

fied with 20% hydrochloric acid to a congo red end-point and extracted twice with 75-ml. portions of ether. The ether extract was washed with water and dried over sodium sulfate. Concentration *in vacuo* left a residue of the stereoisomeric 2-phenylcyclohexanecarboxylic acids which was analyzed by quantitative infrared.

Stability of *cis*-2-Phenylcyclohexanecarboxylic Acid under Debromination Conditions.—A 75-mg. sample (0.368 mmole) of *cis*-2-phenylcyclohexanecarboxylic acid was treated in the same manner as the bromoacid in the corresponding debromination run described above. The percentage conversion to *trans*-2-phenylcyclohexanecarboxylic acid was determined by infrared analysis of the resulting material. These results were used in correcting the ketonization product distribution for isomerization of *cis*-2-phenylcyclohexanecarboxylic acid under reaction conditions. The corrected values are given in Table I.

Quantitative Infrared Analysis.—The analytical method employed in our earlier study⁸ was utilized here. The ratio of *cis*- to *trans*-2-phenylcyclohexanecarboxylic acid in a mixture is given by $R = QF$ where $Q = D''_m D'_t - D'_m D''_t / D'_m D''_c - D''_m D'_c$ and F is determined empirically. The subscripts m, c and t refer to a given mixture, pure *cis* isomer

and pure *trans* isomer, respectively; the superscripts refer to absorption at 7.71 and 7.98 μ .

All analyses were run at a concentration of 40 mg./0.50 ml. of CS₂ in 0.1-mm. cells. The results of analyses of known mixtures given in Table III indicate a probable accuracy of $\pm 0.6\%$ *cis* isomer. In calculating the results in the last two columns of Table III an average value of $F = 1.04$ was used.

Calculation of Differential Free Energy, Enthalpy and Entropy of Activation.—The difference in free energy of activation for the two processes forming *cis*- and *trans*-2-phenylcyclohexanecarboxylic acid was obtained for 20° by using the product distribution obtained in experiment I of Table I and the relation $\Delta\Delta F^\ddagger = -RT \ln(k_c/k_t)$; here it is assumed that both processes have the same kinetic order so that the ratio of products gives the ratio of rates.

The differential enthalpy of activation was obtained by taking the slope of the plot in Fig. 1 equal to $-(\Delta\Delta H^\ddagger / 2.303R)$. The differential entropy of activation resulted from a solution of the relation $\Delta\Delta F^\ddagger_{c-t} = \Delta\Delta H^\ddagger_{c-t} - T\Delta\Delta S^\ddagger_{c-t}$.

EVANSTON, ILL.

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF J. T. BAKER CHEMICAL CO.]

Polymerization of Thiolmethacrylate Esters

BY GENE SUMRELL,¹ JOSEPH BRISKIN, GEORGE E. HAM AND CHARLES H. SCHRAMM

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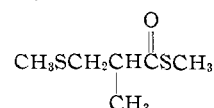
Data from the polymerization of seven thiolmethacrylates are presented. The polymers had higher softening points than those from the analogous methacrylate esters. The primary and secondary alkyl thiolmethacrylates had a tendency to give cross-linked homopolymers and copolymers, a striking difference from the behavior of similar esters in the thiolacrylate series.

The increasing interest in thiolacrylic-type esters prompts us to report some of our findings from polymerization studies of monomers of this type prepared in our laboratories.²⁻⁴ Marvel and co-workers^{3a} have extensively investigated the alkyl thiolacrylate series. Our work has been primarily in the thiolmethacrylate series. We note some similarities and some differences in comparing these two series.

