[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY,[1] PHILADELPHIA, PENNSYLVANIA]

Preparation and Properties of Secondary and Branched-Chain Alkyl Acrylates

BY C. E. REHBERG, W. A. FAUCETTE AND C. H. FISHER

A previous paper[2] described the preparation in high yields of the *n*-alkyl acrylates by alcoholysis of methyl acrylate and gave some information regarding the properties of the monomeric and polymeric *n*-alkyl acrylates. Similar data on acrylic esters prepared from fourteen miscellaneous secondary and branched-chain primary alcohols are reported in the present paper. Seven of these alcohols fall into two homologous series permitting deductions concerning the relation of alcohol group size and structure to polymer properties.

The isopropyl,[3] isobutyl,[3] *s*-butyl,[4,5] isoamyl,[6,7] *s*-amyl[4,5] and capryl[5,8] acrylates had been prepared previously.

TABLE I

PREPARATION AND PROPERTIES OF SECONDARY AND BRANCHED-CHAIN ALKYL ACRYLATES

Expt.	Ester	Yield, %[a]	Conversion, %[b]	Methyl acrylate lost, %	B. p. °C.	B. p. Mm.	$n^{20}D$	d^{20}_4	Mol. refraction Calcd.[c]	Mol. refraction Found	Brittle point of the polymer, °C.
1	Isopropyl		37	10	52	103	1.4060	0.8932	31.09	31.40	0
2	Isobutyl	85	83	13	62	50	1.4150	.8896	35.71	36.09	−24
3	*s*-Butyl	70	67	31	60	50	1.4140	.8914	35.71	35.93	−10
4	2-Methyl-1-butyl	94	83	5	45	10	1.4220	.8871	40.33	40.73	−32
5	3-Methyl-1-butyl	96	96	4	43	7	1.4230	.8911	40.33	40.65	−45
6	3-Pentyl	83	72	5	63	27	1.4210	.8883	40.33	40.59	−16
7	2-Methyl-1-pentyl	79	56	5	88	32	1.4282	.8850	44.95	45.44	−38
8	2-Ethyl-1-butyl	92	88	7	80	20	1.4292	.8912	44.95	45.22	−50
9	4-Methyl-2-pentyl	95	80	0	71	29	1.4220	.8723	44.95	45.52	−15
10	2-Heptyl	89	87	14	66	5.7	1.4282	.8750	49.57	50.08	−38
11	2-Ethyl-1-hexyl	95	95	15	85	8	1.4365	.8852	54.19	54.48	−55
12	2-Octyl	80	80	32	79	5.4	1.4312	.8754	54.19	54.51	−45
13	5-Ethyl-2-nonyl	78	64	16	94	2.2	1.4415	.8758	68.05	68.32	−40
14	2-Methyl-7-ethyl-4-undecyl	78	78	..	96	0.3	1.4448	.8685	81.89	82.22	−20

[a] Based on alcohol not recovered. [b] Based on alcohol put into the reaction mixture. [c] No increment was added for the exaltation caused by the conjugation of double bonds in the acrylyl radical.

Our former[2] and present results (Table I) indicate that many primary and secondary alcohols, both normal and branched, are suitable for preparing the higher acrylic esters by alcoholysis of methyl acrylate. Primary alcohols having two alkyl groups on the beta-carbon atom (Experiments 2, 4, 7, 8, and 11) were used satisfactorily, but whether a primary alcohol (such as neopentyl alcohol) having three such alkyl groups would be suitable is not known. Three secondary branched-chain alcohols (Experiments 9, 13, and 14) were converted satisfactorily into the corresponding acrylates. Inasmuch as di-isopropylcarbinol was unsatisfactory, secondary alcohols having a high degree of branching close to the hydroxyl group seem unsuitable for alcoholysis reactions. An attempt to make tertiary-amyl acrylate by alcoholysis of methyl acrylate was unsuccessful; this result is in agreement with the generally known behavior of tertiary alcohols.

The homologous 2-*n*-alkyl acrylates (Experiments 1, 3, 10, and 12) were similar to the 1-*n*-alkyl acrylates studied previously in that straight lines were obtained by plotting the molecular weight (M) against either the molecular volume (M/d) or M/n. The two straight lines thus obtained with the physical constants ($n^{20}D$ and d^{20}_4) of the monomeric 2-*n*-alkyl acrylates are defined by the equations

$$M/d = 1.1902\ M - 8.42$$
$$M/n = 0.67857\ M + 3.69$$

Polymerized Alkyl Acrylates.—The acrylic esters of Table I were emulsion polymerized under similar conditions, and some of the properties of the polymers were determined. The polymers were generally similar in appearance to the polymerized *n*-1-alkyl acrylates described in a previous paper.[2] All the polymers prepared from the esters listed in Table I were soft, flexible and extensible at room temperature but became brittle at 0°C. or lower. Many of the polymers,

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) C. E. Rehberg and C. H. Fisher, THIS JOURNAL, **66**, 1203 (1944).

(3) A. V. Ipatov, *J. Gen. Chem.* (U. S. S. R.), **10**, 866 (1940).

(4) H. T. Neher, U. S. Patent 2,117,349, May 17, 1938.

(5) Rohm & Haas A.-G., French Patent 818,740–1, Oct. 2, 1937.

