[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

PREPARATION AND PROPERTIES OF MONOMERIC AND POLYMERIC ACRYLIC ESTERS OF ETHER-ALCOHOLS[2]

C. E. REHBERG AND W. A. FAUCETTE[3]

Received May 11, 1949

An earlier paper (1) from this Laboratory reported the acrylic esters of the methyl, ethyl, and butyl monoethers of glycol. They had been made by the pyrolysis of the corresponding α-acetoxypropionates. Only low yields were obtained, and no description of their polymers was given. The present work was intended to develop a more satisfactory method of preparing these and similar esters and to determine some of the properties of their polymers.

Since many acrylic esters had been previously prepared in this Laboratory by the alcoholysis of methyl or ethyl acrylate (2–6), this method was used in the present work. In most cases this method was satisfactory, and the yields were high.

The monomeric esters were colorless, mobile liquids having characteristic mild odors. Table I shows the yields, physical constants and analytical data.

Polymeric esters. In general, the acrylates and methacrylates of ether-alcohols appeared to polymerize much more readily than did the alkyl esters (3–5).

Most of the esters were polymerized in bulk, in emulsion and in solution. The polymers were usually soft, elastic and rubbery, and most of those prepared in solution were tacky. The brittle points of the polymers of several of the alkoxyethyl acrylates were determined and may be compared with those of alkyl acrylates of approximately equal molecular weight: methoxyethyl, −25° (*n*-butyl, −45°); ethoxyethyl, −40° (*n*-amyl, −53°); butoxyethyl, −54° (*n*-heptyl, −59°); and isopropoxyethyl, −28°. These data show that the polymers of the first several *n*-alkoxyethyl acrylates have higher brittle points than the corresponding *n*-alkyl polyacrylates but the difference diminishes as the molecular weight of the monomer increases.

The polymers prepared in solutions of less than about 40% concentration were completely soluble, whereas those prepared in bulk or emulsion usually contained some insoluble, gelled material.

Air-curing of polymers. Exposure of the soluble polymers to air at room temperature for several weeks or at 100–150° for a few hours resulted in the formation of hard, tough, glossy, non-tacky, insoluble and infusible surface films.

Addition of benzoyl peroxide (5%) or soluble cobalt salts, such as the naphthenate or 2-ethylhexoate (0.01–.05%), greatly accelerated the cure, so that some cured in only 8 to 10 minutes at 100°. Large masses or thick films of the polymers cured only on their exposed surfaces, regardless of catalyst, time or

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Presented in part before the Division of Paint, Varnish, and Plastics Chemistry of the American Chemical Society, Atlantic City, N. J., April, 1946.

[3] Present address: Corn Products Refining Company, Argo, Illinois.

