aluminum bromide catalyst only a partial scrambling of the carbon atoms occurred.[12] The differences of the extent of scrambling of the isotopic carbons in *n*-butane and 2-methylbutane was attributed to the respective vapor and liquid phase operations.[12] In the present study the less deep seated scrambling of the C^{14} in ethylcyclohexane as compared with previous experiment[1] can also be attributed to the difference in the two phases of operations.

Experimental

Ethyl-β-C^{14}-cyclohexane used in this work was from the preparation described previously.[1]

Aluminum bromide was prepared according to Walton.[13] As a preliminary purification it was refluxed in an all-glass apparatus with aluminum turnings and then distilled. The receiver test-tubes were immediately sealed after distillations. Further purification and transfer into small ampoules were carried out as described previously,[5] except that a vacuum of 3 mm. by means of an ordinary oil-pump was used instead of a high vacuum.

***sec*-Butyl Bromide Ampoule.**—Freshly distilled *sec*-butyl bromide, b.p. 91.3°, was weighed into a small apparatus, Fig. 1. A was connected to a three-way stopcock which was attached to a vacuum line. Dry nitrogen was passed through the system and B sealed. After *sec*-butyl bromide was frozen with liquid nitrogen bath, the system was evacuated (3 mm.). Admission of nitrogen followed by evacuation was repeated three times.

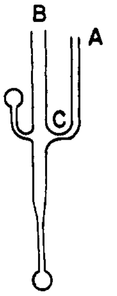

Fig. 1.—*sec*-Butyl bromide ampoule.

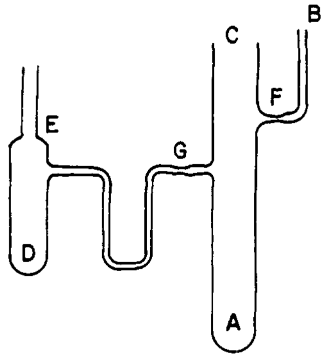

Fig. 2.—Reactor assembly.

Isomerization Reaction.—An apparatus shown in Fig. 2 was used. A weighed amount of ethyl-β-C^{14}-cyclohexane was placed in A with glass beads and a *sec*-butyl bromide ampoule. B was attached to the vacuum line and C sealed. Nitrogen was passed through the apparatus. An aluminum bromide ampoule, cut at its neck, was dropped into D, and E sealed immediately. The system was isolated, the hydrocarbon frozen with a liquid nitrogen-bath and the system evacuated (3 mm.). Admission of nitrogen and evacuation were repeated three times and the system was isolated again. The cooling bath was removed, the solidified hydrocarbon allowed to melt, the bath placed again to freeze the hydrocarbon and the system evacuated. This was repeated twice and F sealed off. The aluminum bromide was distilled from D to A, and G sealed off. The reaction tube was allowed to warm up to the room temperature, gently rotated to dissolve the catalyst, and shaken to break the *sec*-butyl bromide ampoule. The mixture immediately turned yellow at this moment. Then the tube was shaken for a period of time and at the temperature listed in Table I. After the reaction the mixture was clear and colorless with a very small amount of yellow sludge at the bottom. The tube was cut open and the content poured onto ice. The cold aqueous organic mixture was extracted with ether. The ethereal solution was washed with water, 10% sodium carbonate and water, and dried with Drierite overnight. The ether was distilled on an 8 inch Vigreux column. The residue was distilled from a small Claisen flask to give a clear, colorless distillate, maximum b.p. 127°, n^{20}_{D} 1.4291, 80% recovery.

Analysis.—The product for analysis was diluted with inactive 1,2-, 1,3- and 1,4-dimethylcyclohexanes as shown in Table II. The mixture was dehydrogenated by passing twice over 20 ml. of platina–alumina catalyst at 285° at an H.L.S.V. of 0.5. Subsequent chromatography, oxidation of aromatic mixture, separation, purification and decarboxylation of acids, purification of benzene and radioactivity assay, etc., were carried out according to the methods previously described.[1] The results are shown in the tables.

Dehydrogenation of a synthetic mixture of 15% 1,1-dimethylcyclohexane and 85% ethylcyclohexane under the conditions mentioned above did not give toluene, as confirmed by infrared spectrum.

EVANSTON, ILLINOIS

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[12] J. D. Roberts and G. R. Coraor, THIS JOURNAL, **74**, 3586 (1952).

[13] H. F. Walton, "Inorganic Preparations," Prentice–Hall, Inc., New York, N. Y., 1950, pp. 103–105.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY COLLEGE OF FORESTRY AT SYRACUSE UNIVERSITY]

Stereospecific Vinyl Polymerization by Asymmetric Induction[1]

BY NICKY BEREDJICK[2] AND CONRAD SCHUERCH

RECEIVED NOVEMBER 2, 1957

l-α-Methylbenzyl methacrylate has been polymerized and copolymerized with maleic anhydride. The *l*-α-methylbenzyl groups have been removed from the polymer and copolymer by reaction with phosphonium iodide. The resulting polymeric methacrylic acid exhibited some crystallinity and the reduced copolymer had optical activity of opposite sign (+) to that of the polymeric ester. This appears to be the first demonstration that asymmetric induction can produce a degree of stereospecificity in vinyl polymerization.

