[CONTRIBUTION FROM THE POLYMER RESEARCH DEPARTMENT H. D. JUSTI & SON, INC.]

THE PREPARATION OF SOME ESTERS OF METHACRYLIC ACID

JOGINDER LAL AND RICHARD GREEN

Received April 13, 1955

During the last ten years, resin filling materials have been used quite extensively in the dental profession for restoration purposes. One of the defects of currently available materials is excessive shrinkage during polymerization (1). Resin filling compositions comprising slurries obtained by mixing polymer or copolymer powders with methyl methacrylate are polymerized in a Redox activated system at mouth temperature. When a monomer polymerizes, some shrinkage must inevitably take place. Crawford (2) reported a shrinkage of 20.6 per cent during the polymerization of methyl methacrylate at 25°. A similar value has been reported by Nichols and Flowers (3). The per cent shrinkage decreases as the size of the alcohol substituent in the methacrylic ester increases (2, 3). The lower theoretical shrinkage expected during the polymerization of higher esters of methacrylic acid would obviously be an improvement in the resin filling composition. The physical properties such as hardness and brittleness would also be influenced by the methacrylic ester employed.

A very large number of esters of methacrylic acid have been reported in the literature. In the course of this project, a few new esters were synthesized, the preparation and some physical constants of which are reported here.

EXPERIMENTAL

Methacrylic esters of primary and secondary alcohols were best prepared by direct esterification with glacial methacrylic acid; the esters of tertiary alcohols or phenols were prepared by reacting them with methacrylyl chloride.

In direct esterification glacial methacrylic acid and an alcohol were refluxed together in benzene or heptane solution in the presence of a catalyst and an inhibitor. Glacial methacrylic acid was used in 10 per cent excess of the calculated amount to insure complete esterification of the alcohol. For best results, the amount of solvent used was at least one-half of the total volume of reaction mixture. A mixture of 3 g. of hydroquinone and 1 g. of N,N′-di-β-naphthyl-*p*-phenylenediamine per mole of alcohol was used as inhibitor and 3 g. of *p*-toluenesulfonic acid or mixed alkanesulfonic acids per mole of alcohol was used as catalyst. After all the water of esterification had been collected in the trap, the solvent and unreacted methacrylic acid were removed under reduced pressure and the residual liquid was distilled under a vacuum using a Claisen distillation head. The distillate was washed free of acid with dilute sodium hydroxide solution and then was washed with water. It was dried over sodium sulfate, 1 g. of N,N′-di-β-naphthyl-*p*-phenylenediamine per mole of methacrylic ester was added to it, and the product was distilled through a fractionating column under a vacuum. This procedure was found to be preferable to washing the reaction mixture directly with dilute sodium hydroxide solution which very often resulted in emulsions which were hard to handle.

Methacrylic esters of tertiary alcohol or phenol were obtained by the conventional procedure of dropwise addition of methacrylyl chloride to a mixture of alcohol or phenol and a dilute solution of sodium hydroxide, which was mechanically stirred. The temperature of the reaction mixture was maintained at 0–5° by external cooling. After the addition of methacrylyl chloride, stirring was continued for another half hour. The reaction mixture was extracted with ether and the ethereal extract was washed with dilute alkali solution

TABLE I

PHYSICAL CONSTANTS AND ANALYTICAL DATA* FOR METHACRYLIC ESTERS

Compound	B.P.		n_D^{25}	d_4^{25}	Yield, %	Formula	Carbon		Hydrogen		Nitrogen or Sulfur	
	°C.	Mm.					Calc'd	Found	Calc'd	Found	Calc'd	Found
4-Isopropylcyclohexyl methacrylate[a]	82–83	0.7	1.4594	0.9371	22	$C_{13}H_{22}O_2$	74.24	74.22	10.55	10.66	—	—
4-*tert*-Butylcyclohexyl methacrylate[a]	98–99[c]	1.7	1.4626		42	$C_{14}H_{24}O_2$	74.95	74.72	10.78	10.61	—	—
Tetrahydropyran-2-ylmethyl methacrylate[a]	93	2.7	1.4598	1.0237	68	$C_{10}H_{16}O_3$	65.19	65.21	8.75	8.76	—	—
Diisobutylmethyl methacrylate[a]	97	12	1.4298	0.8608	73	$C_{13}H_{24}O_2$	73.54	73.60	11.40	11.52	—	—
1,1-Dimethyl-3-oxobutyl methacrylate[b]	60–61	1	1.4400	0.9747	36	$C_{10}H_{16}O_3$	65.19	65.45	8.75	8.66	—	—
p-Phenylene dimethacrylate[b]	[d]		—	—	60	$C_{14}H_{14}O_4$	68.28	68.28	5.73	5.87	—	—
Bis-4-methacryloxyphenyl ketone[b]	[e]		—	—	30	$C_{21}H_{18}O_5$	71.96	71.81	5.18	5.12	—	—
Bis-4-methacryloxyphenyl sulfone[b]	[f]		—	—	43	$C_{20}H_{18}O_6S$	62.16	62.18	4.61	4.32	8.29	8.30
2-Pyridylmethyl methacrylate[b]	96	1.5	1.5115		40	$C_{10}H_{11}NO_2$	67.78	67.64	6.26	6.41	7.90	7.23
Ethyl methacrylothiolate[b]	75	42	1.4857		66.6	$C_6H_{10}OS$	55.34	55.42	7.64	7.63	24.62	24.12
Phenyl methacrylothiolate[b]	93	1	1.5740		68	$C_{10}H_{10}OS$	67.38	67.51	5.66	5.46	17.98	19.00

