

Preparation and Polymerization of Cycloalkyl Acrylates^{1,2}

By C. E. REHBERG AND W. A. FAUCETTE³

In our earlier work³ it was found that all the alkyl polyacrylates studied had brittle points near room temperature, or lower. It was known that the presence of the cyclohexyl ring in the molecule caused a large rise in the softening point of polymethacrylates.⁴ Hence, it appeared of interest to prepare some cycloalkyl polyacrylates in the hope that they might be of use as rigid plastics.

The monomeric acrylates (Table I) were prepared by the alcoholysis of methyl or ethyl acrylate,⁴ and were polymerized in emulsion. Brittle

low molecular weight. They were discolored and were extremely soft and tacky. Abnormally large amounts of catalyst were required to initiate their polymerization, indicating that some inhibitor remained in the monomer. All the other polymers were hard, white, granular solids, which were readily molded to form clear, colorless sheets.

3,3,5-Trimethylcyclohexyl polymethacrylate has been evaluated as a coating for optical lenses. It is reported to have outstanding resistance to water and to outdoor weathering.⁵

The authors are grateful to C. O. Willits, C. L. Ogg, and their associates for analyses, to Hercules Powder Co., for hydroabietyl alcohol, to Carbide and Carbon Chemicals Corp., for the two forms of

TABLE I
YIELDS, PHYSICAL CONSTANTS AND ANALYSES OF CYCLOALKYL ACRYLATES

Acrylate	Yield, %	Boiling pt. °C.	Mm.	n _D ²⁰	d ₄ ²⁰	Mol. refraction		Sapon. equiv.		Carbon, %		Hydrogen, %		Brittle pt. of polymer, °C.
						Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	
Cyclohexyl	77	75	11	1.4600	0.9796	42.75	43.12	154.2	155.0	70.1	70.2	16
Cyclohexyl ^a	..	182-184	Atm.	1.4673	1.0276	42.75	41.66
2-Methylcyclohexyl	70	69	5	1.4560	.9546	47.37	47.90	168.2	170.5	71.4	71.0	32
3-Methylcyclohexyl	78	74	6	1.4550	.9541	47.37	47.84	168.2	168.1	71.4	70.9	31
4-Methylcyclohexyl	85	55	2	1.4550	.9537	47.37	47.86	168.2	167.8	71.4	71.6	35
3,3,5-Trimethylcyclohexyl ^b	89	72	2	1.4542	.9292	56.60	57.31	196.3	204.1	73.4	73.6	10.3	10.4	48
3,3,5-Trimethylcyclohexyl ^c	50	40	0.2	1.4560	.9346	56.60	57.09	196.3	205.3	73.4	73.3	10.3	10.5	50
4- <i>t</i> -Amylcyclohexyl	85	95	1	1.4705	.9490	65.84	66.00	224.3	222.8	75.0	75.0	10.8	10.8	-8
4-Cyclohexylcyclohexyl ^d	86	115	1	1.4810 ^e	.9500 ^e	68.26	70.80 ^e	236.3	234.0	76.2	76.0	10.2	9.9	35
Hydroabietyl	25	177	0.3	1.5172	1.0181	102.53	102.42	344.5	349.2	28
3,3,5-Trimethylcyclohexyl ^f	88	79	1	1.4560	.9255	61.22	61.77	210.3	213.9	74.2	74.5	10.6	10.7	140

^a Reported by Ipatov, *J. Gen. Chem. (USSR)*, **15**, 639 (1945) [*C. A.*, **40**, 5697 (1946)]. ^b Made from alcohol of m. p. 35°. ^c Made from alcohol of m. p. 51°. ^d M. p., 41°. ^e At 50°. ^f Methacrylate made from alcohol of m. p. 35°.

points were determined as previously described.³ The one methacrylate was prepared (from methyl methacrylate) for comparison with the corresponding acrylate.

The two isomeric forms of 3,3,5-trimethylcyclohexanol (m. p. 35° and 51°) formed monomeric esters which showed small, but probably significant, differences in refractive index and density (Table I). Attempts to determine their melting points were indecisive; both samples became glass-like at about -50° without passing through any sharp transition point. The small difference in the brittle points of the polymers is not considered significant.

The 4-cyclohexylcyclohexyl ester was a colorless solid, melting at 41°. Excepting monomeric hydroabietyl acrylate, which was slightly colored and exceedingly viscous, the esters were colorless, mobile, or slightly oily liquids having mild, pleasant, terpene-like odors.

The hydroabietyl and the 4-*t*-amyl- and 4-cyclohexylcyclohexyl polyacrylates appeared to be of

3,3,5-trimethylcyclohexanol, to the Dow Chemical Co., for 4-cyclohexylcyclohexanol, and to Sharples Chemicals, Inc., for 4-*t*-amylcyclohexanol.

(5) Coles, Schulz, Levy and Wheatley, *Modern Plastics*, **25**, No. 11, 123 (1948).

EASTERN REGIONAL RESEARCH LABORATORY
PHILADELPHIA 18, PENNA. RECEIVED MARCH 16, 1950

Formation of *m*-Toluidine by a New Synthetic Route

By DAVID A. SALZBERG

In setting up a research program in this Laboratory on the metabolism of carcinogenic azo dyes, interest was centered on the greatly enhanced carcinogenic activity of 3'-methyl-*p*-dimethylaminoazobenzene¹ over the parent compound *p*-dimethylaminoazobenzene. It was felt that much could be learned by incorporating isotopic carbon (C¹⁴) in the 3'-methyl group of the former dye and determining its metabolic fate in the rat, where diets containing 0.06% of the dye result in liver tumors in ten to twelve weeks.

The dye is readily prepared by coupling diazotized *m*-toluidine with dimethylaniline and thus the problem was to synthesize *m*-toluidine labeled with C¹⁴ in the methyl group. Benzoic acid containing C¹⁴ in the carboxyl group is obtainable by

(1) Miller and Baumann, *Cancer Research*, **5**, 227 (1945).

(1) From the Eastern Regional Research Laboratory, one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) Presented before the Organic Chemistry Division of the American Chemical Society at the 117th National Meeting, Philadelphia, Pa., April, 1950.

(3) Rehberg and Fisher, *Ind. Eng. Chem.*, **40**, 1429 (1948).

(4) E. I. du Pont de Nemours and Co., *ibid.*, **28**, 1160 (1936).