The probable presence of stereoisomeric structures in vinyl polymers having the structure $(-CH_2CR_1R_2-)_n$ has been recognized for many years,[3-6] and has been considered the case of the generally poor crystallinity of polystyrene, polyvinyl acetate, polymethacrylates, acrylates and the

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[1] Presented at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956. Abstracted from a portion of a thesis presented by Nicky Beredjick in partial fulfillment of the requirements of Ph.D. at the State University College of Forestry.

[2] Standard Oil Co. (Indiana), Whiting, Indiana.

[3] H. Staudinger, "Die Hochmolekularen Organische Verbindungen," Julius Springer, Berlin, 1932, p. 114.

[4] P. J. Flory, "Principles of Polymer Chemistry," Cornell Univ. Press, Ithaca, N. Y., 1953, p. 56.

[5] C. S. Marvel, "Chemistry of Large Molecules," Interscience Publishers, Inc., 1943, p. 240.

[6] M. L. Huggins, paper presented at the Rochester Meeting of the A.C.S., June 24, 1944.

like. Polyoxymethylene, polyvinylidene chloride and high molecular weight paraffins with no asymmetric atoms in contrast exhibit a much higher degree of crystallinity. The explanation for this difference has been that steric dissimilarities between segments of asymmetrically substituted polymer chains decrease the probability of formation of crystalline regions of identical units, and it has even been suggested that differences in stereoisomerism may affect properties of polymers in dilute solution.[7,8]

The belief that the stereoisomerism of high polymers has an important effect upon their physical properties has by now been verified by the extensive research of Natta's school[9-12] with important contributions by Schildknecht[13,14] and others.[15-19] In their work polymers have been synthesized with long sequences of mers having a regular distribution of configurations and greatly enhanced crystallinity. The closely related problem of preparing a polymer or copolymer with an excess of one configuration in the backbone of the polymer chain and exhibiting optical activity has however not been solved heretofore although it was first attacked unsuccessfully about sixty years ago.[20]

Walden prepared optically active diamyl itaconate and found no significant change in optical rotation on its polymerization.[20] It is of some interest that this was described some years later as a result obvious from the association theory of polymer structure.[21] Marvel and co-workers attempted to induce optical activity in the synthesis of polystyrene, polymethyl methacrylate and polyacrylonitrile by the use of optically active free radical sources in the initiation step. However the resulting polymer showed no optical activity.[22] Marvel and Overberger also polymerized optically active derivatives of styrene so that the propagation steps were under the influence of an asymmetric center. In the first attempt, no significant change in optical rotation was found during the polymerization of *p*-vinylbenzyl *d-sec*-butyl ether.[23] In a second attempt *d-sec*-butyl *p*-vinylbenzoate was polymerized, and the polyester hydrolyzed to the polyacid, thus removing the optically active inducing agent. The resulting polymer proved to be optically inactive.[24]

In a somewhat similar synthesis Overberger and Palmer polymerized a styrene derivative containing an asymmetric center substituted in the *o*-position of the benzene ring: *o*-vinylbenzyl *d-sec*-butyl sulfide. The monomer was also copolymerized with methyl methacrylate. Following desulfurization at 150° with nickel and loss of the original centers of asymmetry neither polymer nor copolymer exhibited crystallinity or optical activity.[25]

The interesting polymerizations of *l*-propylene oxide by Price and co-workers to obtain optically active polymers represent a somewhat different approach. No asymmetry was induced in these reactions for the optical activity of the polymer is due to the conservation of the original asymmetric centers in the monomer, *l*-propylene oxide, during the polymerization reaction.[26,27]

As a result of these earlier synthetic attempts and theoretical interpretations[28,29] of the stereoisomerism of addition polymerization, the requirements for optical activity in polymers are now more clear. Frisch, Schuerch and Szwarc have emphasized that the optical activity which can be induced by the use of an asymmetric initiator is negligible even when the propagation is highly stereospecific. Their calculations show that even with a propagation process which is 90% stereospecific such a method can produce only five asymmetric centers of one configuration in excess of the other in each polymer chain. Qualitatively, the reason is that the probabilities of propagation reactions 1 and 4 are identical and the probabilities of reactions 2 and 3 are identical

$$\sim\sim\sim m^{+}\cdot + M \longrightarrow \sim\sim\sim m^{+}m^{+}\cdot \tag{1}$$

$$\sim\sim\sim m^{+}\cdot + M \longrightarrow \sim\sim\sim m^{+}m^{-}\cdot \tag{2}$$

$$\sim\sim\sim m^{-}\cdot + M \longrightarrow \sim\sim\sim m^{-}m^{+}\cdot \tag{3}$$

$$\sim\sim\sim m^{-}\cdot + M \longrightarrow \sim\sim\sim m^{-}m^{-}\cdot \tag{4}$$

Therefore any radicals of negative configuration which are formed will propagate their kind just as efficiently as the positive radicals and after a very few propagation steps the number of negative radicals on the end of growing chains will have essentially equalled the number of growing positive radicals.