A striking difference was the tendency of the primary and secondary alkyl thiolmethacrylates to give insoluble and presumably cross-linked homopolymers and copolymers, whereas such behavior apparently did not occur in the thiolacrylate series. Marvel reports soluble homopolymers of a variety of primary and secondary alkyl thiolacrylates in conversions of 50-70%. Much copolymerization data are given with a variety of comonomers including styrene, with no mention of cross-linking. In our work, we obtained soluble homopolymers of methyl, ethyl and isopropyl thiolmethacrylate in conversions of 20-25%, but at higher conversions the polymers exhibited swelling in a variety of organic

solvents, but did not dissolve. A slight tendency to give insoluble copolymers with styrene was also noted. This tendency was much greater with methyl methacrylate and some of the data are given in the Experimental section. Since we did not obtain insoluble homopolymers or copolymers with tert-butyl thiolmethacrylate, or with the aryl thiolmethacrylates, we are inclined to associate the cross-linking with the presence of a hydrogen attached to the carbon next to the sulfur atom in the thiol ester grouping. If chain transfer occurs readily at this point, the results would be equivalent to having a bifunctional monomer which would be expected to give cross-linked polymers.

The fact that we were able to produce insoluble poly-(methyl methacrylate) polymers (see Experimental) in the presence of as little as 1% by weight of methyl 2-methyl-3-thiomethoxythiolpropionate



is further evidence of active chain transfer at the site mentioned above. It is known⁵ that aliphatic sulfides may be incorporated into poly-(methyl methacrylate), but we are not aware of any evidence that crosslinked polymers are ever obtained using simple alkyl sulfides. Since cross-linking requires that the agent become attached to polymer chains in at least two places, it is of interest to consider the points at which the above pictured

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(2) For the preparation of these monomers see G. Sumrell, G. E. Ham and E. D. Hornbaker. *THIS JOURNAL*, **80**, 2509 (1958).

(3) We are aware of the following literature bearing on this subject: (a) C. S. Marvel, S. L. Jacobs, W. K. Taft and B. G. Labbe, *J. Polymer Sci.*, **19**, 59 (1956); (b) S. L. Jacobs, Ph.D. Thesis, University of Illinois; *C. A.*, **49**, 10894 (1955); (c) M. M. Koton, T. M. Kiselyeva and K. S. Podgorskaya, *Zhur. Obshchei Khim.*, **26**, 475 (1956); *C. A.*, **50**, 13815 (1956); (d) G. Braude, *J. Org. Chem.*, **22**, 1675 (1957); (e) W. Reppe, *Ann.*, **582**, 13 (1953).

(4) L. A. Mikeska, U. S. Patent 2,475,246, July 5, 1949, assigned to Standard Oil Development Co.

(5) B. M. Marks, U. S. Patent 2,565,141, August 21, 1951, assigned to E. I. du Pont de Nemours and Co.

compound may be incorporated into a polymer chain. Neither our data nor evidence from the literature is sufficient to establish positively that chain transfer occurs, under the conditions of our experiments, in the vicinity of the sulfide portion of the molecule in this thiol ester. It appears likely that it does. It also appears likely that more than one chain transfer can occur at the thiol methyl group. It thus is not surprising that this compound should be an effective cross-linking agent. However, we are at present unable to offer an explanation as to why cross-linking did not occur in the preparation of polymers from the primary and secondary alkyl thiolacrylates.^{3a}

It might be mentioned in passing that when we prepared methyl thiolmethacrylate by the method employed by Marvel in the preparation of the thiolacrylates, *i.e.*, by removing bromine from the dibromo compound with sodium iodide, we were not able to remove iodine from the resulting monomer sufficiently for satisfactory polymerization studies. Even after several fractionations, the monomer continued to split out iodine (apparent from its color) when heat was applied during polymerization. The iodine acted as a powerful inhibitor. The methyl thiolmethacrylate used in our polymerizations was prepared by an alternate method (see reference 1 for these preparations).

It was observed by Marvel and co-workers that homopolymers from alkyl thiolacrylate esters have higher softening points than the corresponding polymers from alkyl acrylates.^{3a} We made the same observation in the thiolmethacrylate series, as compared with methacrylates. A comparison of the softening points in these two series is presented in Table I. The softening points of two thiolacrylate homopolymers are included. As would be expected, these values are considerably lower than those of the corresponding thiolmethacrylate polymers.