TABLE I
ACRYLIC ESTERS OF ETHER-ALCOHOLS

ACRYLATE	B.P., °C.	MM.	YIELD, %	n_D^{20}	d_4^{20}	MOL. REFRACTION		SAPON. EQ.		ANALYSES			
										C		H	
						Calc'd	Found	Calc'd	Found	Calc'd	Found	Calc'd	Found
2-Methoxyethyl[a]	59	12	96	1.4272	1.0131	32.74	33.00	130.1	128.3	55.4	55.2	7.7	7.8
2-Ethoxyethyl[a]	78	23	96	1.4282	0.9819	37.36	37.79	144.2	144.4	58.3	58.3	8.4	8.4
2-(2-Chloroethoxy)ethyl	74	0.8	63	1.4580	1.1471	42.22	42.49	89.3	91.7	47.1	47.4	6.2	6.6
2-Isopropoxyethyl[a]	82	19	95	1.4258	0.9549	41.97	42.44	158.2	158.6	60.7	60.8	8.9	9.2
2-Butoxyethyl[a]	64	2	95	1.4323	0.9497	46.59	47.07	172.2	173.3	62.8	62.7	9.4	9.3
2-(2-Ethylhexoxy)ethyl	87	0.5	90	1.4408	0.9215	65.06	65.40	228.3	226.2	68.4	68.9	10.6	10.9
2-Phenoxyethyl	84	0.2	92	1.5200	1.1037	52.23	52.94	192.2	193.4	68.7	69.2	6.3	6.4
2-Benzyloxyethyl	118	2.3	68	1.5075	1.0741	56.84	57.20	206.2	208.1	69.9	69.8		
2-(*p*-*tert*-Butylphenoxy)ethyl	117	0.1	83	1.5093	1.0326	70.70	71.84	248.3	242.1	72.5	71.7		
2-(2,4-Di-*tert*-amylphenoxy)ethyl[b]	165	0.8	80	1.4905$^{54°}$	0.9612$^{54°}$	98.41	100.10	332.5	335.6	75.9	76.5	9.7	9.8
2-(2-Methoxyethoxy)ethyl	86	4.6	61	1.4392	1.0421	43.62	43.98	174.2	175.6	55.2	55.2	8.1	8.2
2-(2-Ethoxyethoxy)ethyl	45	0.15	78	1.4390	1.0145	48.23	48.80	188.2	188.6	57.4	57.4		
2-(2-Butoxyethoxy)ethyl	103	2.3	81	1.4394	0.9821	57.47	57.97	216.3	214.6	61.1	61.1		
2-(2-Phenoxyethoxy)ethyl	118	0.3	80	1.5108	1.1103	63.11	63.74	236.3	240.0	66.1	66.1	6.8	6.8
2-Isopropoxyethyl[c]	73	6	65	1.4278	0.9430	46.59	46.97	172.2	173.9	62.8	62.9		
Tetrahydrofurfuryl[d]	87	9	91	1.4580	1.0643	39.77	40.05						
Tetrahydrofurfuryl[c]	52	0.4	86	1.4585	1.0435	44.39	44.54	170.2	169.2	63.5	63.6		
p-Methoxybenzyl	100	0.1	67	1.5260	1.1061	52.23	53.34	192.2	194.0	68.7	69.2	6.3	6.5

[a] Brittle points of the polymers were: Methoxyethyl, −25°; ethoxyethyl, −40°; isopropoxyethyl, −28°; and butoxyethyl, −54°. [b] Melting point, 42°. [c] Methacrylate. [d] Previously reported by Claborn (8).

temperature. This indicated that an oxidation reaction was involved; hence it seemed likely that the ether linkage in the alcohol radical was responsible. In accord with this theory, it was found that polyvinyl isopropyl ether and polyvinyl *n*-butyl ether could be air-cured, though the latter reacted slowly.

A series of copolymers of isopropoxyethyl and isobutyl acrylates containing various percentages of the isobutyl ester was prepared. When cured at 100°, with a trace of cobalt octoate, the rate of cure was roughly inversely proportional to the percentage of isobutyl acrylate in the copolymer. It was noted, however, that pure isobutyl polyacrylate could be cured by baking, though the rate was low. Following this surprising result, it was found that methyl, butyl, and 4-methyl-2-pentyl polyacrylates could be air-cured. On the other hand, cyclohexyl polyacrylate, methyl and *n*-butyl polymethacrylates, polystyrene, polyvinyl acetate, and glyceryl phthalate showed no perceptible rate of cure. It has been reported (7) that ethyl polyacrylate can be cured with benzoyl peroxide.

Quantitative comparison of the rates of cure of the various resins is difficult, but the following generalizations appear justified: (a) the presence of an ether linkage enormously increases the rate of cure, and with two ether linkages in the repeating unit the rate is even higher than with one; (b) compounds having branched alkyl groups have a higher rate of cure than those containing only straight chains; (c) the presence of aromatic groups lowers the rate of cure; (d) polyacrylic esters cure faster than polymethacrylic esters, especially in the absence of ether linkages; (e) peroxides and cobalt salts, especially the latter, greatly increase the rate of cure. In the absence of catalysts, only the polyacrylates and polymethacrylates of the ether-alcohols could be cured at a perceptible rate.

The mechanism of the curing process is largely unknown. The fact that it occurs only in the presence of oxygen and is catalyzed by oxidation catalysts indicates that it is an oxidation reaction. Further evidence is furnished by the elementary analysis of the cured resin. An unsupported film of isopropoxyethyl acrylate was highly cured by baking for several days at 150°. The elementary analysis then showed that, on the basis of unchanged carbon content, each monomer unit had lost two hydrogen atoms and gained 1.3 oxygen atoms.