A significant excess of one configuration will therefore only be achieved by influencing the propagation reaction directly, not the initiation process. However, even if a polymer is prepared with propagation under the influence of an optically active agent, a number of practical factors must be taken into account in order to induce measurable optical activity in the final polymer.

In radical additions on 1-substituted cyclohexenes, the thermodynamically less stable product predominates, the reaction is under kinetic control

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[7] T. Alfrey, A. Bartovics and H. Mark, THIS JOURNAL, **65**, 2319 (1943).

[8] M. L. Huggins, *ibid.*, **66**, 1991 (1944).

[9] G. Natta, P. Pino, P. Corradini, F. Danusso, E. Mantica, G. Mazzanti and G. Moraglio, *ibid.*, **77**, 1708 (1955).

[10] G. Natta, *J. Polymer Sci.*, **16**, 82, 142 (1955).

[11] G. Natta and P. Corradini, *Atti acad. mazl. Lincei*, **352**, 73 (1955).

[12] G. Natta and P. Corradini, *Redn. acad. mazl. Lincei*, **8**, 18, no. 1, 19 (1955).

[13] C. E. Schildknecht, S. T. Gross and A. O. Zoss, *Ind. Eng. Chem.*, **41**, 1998 (1949).

[14] C. E. Schildknecht, A. O. Zoss and F. Grosser, *ibid.*, **41**, 2891 (1949).

[15] S. H. Muthana and H. Mark, *J. Polymer Sci.*, **4**, 531 (1949).

[16] J. M. Lambert and A. O. Zoss, *Ind. Eng. Chem.*, **40**, 2104 (1948).

[17] C. W. Bunn and E. R. Howells, *J. Polymer Sci.*, **18**, 88, 307 (1955).

[18] J. L. R. Williams, J. VanDenBerghe, W. J. Dulmage and K. R. Dunham, THIS JOURNAL, **78**, 1260 (1956).

[19] J. L. R. Williams, J. VanDenBerghe, K. R. Dunham and W. J. Dulmage, *ibid.*, **79**, 1716 (1957).

[20] P. Walden, *Z. physik. Chem.*, **20**, 383 (1896).

[21] H. H. Landolt, "Optical Activity and Chemical Composition," translated by John McCrae, Whittaker, London, 1899, p. 27.

[22] C. S. Marvel, R. L. Frank and E. Prill, THIS JOURNAL, **65**, 1647 (1943).

[23] C. S. Marvel and C. G. Overberger, *ibid.*, **66**, 475 (1949).

[24] C. S. Marvel and C. G. Overberger, *ibid.*, **68**, 2106 (1946).

[25] C. G. Overberger and L. C. Palmer, *ibid.*, **78**, 666 (1956).

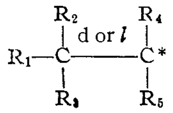
[26] C. C. Price, M. Osgan, R. E. Hughes and C. Shambelan, *ibid.*, **78**, 690 (1956).

[27] C. C. Price and M. Osgan, *ibid.*, **78**, 4787 (1956).

[28] H. L. Frisch, C. Schuerch and M. Szwarc, *J. Polymer Sci.*, **11**, 559 (1953).

[29] C. L. Arcus, *J. Chem. Soc.*, 2801 (1955); 1189 (1957).

and a high degree of specificity appears to depend upon the lifetime of the intermediate radical.[30] It is however not necessary that radical racemization be avoided for stereospecific addition to be observed. It has been pointed out by Hammett[31] that a reaction proceeding *via* an intermediate radical or ion of the type



$$R_1-\underset{\underset{R_3}{|}}{\overset{\overset{R_2}{|}}{C}}\overset{d\text{ or }l}{\text{——}}\underset{\underset{R_5}{|}}{\overset{\overset{R_4}{|}}{C}}{}^{*}$$

where C* represents a carbonium ion, carbanion or radical, irrespective of the configuration of this intermediate, leads to two diastereoisomeric products, which may be expected to be formed with different rates. It should be noted in this connection that the two diastereoisomeric transition states corresponding to the two products will be formed with a difference in activation energy.[32] Therefore just as in diene polymerization[33-35] the stereospecificity of polymerization will be temperature dependent and will be increased at low temperature. In asymmetric syntheses on small molecules[36,37] it has been observed that stereospecificity increases with lowering temperature. Consequently, our polymerizations were carried out at the lowest practical temperature for the system, *ca.* 30°.

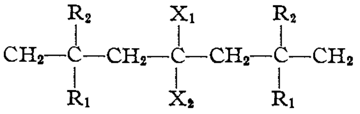
Qualitatively asymmetric induction would also be expected to be most effective when differences in size are great between the four groups forming the original inducing center and when the inducing center is as close as possible to the locus of reaction being converted into a new point of asymmetry.[32] In the classical work on asymmetric induction, addition reactions on the carbonyl function of esters of α-keto acids and optically active secondary alcohols have led to an excess of one configuration in the products. The polymerization of similar esters of α,β-unsaturated acids constitutes a close analogy to this work with an asymmetric carbon atom only two atoms removed from the C=C group undergoing polymerization. In a vinyl ether the asymmetric center may of course be only one atom removed from the vinyl group and this structure may be more advantageous for a demonstration of induced asymmetry by vinyl polymerization.