* Microanalyses by Doctors G. Weiler and F. P. Strauss, Oxford, England. [a] Prepared by direct esterification of methacrylic acid with the corresponding alcohol. [b] Prepared by reaction of methacrylyl chloride with the corresponding alcohol or phenol. [c] Also m.p. 30.5–31°. [d] M.p. 91–92°. [e] M.p. 112–112.5°. [f] Polymerizes at 100° without melting.

and finally with water. It was dried over sodium sulfate and, after the addition of N,N′-di-β-naphthyl-p-phenylenediamine, ether was removed by distillation and the residual liquid was fractionally distilled.

Preparation of methacrylyl chloride. Methacrylyl chloride was prepared by reacting at room temperature 258 g. (3 moles) of glacial methacrylic acid and 357 g. (3 moles) of thionyl chloride in the presence of 1.5 g. of cuprous chloride. When the evolution of gases had ceased, the light brown liquid was gently refluxed for one hour and then was distilled through a 1-meter column packed with glass helices. The water-white fraction boiling at 98.4° at 772 mm. was collected as the product. Yield 58–70%, n_D^{25} 1.4405.

Anal. Calc'd for C_4H_5ClO: C, 45.95; H, 4.82; Cl, 33.92.
Found: C, 46.15; H, 5.00; Cl, 34.10.

The preparation of methacrylyl chloride has been reported by a number of other methods (4–7); we found the above described method to be quite convenient for obtaining product of high purity.

Physical constants and analytical data for the various esters of methacrylic acid are shown in Table I.

Polymerization of polymer-monomer slurries. Methyl polymethacrylate was used for making slurries with the various liquid monomeric methacrylic esters. The polymer was obtained by the suspension polymerization of methyl methacrylate and was finely ground under liquid nitrogen. The polymer was thoroughly mixed with 2 per cent by weight of benzoyl peroxide by rolling in a ball-mill for six hours. Each of the various liquid methacrylic esters reported in this paper was activated by the addition of 0.5 per cent by weight of N,N-dimethyl-p-toluidine.

Methyl polymethacrylate powder (2 g.) containing the catalyst was mixed with 1 ml. of each of the activated monomers. The resulting slurries were spatulated thoroughly. None of the slurries polymerized to a hard mass in less than an hour at 37°. In some cases, the slurries did not polymerize even after standing for 24 hours. These results are in marked contrast to the rapid polymerization in less than 10 minutes of similarly Redox activated slurries comprising methyl methacrylate and methyl polymethacrylate.

Substitution of methyl polymethacrylate by a co-polymer of equal parts by weight of methyl methacrylate and ethyl methacrylate in the formulation of slurries did not materially change the results.

The purpose of our investigation was the rapid polymerization of slurries employing higher esters of methacrylic acid and subsequent study about the shrinkage during polymerization of these methacrylic esters either alone or in the form of slurries. In view of the very slow rate of the polymerization of the slurries and their doubtful usefulness for dental applications, studies about shrinkage during polymerization were not carried out.

This research has been carried out under Contract AF 18(600)-461 between U. S. Air Force—School of Aviation Medicine and H. D. Justi and Son, Inc., Philadelphia, Pennsylvania. The authors are grateful to Professor Frederick R. Eirich for much helpful guidance.

SUMMARY

The preparation and physical constants of some new esters of methacrylic acid have been described. These esters were prepared by direct esterification of primary or secondary alcohols with methacrylic acid, or by the reaction of methacrylyl chloride with tertiary alcohols or phenols. Liquid methacrylic esters when mixed with methyl polymethacrylate gave slurries which polymerized extremely slowly with a Redox activated system.

PHILADELPHIA 4, PENNA.

REFERENCES

(1) Smith and Schoonover, *J. Am. Dent. Assoc.*, **46**, 540 (1953).
(2) Crawford, *J. Soc. Chem. Ind. (London)*, **68**, 201 (1949).
(3) Nichols and Flowers, *Ind. Eng. Chem.*, **42**, 292 (1950).
(4) Haworth, Gregory, and Wiggins, *J. Chem. Soc.*, 448 (1946).
(5) Rehberg, Dixon, and Fisher, *J. Am. Chem. Soc.*, **67**, 208 (1945).
(6) Patai, Bentov, and Reichman, *J. Am. Chem. Soc.*, **74**, 845 (1952).
(7) Heyboer and Staverman, *Rec. trav. chim.*, **69**, 787 (1950).

NOTICE TO AUTHORS

On and after September 1, 1955, the Journal will accept *Notes*; the Journal will accept *Communications to the Editor* received on or after November 1, 1955 for publication in Volume 21. See revised Notice to Authors for details.

Effective with Volume 21, the Journal will use a double column format with a page size approximately 6½″ by 9″. Authors should consider this in connection with graph sizes, and table compositions.