Properties of the cured resins. The cured films were hard, smooth, glossy, clear, transparent, light colored, and flexible. They showed excellent adhesion to wood, glass, and metals, with little or no effect after prolonged immersion in toluene, hexane, acetone, or ethyl acetate. Water and ethyl alcohol produced some swelling and softening of the films but did not loosen them or produce any permanent visible change. Dilute alkaline solutions, such as a 1% solution of sodium carbonate or even soapy water, attacked the cured films vigorously and dissolved or disintegrated most of them within 10 to 15 minutes. This sensitivity to alkali appeared to be proportional to the degree of cure. Highly cured films were partially or wholly dissolved by aqueous alkali, and from such solutions a gummy precipitate could be recovered by acidification. From these observations, it appears that alkali degrades the cured resin in some way that produces carboxyl groups. That this is not saponification of the acrylate ester groups is shown by the fact that the uncured resin is resistant to alkali, and also by the fact that resins, such as the vinyl ethers, which contain no ester groups show similar alkali sensitivity. All air-cured polymers, including the alkyl acrylates, behaved similarly.

Even highly cured films retained excellent toughness and flexibility. Thus, an unsupported film of isopropoxyethyl polyacrylate baked for 24 hours at 100° could be folded and creased without cracking. Cured films stored at room temperature for 3 years showed no visible change.

EXPERIMENTAL

Alcohols. Most of the alcohols used are commercially available; before they were used they were fractionally distilled. Because commercial methyl and ethyl monoethers of diethylene glycol (Methyl Carbitol and Carbitol) contain considerable glycol, purification by distillation is difficult, particularly with the latter compound. We are indebted to the Carbide and Carbon Chemicals Corporation for a glycol-free sample of Carbitol which was used in the present work; to Sharples Chemicals, Inc. for 2,4-di-*tert*-amylphenoxyethanol, and to Dow Chemical Company for *p*-*tert*-butylphenoxyethanol.

Monomeric esters. The acrylic and methacrylic esters were prepared by the alcoholysis of the methyl or ethyl ester (2–6). The ethyl ester is preferred for making acrylic esters because (a) it has a higher boiling point than methyl acrylate; hence a higher reaction temperature and faster reaction are obtained by its use; (b) the ethanol-ethyl acrylate azeotrope contains much less ester than the methanol-methyl acrylate azeotrope (5); and (c) the wider spread in boiling point between the ester and its azeotrope (32° for ethyl and 17° for methyl) facilitates the distillation of the azeotrope without unnecessary loss of ester in the distillate (5).

Premature polymerization in the still-pot or fractionating column was sometimes troublesome, especially if glycol was present. When exposed to air, both the acrylic esters and the ether-alcohols readily form peroxides which catalyze polymerization; hence the starting materials should be freshly distilled. Air should be rigidly excluded from the still throughout the operation. It was found helpful to pass a fine stream of carbon dioxide into the still-pot through a capillary bubbler tube during the distillation. The monomers were clear, colorless liquids which could be stored indefinitely without inhibitors if kept in a refrigerator at 0–5°. Table I shows yields and other data on the monomers.

Many of these compounds were difficult to analyze for carbon and hydrogen because of frequent explosions in the combustion tube. Although samples of only about 15 to 20 mg. were used, in several instances the tube was shattered by the explosion. Probably this behavior was due to formation of peroxides by the action of oxygen on the ether-esters. In several instances carbon was determined by wet oxidation. We are indebted to C. O. Willits, C. L. Ogg, and their associates, the Analytical and Physical Chemistry Division of this Laboratory for analyses.

Polymerization. The usual procedure was to dissolve 25 g. of monomer and 0.125 g. of benzoyl peroxide in 50 g. of ethyl acetate and boil the solution under a reflux condenser. Polymerization began immediately and resulted in vigorous refluxing for a few minutes. Refluxing was continued for 3 hours, though there was no visible change after 15 to 20 minutes.

Most of the monomers when polymerized in emulsion gave polymers which were insoluble, or only partially soluble, in organic solvents. The acrylates of glycol monoalkyl ethers thus polymerized were soft and rubbery, although not especially tacky. All the acrylates of monoethers of diethylene glycol gave gelled, insoluble polymers.

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