A consideration of these factors led to the choice of method of induction, of reaction conditions, and of the optically active monomer used in this research.

The amount of optical activity a polymer exhibits will obviously depend not only on the specificity of polymerization but also upon the final structure of the polymer. Now optical activity is determined mainly by groups which are in the immediate vicinity of an asymmetric carbon and as the point of structural dissimilarity is moved farther from the asymmetric center, the optical activity decreases rapidly to a negligible value.[28] In a series of about one hundred compounds listed in reference 38 there are several examples in which single functional groups constitute the only point of structural dissimilarity in a molecule. When the group is four or more carbon atoms away from the asymmetric center, the optical activity is a small fraction of that observed when the same group is adjacent to the asymmetric center. The same principle can be used to correlate the optical activity of phytol and some of its derivatives.[39]

In a homopolymer the differences in structure between the two ends of the polymer attached to any asymmetric center are limited to end groups, the lengths of the chains and the configurations of the substituted carbons on adjacent mers. These would be expected to cause a negligible optical activity. Therefore, while a homopolymer which has been propagated under the influence of an asymmetric center may have longer sequences of a single configuration than one prepared without this influence and may exhibit isotacticity, it will not be expected to show induced optical activity.[28]

Similarly, a copolymer propagated under the influence of an optically active agent will exhibit measurable optical activity due to the structure of the vinyl backbone only if the copolymer has points of structural dissimilarity *near* the asymmetric carbon atoms. In the case of a copolymer produced from two monomers of general structure $CH_2{=}CR_1R_2$, $CH_2{=}CX_1X_2$ it is therefore necessary to consider the effect of unfavorable reactivity ratios. Alfrey, Bohrer and Mark[40] have shown that in a 50–50 random copolymer ($r_1r_2 = 1$), half of all the mers are isolated, that is, are in alternating sequences. In any real case, for example, styrene (M_1) and methyl methacrylate (M_2) ($r_1 = 0.52$, $r_2 = 0.48$), the tendency to alternation is even greater. The vinyl chain of such a copolymer is identical for a distance of at least three carbons on either side of the substituted carbon of an isolated mer. Isolated mers will therefore contribute little to the optical activity of the copolymer. In sequences containing two identical mers, however, both mers will be attached to two different groups and both may contribute to the optical activity. In longer uninterrupted sequences of a single kind of mer only the terminal mers may contribute very much to the optical activity and all others will be nearly inactive. It seems probable therefore that few mers in the copolymer synthesized by Overberger and Palmer would contribute much to optical activity. The lack of isotacticity in the polymer may also have been due to the presence of a benzylic hydrogen on the asymmetric center which may have racemized under their drastic conditions of desulfurization.



$$CH_2-\underset{\underset{R_1}{|}}{\overset{\overset{R_2}{|}}{C}}-CH_2-\underset{\underset{X_2}{|}}{\overset{\overset{X_1}{|}}{C}}-CH_2-\underset{\underset{R_1}{|}}{\overset{\overset{R_2}{|}}{C}}-CH_2$$

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(30) H. L. Goering, D. I. Relyea and D. W. Larsen, THIS JOURNAL, **78**, 348 (1956).

(31) L. P. Hammett. "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 66 and 178.

(32) E. E. Turner, *et al.*, *J. Chem. Soc.*, 3365, 5169 (1949); 3219, 3223, 3227 (1951).

(33) R. R. Hampton, *Anal. Chem.*, **21**, 923 (1949).

(34) W. S. Richardson and A. Sacher, *J. Polymer Sci.*, **10**, 353 (1953).

(35) E. J. Hart and A. W. Meyer, THIS JOURNAL, **71**, 1980 (1949).

(36) H. S. Mosher and E. LaCombe, *ibid.*, **72**, 3994 (1950).

(37) R. L. Letsinger, *ibid.*, **72**, 4842 (1950).

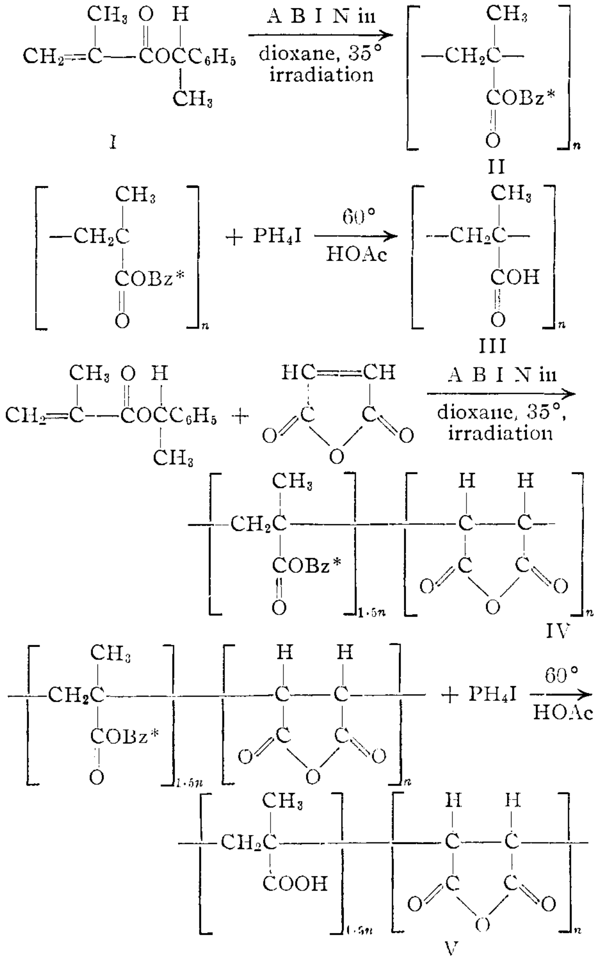
(38) R. E. Marker, *ibid.*, **58**, 976 (1936).