(6) P. P. Kobeko, M. M. Koton and F. S. Florinskii, *J. Applied Chem.* (U. S. S. R.), **12**, 313 (1939).

(7) C. Moureu, M. Murat and L. Tampier, *Ann. chim.*, **15**, 221 (1921).

(8) Rohm & Haas A.-G., British Patent 491,800, Sept. 8, 1938.

particularly those having low brittle points, were very tacky.

Several conclusions regarding the relation between the structure of the monomer and the brittle point of the polymer seem warranted. In any homologous series, an increase in the length of the principal chain of the alkyl group to about eight carbon atoms lowered the brittle point. On the basis of observations made with acrylic esters of the primary *n*-alkanols, it would be expected that further lengthening of the chain would raise the brittle point (Fig. 1). Differences in properties within a homologous series may be due in part to differences in molecular weight of the polymers, since the polymers of the higher alkyl acrylates may have lower molecular weights than polymethyl acrylate.[9]

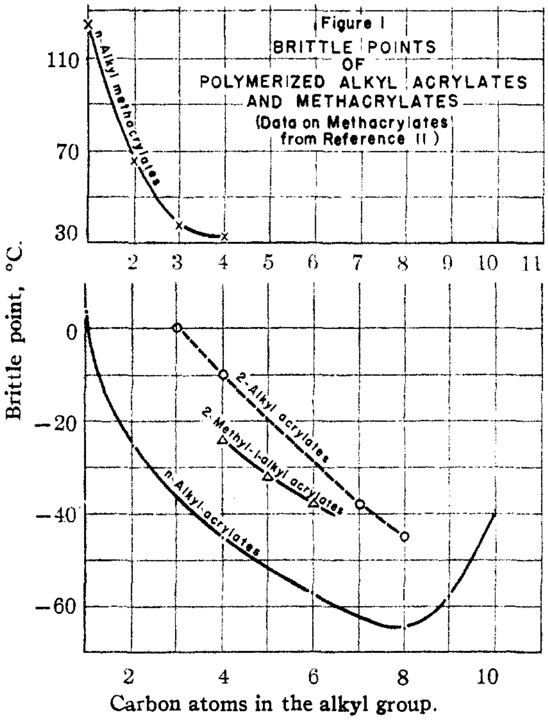

Fig. 1.—See top on drawing.

Isomeric variations in the alkyl group also cause the brittle point to change regularly. The esters of unbranched secondary alcohols had considerably higher brittle points than the isomeric esters prepared from primary *n*-alkanols (Fig. 1). This difference ranged from 36° for the *n*-propyl and isopropyl esters to 20° for the *n*-octyl and 2-octyl esters. The tertiary butyl ester[10] has a much higher brittle point than *s*-butyl acrylate.

Branching in the alkyl group also raises the brittle point. If a methyl group is located on the beta-carbon atom of the alkyl group (Experiments 2 and 7, Table I) the brittle point is raised approximately 20° above that of the isomeric 1-*n*-alkyl ester; the increase in brittle point is only about 10° if an ethyl group is placed in the beta position (Experiments 8 and 11, Table I).

All the esters prepared from alcohols having eight or less carbon atoms had brittle points higher than those of the isomeric 1-*n*-alkyl acrylates (Fig. 1). The polymeric esters prepared from a secondary and branched undecanol and tetradecanol, however, were exceptional in that their brittle points (Experiments 13 and 14, Table I) were lower than those of the isomeric normal primary esters.

As is well known, acrylic esters have brittle points much lower than those of the corresponding methacrylic esters[11] (Fig. 1).

Experimental

The alkyl acrylates were prepared from methyl acrylate by a previously described procedure.[2] Some of the secondary alcohols (particularly 2-heptyl, 2-octyl, and 3-pentyl) reacted readily, whereas others reacted slowly or not at all. Isopropyl alcohol reacted more slowly than any of the other secondary alcohols except diisopropylcarbinol, whose reaction rate was negligible. The ester of 2-methyl-7-ethyl-4-undecanol was difficult to distil from its reaction mixture because of its tendency to decompose[12] into acrylic acid and the corresponding olefin.

The monomeric acrylic esters were emulsion polymerized as before[2] with the exception that any monomer (approximately 2%) remaining in the emulsion was removed by steam distillation. The brittle points were determined by flexing samples in an ethanol bath (cooled with solid carbon dioxide) and noting the temperature at which breakage occurred.

Summary

Various secondary and branched-chain alkyl acrylates were prepared in high yields by the alcoholysis of methyl acrylate. Certain properties of the monomeric and polymeric acrylic esters were determined. A brief discussion of the relation between structure of the monomer and properties of the polymer is given.

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[9] P. O. Powers, "Synthetic Resins and Rubbers," John Wiley & Sons, Inc., New York, N. Y., 1943, 296 pp.

[10] H. T. Neher, *Ind. Eng. Chem.*, **28**, 267 (1936).

[11] E. I. du Pont de Nemours & Co., Inc., *Ind. Eng. Chem.*, **28**, 1160 (1936).

[12] W. P. Ratchford, C. E. Rehberg, and C. H. Fisher, "Preparation of Acrylic and Methacrylic Acids by the Pyrolysis of Their Alkyl Esters," submitted for publication in This Journal.