfate as the initiator, the cumene hydroperoxide recipe,<sup>7</sup> and the emulsion recipe with azobisisobutyronitrile as the initiator in Triton X-100 emulsion<sup>8</sup> to which had been added about 0.1% of Daxad 11 (an emulsion stabilizer produced by the Dewey and Almy Company). The experimental results are summarized in Table II. The melting points reported were taken on a copper bar by the procedure recommended by Beaman and Cramer.<sup>9</sup>

Samples E<sub>8</sub>, E<sub>71</sub>, E<sub>72</sub>, E<sub>73</sub>, E<sub>74</sub>, and E<sub>89</sub> were tested to see if the ester component had improved the plasticity of the copolymer over that of a sample of polyvinylidene chloride (E<sub>29</sub>). All samples carbonized in a Carver press at 160° under conditions normally used for molding the commercial stabilized polyvinylidene chloride.

We are indebted to Dr. R. F. Dunbrook of the Firestone Tire and Rubber Company for examining these samples. Micro analyses were performed by Mr. J. Nemeth, University of Illinois, Urbana, Illinois; Micro-Tech Laboratories, Skokie, Illinois; and Clark Microanalytical Laboratory, Urbana, Illinois. Mr. James Brader of the University of Illinois performed the infrared analyses.

### References

1. This is a partial report of work done under contract with three Utilization Research and Development Divisions, Agricultural Research Service, U.S. Department of Agriculture, and authorized by the Research and Marketing Act. The contract was supervised by Dr. J. C. Cowan of the Northern Division.
2. Educational exchange visitor from the University of Brazil, Rio de Janeiro, Brazil, supported by the Department of State under authority of Public Law 402 (Smith-Mundt Act, 80th Congress).
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### Synopsis

Reactivity ratios for the copolymerization of trimethyl aconitate and vinylidene chloride have been determined. Some copolymers of vinylidene chloride with trimethyl, triethyl, and tri-*n*-butyl aconitate have been reported. The stabilizing effect of aconitic esters on the color of polyvinylidene chloride has been confirmed.

### Résumé

Les rapports de réactivité de la copolymérisation de l'aconitate de triméthyle et du chlorure de vinylidène ont été déterminés. Quelques copolymères du chlorure de vinylène avec les aconitates de triméthyle, triéthyle et de tri-*n*-butyle ont été décrits. L'effet stabilisant des esters aconitiques sur la couleur du chlorure de polyvinylène a été confirmé.

### Zusammenfassung

Reaktivitätsverhältnisse für die Copolymerisation von Trimethyl-aconitat und Vinylidenchlorid wurden bestimmt. Einige Copolymere von Vinylidenchlorid mit Trimethyl-, Triäthyl- und Tri-*n*-butyl-Aconitat wurden gegeben. Die stabilisierende Wirkung von aconitischen Estern auf die Farbe von Polyvinylidenchlorid wurde bestätigt.

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