(39) N. Beredjick and C. Schuerch, *J. Org. Chem.*, **22**, 469 (1957).

(40) T. Alfrey, Jr., J. J. Bohrer and H. Mark, "Copolymerization," Interscience Publishers, Inc., New York, N. Y., 1952, pp. 134–137.

A simpler system with which to deal is a copolymer of a 1-substituted or 1,1-disubstituted olefin and a 1,2-disubstituted olefin. If the pair have reactivity ratios which indicate a high degree of alternation, the resulting copolymer should have nearly every mer isolated and each substituted atom in the vinyl chain surrounded by four different groups. If an excess of one configuration is produced it should be demonstrated in this case in optical activity. This was the kind of system chosen for the present investigation:

l-α-Methylbenzyl methacrylate, (I) $[\alpha]$ -41.48°, $[M]^{25}\text{D}$ -78.8° was polymerized with α,α′-azobisisobutyronitrile as initiator to poly-*l*-α-methylbenzyl methacrylate, (II) $[\alpha]$ -77.4°, $[M]^{25}\text{D}$ -147°. The latter was allowed to react with phosphonium iodide to give polymethacrylic acid (III), $[\alpha]\,0^\circ$. Compound I, $[\alpha]\,-41.48^\circ$, $[M]^{25}\text{D}$ -78.8°, was copolymerized with maleic anhydride (IV) to a 1.5–1 *l*-α-methylbenzyl methacrylate–maleic anhydride copolymer (V), $[\alpha]$ -50.2° $[M]^{25}\text{D}$ -128°. Compound V was allowed to react with phosphonium iodide to a 1.5–1 copolymer of methacrylic acid–maleic anhydride (VI) of opposite rotation, $[\alpha]$ $+23^\circ$, $[M]^{25}\text{D}$ $+34.8^\circ$.



I

II

III

IV

V

The results listed here and in the experimental on the copolymer represent a somewhat better sample produced in slightly larger quantities than that initially reported on.[41] The carbon content of this copolymer is the same as theoretical and the hydrogen value is only slightly high. The rotation is perhaps greater than the initial preparation, but the difference is within experimental error. The *d,l*- and *l*-polymer and *l*-copolymer were examined by X-ray diffraction before and after the removal of α-methylbenzyl groups. Because of the small quantity of material, difficulty was experienced in preparing proper samples. However, some crystallinity was observed in the case of the polymer prepared from *l*-α-methylbenzyl methacrylate after removal of *l*-α-methylbenzyl group. This is the product in which crystallinity is most likely since the backbone is most regular and the bulky side chains, which might not fit into a crystal lattice, have been removed.[42] No attempts to find specific conditions for the production of maximum crystallinity were made.[43]

The copolymer of *l*-α-methylbenzyl methacrylate and maleic anhydride appeared completely amorphous even after removal of the α-methylbenzyl groups. Here the crystallinity of the regions of similar configuration is undoubtedly slight because of the complexity of structure. However, the optical activity of the product demonstrates the presence of a preferred configuration of many of the backbone carbon atoms which are surrounded with four different adjacent groups.

These results are entirely consistent with the view that *l*-α-methylbenzyl methacrylate is preferentially converted into one diastereoisomer in excess of the other whether adding to a *l*-α-methylbenzyl methacrylate monomer or to a maleic anhydride monomer. Since each step of the propagation reaction is under the influence of identical groups, it appears that the configurations of induced asymmetric centers in the orderly regions of the vinyl chains should be identical or that the crystalline regions of this polymethacrylic acid should be isotactic.

It is not at present possible to estimate how great an excess of one configuration has been induced in this polymerization. It should be noted, however, that the reduced copolymer reported above has a molecular rotation (based on methacrylate residues) about one-fourth of that of the corresponding α-methylbenzyl polymeric esters and that the activity of the original alcohol which acted as an inducing agent was only about three-fourths of that of the pure enantiomorph.

Acknowledgment.—We wish to express our appreciation to the National Science Foundation for financial support of this work and to Professor Aiden King of Syracuse University for several X-ray analyses.

Experimental

Materials.[44]—Purified[45] dioxane (Fisher Scientific Co., C.P. grade), freshly redistilled and peroxide free was used as solvent in all polymerization experiments.