TABLE I
SOFTENING POINTS OF HOMOPOLYMERS OF METHACRYLATE
AND THIOLACRYLIC-TYPE ESTERS, °C.

R group in ester	Thiol- acrylate	Methacrylate	Thiol- methacrylate
Methyl		144	152
Ethyl		65 ^a	127
<i>i</i> -Propyl		95 ^a	140
<i>t</i> -Butyl	98		193
Phenyl	101	152 ^b	169
4-Chlorophenyl		154 ^b	172
Pentachlorophenyl		>250	>250

^a Data from Anonymous, *Ind. Eng. Chem.*, **28**, 1161 (1936). ^b Unpublished data from our laboratories.

While the crude polymers prepared in our work were odorous from traces of monomer still present, precipitation of these polymers from chloroform-methanol gave materials which were odorless. Compression molding of the homopolymers gave clear transparent disks or bars which, in several cases (see Experimental), were resistant to steam sterilization at 121°. These all proved to be too brittle for heat distortion data to be obtained. Preliminary work showed that several of the thiomethacrylate esters copolymerized readily

with methyl methacrylate to give tough clear copolymers with increased heat resistance over poly-(methyl methacrylate).

TABLE II
POLYMERIZATION CONDITIONS FOR NEW HOMOPOLYMERS

Monomer	Grams	AIBN wt. %	Temp., °C.	Time, hours	Conver- sion %	[η]
Me TM ^d	32	None	60	14	25	1.03
Et TM	10	None	60	12 ^e	20	0.52
<i>i</i> -Pr TM	15	None	60	12	20	.54
<i>t</i> -Bu TM	62	0.1	60	96	66	.24
Ph TM	40 ^b	None	60	24	52	.32
4-ClPh TM	6	None	60	24	37	.23
C ₆ Cl ₅ TM	10	0.5	105	48	e	e
<i>t</i> -Bu TA ^d	11	None	60	24	23	0.28
Ph TA ^a	28	None	60	24	64	0.29

^a Became viscous from polymerization on standing several hours at room temperature prior to heating. ^b Sample partially gelled on storage overnight at 5°. ^c Another similar sample which was maintained at 60° for 6 days gave an insoluble polymer; above sample was soluble in 50 ml. in chloroform. ^d TM = thiolmethacrylate, TA = thiolacrylate. ^e See Experimental.

Experimental

Polymerizations and Processing of Polymers.—The liquid monomers were stored with a trace of iodine (0.01–0.1%) to prevent polymerization. When such a monomer was used to prepare a polymer, the charge of monomer or mixed monomers was washed with a few drops of concentrated aqueous sodium thiosulfate to remove the iodine. Then a small amount of sodium sulfate was added and the monomer charge was decanted.

Polymerizations were carried out in screwcapped vials or bottles of sufficient size that the monomer charge filled them half to three-fourths full. Aluminum foil was placed between the cap and the vial or bottle. After the monomer charge and catalyst had been added, the container was flushed with nitrogen before capping. The polymerizations were carried out as described. The resulting polymers were dissolved in enough chloroform to give approximately a 5% solution. The latter was poured with stirring into 5 volumes of methanol. The precipitated polymer was filtered, washed thoroughly with methanol and dried. The softening points were determined on a Parr melting point apparatus. The intrinsic viscosities were determined in the usual way⁶ using dioxane as a solvent and a constant temperature bath regulated to 20 ± 0.02°.

Methyl Thiolmethacrylic Polymers.—A sample of 10 g. of methyl thiolmethacrylate was heated at 60° for 48 hours with 0.1% of azodiisobutyronitrile, giving a clear hard solid which smelled of the monomer. The solid exhibited swelling in chloroform, benzene and other organic solvents, but did not dissolve appreciably. Another sample of 32 g. of this monomer was heated without a catalyst for 14 hours at 60°, giving a soft clear gel which readily dissolved in chloroform. Precipitation in methanol gave 8 g. (25%) of the polymer, which had an intrinsic viscosity of 1.03 and S.P. 152°. Compression molding gave a clear transparent disk which exhibited no surface flow when heated in steam at 121°. The precipitated polymer possessed no odor.