α,α′-Azo-bis-isobutyronitrile (Eastman Kodak Co.) was twice recrystallized from ether to m.p. 101°. *d,l*-α-Methyl-

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[41] N. Beredjick and C. Schuerch, THIS JOURNAL, **78**, 2646 (1956).

[42] A. V. Tobolsky, *Am. Scientist*, **45**, 37 (1957).

[43] Leo Mandelkern, "The Crystallization of Flexible Polymer Molecules," *Chem. Revs.*, **56**, 908 (1956).

[44] All melting points are uncorrected. Microanalyses were performed by Dr. K. Ritter, Basel, Switzerland.

[45] "A Textbook of Practical Organic Chemistry," by A. J. Vogel, Longmans, Green and Co., New York, N. Y., 1948, p. 175.

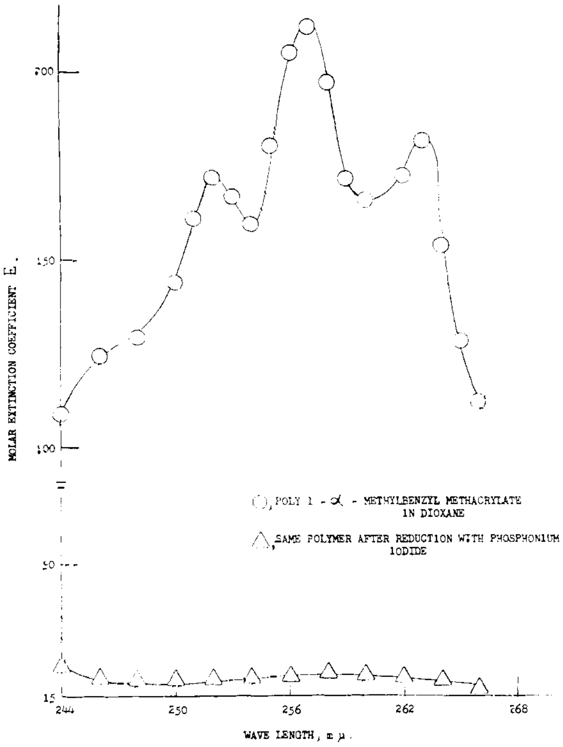

Fig. 1.—Ultraviolet absorption spectrum.

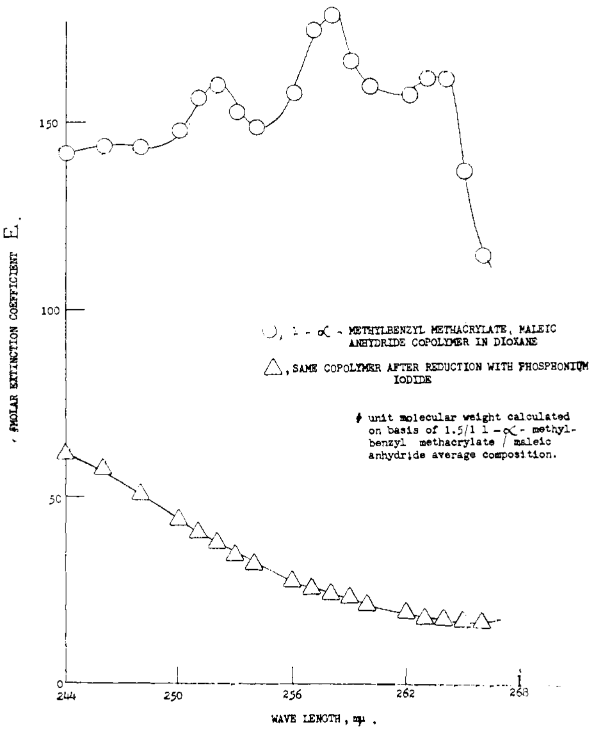

Fig. 2.—Ultraviolet absorption spectrum.

benzyl alcohol (Eastman Kodak Co.) was dried over magnesium sulfate, distilled and the fraction boiling at 60.5–61.0° and 3 mm. pressure resolved by the method of Downer and Kenyon.[46] The ultraviolet absorption spectrum showed characteristic peaks at 249, 255 and 261 mμ. Methacrylic acid glacial (Monomer-Polymer, Inc.) was used without further purification. Maleic anhydride (Fisher Scientific Co., C.P. grade) was twice recrystallized from chloroform to m.p. 53°. Phosphonium iodide[47] was prepared in high yields in a modified apparatus.[48] Methacrylyl chloride was prepared according to Rehberg, *et al.*[49] All synthetic preparations were first made with optically inactive materials to determine optimum reaction conditions and yields.

***l*-α-Methylbenzyl Methacrylate (I).**—*l*-α-Methylbenzyl alcohol (24.5 g., 0.2 mole, $[\alpha]^{27}\text{D}$ −31.8°) and pyridine (24.0 g., 0.3 mole) were placed in a three-necked flask with efficient stirrer, condenser and dropping funnel in an ice-bath. Methacrylyl chloride (16.1 g., 0.2 mole) was added dropwise for one hour. Stirring was continued at 0° for an additional hour. The mixture was washed with 100 ml. of dilute HCl (1:10 by volume) at ice-bath temperature and extracted with ether. The extract was washed with water to neutrality, dried, the ether evaporated and the residue vacuum-distilled in the presence of hydroquinone. *l*-α-Methylbenzyl methacrylate (12.2 g.) (I), b.p. 92° at 3–4 mm., was obtained in 65% yield, $n^{25}\text{D}$ 1.515, $d^{25}{}_{25}$ 1.01, $[\alpha]^{25}\text{D}$ −41.48°, [M] −78.8° (l = 0.5d ec., pure liquid).

Anal. Calcd. for $C_{12}H_{15}O_2$: C, 75.78; H, 7.4. Found: C, 75.9; H, 7.8.

Poly-*l*-α-methylbenzyl Methacrylate (II).—*l*-α-Methylbenzyl methacrylate (0.687 g., 3.6 × 10^{-3} mole, $[\alpha]^{25}\text{D}$ −41.48°) and 0.040 g. (2.44 × 10^{-4} mole) of α,α′-azobisisobutyronitrile were dissolved in 3 ml. of dioxane and placed in a 50-ml. flask equipped with a side finger for a thermometer well. The solution was frozen and degassed three times *in vacuo*, evacuated to 10^{-5} mm. and sealed. Decomposition of α,α′-azobisisobutyronitrile (absorption peak 3500 A.) was photosensitized by[50] illumination from a shielded AH4 Hanovia mercury lamp (General Electric). Its light was directed onto the flask through a 15-cm. long black walled tube, 4 cm. in diameter. The temperature registered in the flask was 30–35°, depending upon the distance between the reaction flask and the light source.

The reaction mixture was exposed to eight hours of continuous radiation. The polymer was precipitated three times into petroleum ether (Fisher b.p. 35.5–55°), dissolved in dioxane and freeze-dried for 24 to 48 hours, then dried to constant weight at 60° in a vacuum oven. Poly-*l*-α-methylbenzyl methacrylate (II) was obtained in a yield of 67% (0.456 g.), $[\alpha]^{25}\text{D}$ −77.4°, [M] −147° (l 0.5, c 2.2, α −0.87°), m.p. 136–139°. The ultraviolet absorption spectrum showed characteristic peaks at 252, 257 and 263 μm. (Fig. 1). A film cast from dioxane showed no evidence of crystallinity by X-ray diffraction.

Anal. Calcd. for $(C_{12}H_{14}O_2)_n$: C, 75.7; H, 7.4. Found: C, 75.2; H, 7.7.

Reaction of Poly-*l*-α-methylbenzyl Methacrylate (II) with Phosphonium Iodide.—Poly-*l*-α-methylbenzyl methacrylate (0.300 g., $[\alpha]^{25}\text{D}$ −77.4°) was dissolved in 25–30 ml. of acetic acid in a 50-ml. flask equipped with a side-arm, through which a steady stream of dry hydrogen was bubbled through the bulk of the solution. The solution was heated to 60° and 2.00 g. of phosphonium iodide added in small portions during the period of one hour, then kept at 60° and under constant hydrogen bubbling for another hour.

The polymer was precipitated three times into ligroin (Fisher b.p. range 60–90°) and twice into absolute diethyl ether. The fine bulky precipitate was centrifuged off, dissolved in dioxane, freeze-dried for 24–48 hours and dried to constant weight in a 60° vacuum oven.

Polymethacrylic acid (III) (0.114 g., yield 84%) was obtained. The ultraviolet absorption spectrum showed no characteristic peaks for the α-methylbenzyl group (Fig. 1); m.p. 260–270° dec. No optical activity was detected (l 0.5, c 3, α 0).

A film cast from dioxane solution gave some evidence of crystallinity, by the X-ray diffraction method, but indicated that the polymer was largely amorphous.

Anal. Calcd. for $(C_4H_6O_2)_n$: C, 55.9; H, 7.0. Found: C, 55.68; H, 7.5.

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A sample of polymer III reduced in the above manner (0.0091 g.) was dissolved in 7 ml. of wet dioxane in a weighing flask; 1.75 ml. of 0.1 *N* sodium hydroxide was added and the solution warmed to 65° for 1.5 hours. It was then cooled and back-titrated potentiometrically with 0.1 *N* HCl; neut. equiv. calcd. 86.0, found 84.6.

Copolymerization of *l*-α-Methylbenzyl Methacrylate and Maleic Anhydride.—*l*-α-Methylbenzyl methacrylate ($[\alpha]^{25}D$ −41.48, 0.349 g., 1.83×10^{-3} mole), maleic anhydride (0.535 g., 5.46×10^{-3} mole) and α,α'-azobisisobutyronitrile (0.020 g., 0.12×10^{-3} mole) were dissolved in 3 ml. of dioxane, processed as before and irradiated for 80 hours at 30–35°. The resulting viscous solution was precipitated four times in petroleum ether to remove unreacted maleic anhydride, freeze-dried from dioxane for 24–48 hours and dried to constant weight in a 60° vacuum oven; 0.2126 g. of copolymer was obtained. The copolymer showed characteristic peaks of absorption at 252, 258 and 263 mμ (Fig. 2); $[\alpha]^{25}D$ −50.2° (*c* 2.1 in dioxane, *l* 0.5) and [M] −128°. A dioxane solution cast film showed no evidence of crystallinity by X-ray diffraction.