A copolymer was prepared by heating 15 g. of methyl thiolmethacrylate and 35 g. of methyl methacrylate with 0.1% of azodiisobutyronitrile for 24 hours at 60°. The clear hard polymer swelled in chloroform, but did not dissolve. Another copolymer was prepared by heating 5 g. of methyl thiolmethacrylate and 45 g. of methyl methacrylate without a catalyst for 10 days at 60°. Gelation occurred in 6 days. The resulting polymer was soluble in chloroform. Precipitation from methanol gave 36 g. (72%) of material which had an intrinsic viscosity of 1.31 and S.P. 154°. Compression molding gave a clear tough

(6) See P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, pp. 308–310.

(7) This material analyzed for 2.37% sulfur, indicating the incorporation of 8.35% of methyl thiolmethacrylate in the copolymer.

bar which had an ASTM heat distortion of 110°. By comparison, a bar of poly-(methyl methacrylate), molded from polymer with an intrinsic viscosity of 0.72 and S.P. 144°, had an ASTM heat distortion of 102°.

Isopropyl Thioldimethacrylate Homopolymer.—A sample of 59 g. of isopropyl thioldimethacrylate was heated at 80° for 11 days without a catalyst, giving a transparent waxy solid. Gelation had occurred in 3 days. The material exhibited swelling in a variety of organic solvents, including chloroform, carbon tetrachloride, benzene, acetone, dimethylformamide and dimethyl sulfoxide. However, the major part of it did not dissolve. The entire mass (after evaporation of solvent) was treated with methanol, giving 37.5 g. (63%) of white solid which had S.P. 127°. The unpleasant odor of the monomer was not completely removed.

Another sample of 15 g. of this monomer was heated at 60° without a catalyst for 72 hours, giving a clear soft gel. This material also displayed swelling in chloroform, giving a jelly-like mass when allowed to stand with 900 ml. of the solvent. The polymer was distributed throughout the 900 ml. of chloroform, giving a gel which was too thick for pouring.

A third sample (15 g.) of this monomer was heated at 60° for 12 hours without a catalyst. The still fluid material was dissolved in 50 ml. of chloroform and poured with stirring into 250 ml. of methanol, giving 3 g. (20%) of white powdery material which had an intrinsic viscosity of 0.54 and S.P. 140°. This precipitated polymer was free of the odor of the monomer.

***t*-Butyl Thioldimethacrylate Polymers.**—A sample of 62 g. of *t*-butyl thioldimethacrylate was heated at 60° for 4 days with 0.1% of azodiisobutyronitrile. Gelation occurred in 12 hours. The material dissolved readily in 1200 ml. of chloroform. Precipitation from 6000 ml. of methanol gave 41 g. (66%) of white, odorless powder. This material had an intrinsic viscosity of 0.24 and S.P. 193°. Compression molding gave a clear brittle specimen which did not exhibit surface flow when heated in steam at 121°.

This monomer copolymerized readily with methyl methacrylate giving clear copolymers up to about 40 weight per cent. of the thiol ester. Larger amounts of thiol ester gave hazy and increasingly brittle materials. On one run, a mixture of 5 g. of *t*-butyl thioldimethacrylate and 45 g. of methyl methacrylate was heated at 60° for 5 days without a catalyst. Precipitation gave 36.7 g. (73%) of copolymer which had an intrinsic viscosity of 1.63 and S.P. 154°. Compression molding gave a clear tough bar which had an ASTM heat distortion of 112°. ⁸

(8) This material analyzed for 2.16% sulfur, indicating the incorporation of 10.7% of the thiol ester in the copolymer.