Anal. Calcd. for $(CH_2C(CH_3)COOCH(CH_3)C_6H_5)_{1.5n}$–$(C_4H_2O_3)_n$: C, 69.0; H, 6.01. Found: C, 68.94; H, 6.13.

Reaction of α-Methylbenzyl Methacrylate–Maleic Anhydride Copolymer (V)–(VI) with Phosphonium Iodide.—Poly-*l*-α-methylbenzyl methacrylate–maleic anhydride copolymer (V) (0.150 g., $[\alpha]^{25}D$ −50.2°) was dissolved in 10 ml. of glacial acetic acid and allowed to react in the manner described above with 0.450 g. of phosphonium iodide. The solution was cooled to room temperature, the reduced copolymer precipitated in a curdy flocculent form in absolute ether and left to settle for 24 hr. It was then centrifuged off, redissolved in dioxane and reprecipitated in absolute ether four to six times to remove traces of iodine, freeze-dried from dioxane for 24–48 hours and dried to constant weight in a 60° vacuum oven; 0.060 g. of reduced copolymer (VI) was obtained in 67.5% yield. The ultraviolet absorption spectrum of VI (Fig. 2) showed no characteristic peaks for the α-methylbenzyl group.

Anal. Calcd. for $(CH_2C(CH_3)(COOH))_{1.5n}(C_4H_2O_3)$: C, 52.9; H, 6.1. Found: C, 52.9; H, 4.9.

A 2% solution in dioxane was examined for optical activity (*l* 0.5 dec.). It showed an angular rotation of $\alpha = +0.22 \pm 0.05°$, specific rotation $[\alpha]^{25}D$ +23° and molecular rotation [M] +34.8°. A film cast from dioxane showed no evidence of crystallinity by the X-ray diffraction method.

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[CONTRIBUTION FROM THE POLYMER RESEARCH DEPARTMENT, RESEARCH DIVISION, STAMFORD LABORATORIES, AMERICAN CYANAMID CO.]

The Dimers of Ring Substituted α-Methylstyrenes[1]

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The course of the acid-catalyzed dimerization of α-methylstyrenes containing the following ring substituents is described: p-CH_3, p-COOH, p-NH_2 and m-CH_2. Depending on conditions, two types of dimers are formed. These are open chain unsaturated dimers (IV and V) and cyclic substituted phenylindanes (VI). The former are converted readily into the latter by more vigorous acid treatment. The basis for assignment of structures to these various dimers is presented.

The acid-catalyzed dimerization of both styrene and α-methylstyrene has been known for many years.[2–6] Recent kinetic data indicate that the course of the styrene dimerization follows the scheme shown in Fig. 1.[5] Essentially, the reaction proceeds *via* the protonation of styrene monomer to form the styrylcarbonium ion IIa which adds a molecule of monomer to yield the dimer carbonium ion IIIa. The latter can (1) add additional monomer units to form polymer, (2) eject a proton to yield the unsaturated dimer IVa or (3) undergo an intramolecular alkylation to afford the cyclic dimer VIa. By regulating the acidic strength of the catalyst, excellent yields of either dimer may be obtained.[5]

The dimerization of α-methylstyrene (Ib) and α,p-dimethylstyrene (Ic) has not been investigated as thoroughly as the dimerization of styrene. Nevertheless, it is more than likely that these two monomers dimerize in a fashion analogous to styrene since they both afford after acid treatment the corresponding unsaturated and cyclic dimers (see Fig. 1). Furthermore, in both cases the unsaturated dimers are converted readily to the saturated cyclic forms VIb and VIc by more vigorous acid treatment.[3,7]

Unlike styrene, the α-methylstyrenes can form two unsaturated dimers (IV and V) depending upon which carbon atom in intermediate III loses the proton. In the case of α,p-dimethylstyrene both unsaturated dimers IVc and Vc have been identified by degradation experiments.[7] Similarly, with α-methylstyrene it is more than likely that a mixture of IVb and Vb is formed in spite of the fact that only IVb has been established by degradation studies.[3]

The present work expands the scope of the dimerization reaction to include other ring substituted α-methylstyrenes.

It was reported in 1883 that dilute hydrochloric acid readily dehydrated p-(1-hydroxy-1-methylethyl)-benzoic acid to yield p-isopropenylbenzoic acid (Id, m.p. 161°), while concentrated hydrochloric acid at elevated temperatures produced an "isomer" of m.p. 255–260°.[8] This work was repeated and it was found that the higher melting acid melted over a wide range (245–265°), and that the melting point did not change appreciably after repeated recrystallizations. The infrared spectrum of this higher melting acid suggested the presence of olefinic unsaturation including terminal olefinic unsaturation. Moreover, a more rigorous acid treatment converted it to the cyclic isomer

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