Pentachlorophenyl Thioldimethacrylate Homopolymer.—A sample of 10 g. of pentachlorophenyl thioldimethacrylate was heated at 105° for 48 hours with 0.5% of azodiisobutyronitrile, giving a yellow transparent solid which was quite brittle. This material was treated with 800 ml. of chloroform for several days, with no swelling and little solution occurring. Filtration gave back 6.5 g. of undissolved polymer which did not soften at 250°, the upper limit of our apparatus. An attempt to dissolve 0.1 g. in 100 ml. of chloroform failed. Compression molding gave a clear brittle specimen which did not show surface flow when heated in steam at 121°.

Cross-linking of Poly-(methyl Methacrylate) Using Methyl 2-Methyl-3-thiomethoxythiolpropionate.—Several runs were carried out in which methyl methacrylate was heated with a catalyst under varying conditions with 1–10% by weight of the methyl mercaptan addition product of methyl thioldimethacrylate, yielding insoluble polymers. When such experiments were carried out without a catalyst, the addition product proved to be an effective inhibitor to polymerization. The following run is illustrative of such runs:

A mixture of 20 g. of methyl methacrylate, 0.2 g. of the addition product and 0.02 g. of azodiisobutyronitrile was heated for 24 hours at 50°. The resulting solid was allowed to stand with 700 ml. of chloroform for several days. It soon swelled to several times its original size, giving a soft gel which did not further change. The supernatant chloroform was decanted and the gel stirred in a blender with methanol. The precipitated white solid was further washed with methanol and dried. It amounted to 14 g. (70%) and had S.P. 153°. An attempt to dissolve 0.1 g. in 100 ml. of chloroform gave swelling of the individual particles, but solution did not occur.

In another similar experiment, carried out at the same time under identical conditions, the amount of addition product was reduced to 0.07 g. This polymer was readily soluble in 400 ml. of chloroform. Precipitation in methanol gave 17 g. (85%) of polymer which had an intrinsic viscosity of 2.08 and S.P. 152°. A control, in which the addition product was omitted, gave 18 g. (90%) of poly-(methyl methacrylate) which had an intrinsic viscosity of 3.70 and S.P. 144°. Thus, at the lower concentration, the mercaptan addition product acted as a chain transfer agent, reducing the molecular weight of the polymer, but did not cross-link it.

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[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF J. T. BAKER CHEMICAL CO.]

Preparation and Polymerization of Some New Aryl Methacrylates¹

BY GENE SUMRELL,² PAUL G. CAMPBELL, GEORGE E. HAM AND CHARLES H. SCHRAMM

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A number of new halogenated phenyl methacrylates have been prepared and polymerized. The relationship of softening points of the polymers to structure of the monomers is discussed. Difficulties experienced in the preparation of the 2,6-disubstituted phenyl esters is discussed, and a method of preparation is described. This method involves a modified Schotten-Baumann reaction in which methanolic sodium hydroxide is used instead of the aqueous reagent.

Although aliphatic esters of methacrylic acid have been extensively investigated, relatively few aryl methacrylates have been reported in the literature. We are aware of only two halogenated phenyl methacrylates having been previously prepared, *i.e.*, 4-chlorophenyl and 2,4-dichlorophenyl methacrylate.³ The possibility that halogenated

phenyl methacrylates could be used in the preparation of flame resistant polymers prompted us to prepare a series of chlorinated and brominated phenyl methacrylates. Some of the properties of homopolymers of these materials are presented here. We found that even the monomers containing one or more bromines were quite resistant to burning. At least three chlorines were necessary in the aryl methacrylates and their homopolymers to give marked resistance to burning. The halogenated phenyl methacrylates all gave clear transparent polymers when heated alone or in the pres-

(1) The antibacterial and antifungal properties of some of the compounds described in this paper are being reported elsewhere.

(2) To whom inquiries for reprints should be sent. Southwest Research Institute, 8500 Culebra Rd., San Antonio 6, Tex.

(3) S. Patai, M. Bentov and M. E. Reichmann, *THIS JOURNAL*, **74**, 845 (1952).