**541.** *Stereoisomerism of Addition Polymers. Part III.[1] The Optical Rotatory Power of Poly[(+)-1 : 3-Dimethylbutyl Methacrylate] and of Copolymers with Methyl Methacrylate.*

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Polymers of (+)-1 : 3-dimethylbutyl methacrylate, and copolymers with methyl methacrylate, have been prepared, and the rotatory power of their solutions in *sym*-tetrachloroethane measured. Change in concentration of solutions, in molecular weight, and from benzoyl peroxide to αα'-azoisobutyronitrile as initiator, have little effect on optical rotation.

The use of molecular-rotation differences leads to the conclusion that dissymmetric secondary coiling of the main chain in these polymers contributes to the rotatory power.

In furtherance of a study of addition-polymer stereoisomerism, a theoretical treatment of which was given earlier,[1,2] the optical rotatory powers of a group of polymethacrylates have been investigated and related to aspects of molecular structure. References in the literature to optically active polymers have been discussed in Part II; to these is added the preparation and polymerisation of (+)-s-butyl α-chloroacrylate.[3] In no case were the authors primarily interested in rotatory power, and values for only a single wavelength and concentration are usually given for each polymer specimen.

In the present work (+)-1 : 3-dimethylbutyl methacrylate has been prepared by the reaction of methacryloyl chloride with (+)-1 : 3-dimethylbutanol. This alcohol was selected because its rotatory dispersion in the visible region is simple, and it is of low molecular weight and can readily be resolved;[4] further, the (±)-methacrylate had earlier been prepared and polymerised by Crawford.[5] The (+)-methacrylate was polymerised by initiation with benzoyl peroxide, and the rotatory power to visible light of five wavelengths determined. Similar measurements have been made on polymer initiated with αα'-azoisobutyronitrile, and on copolymers of the (+)-methacrylate with methyl methacrylate. Solutions in *sym*-tetrachloroethane have been used throughout.

In order to apply the method of molecular-rotation differences, (+)-1 : 3-dimethylbutyl

[1] Part II, Arcus, *J.*, 1957, 1189.
[2] Part I, Arcus, *J.*, 1955, 2801.
[3] Crawford and Plant, *J.*, 1952, 4492.
[4] Kenyon and Strauss, *J.*, 1949, 2153.
[5] Crawford, *J. Soc. Chem. Ind.*, 1949, **68**, 201.

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pivalate has been prepared. Differences have been determined for the series of five wavelengths, in preference to the use of a single wavelength, in order to provide a check on the possible incidence of anomalous dispersion.

## EXPERIMENTAL

Rotations are at 25°; those of undiluted liquid compounds are for $l$ 1·0, and those of solutions for $l$ 2·0, unless otherwise stated.

Pyridine, dried with, then distilled from, potassium hydroxide, was passed down a column of alumina in order to remove peroxides.

*sym*-Tetrachloroethane (400 ml.) was repeatedly stirred with 50 ml. portions of sulphuric acid, with heating on a steam-bath, then steam-distilled, dried ($CaCl_2$), and distilled; it had b. p. 144—146°, $d_4^{25}$ 1·587.

Methacryloyl chloride, b. p. 96—98°, and pivaloyl chloride, b. p. 105—106°, were prepared by the reaction of methacrylic acid (b. p. 100°/70 mm.) with benzenesulphonyl chloride, and of pivalic acid (b. p. 165°) with benzoyl chloride, according to directions by Heyboer and Staverman [6] and Brown [7] respectively.

(±)-1 : 3-Dimethylbutanol was dried ($K_2CO_3$) and distilled through a Vigreux column; it had b. p. 128—130°. Three resolutions by Kenyon and Strauss's method [4] yielded (+)-1 : 3-dimethylbutanol having $\alpha_{5893}^{24}$ +16·76°, $\alpha_{5893}$ +16·58°, $\alpha_{5893}$ +16·80°.

Pivaloyl chloride (9·6 g.) was added to an ice-cold mixture of pyridine (12·6 g.) and (+)-1 : 3-dimethylbutanol (8·2 g.) containing a little copper powder. The whole was boiled for $1\frac{1}{4}$ hr.; after cooling, it was added to dilute hydrochloric acid. The product was extracted with light petroleum (b. p. 40—60°) and twice distilled, yielding (+)-1 : 3-*dimethylbutyl pivalate* (11·8 g.), b. p. 77—78°/22 mm., $n_D^{23}$ 1·4070, $\alpha_{5893}^{24}$ 19·59° (Found: C, 70·8; H, 11·65. $C_{11}H_{22}O_2$ requires C, 70·9; H, 11·9%).

Methacryloyl chloride (17·3 g.) was added to an ice-cold, stirred mixture of (+)-1 : 3-dimethylbutanol (16·3 g.), pyridine (15·8 g.), and t-butylcatechol (0·4 g.). The mixture was kept at 85° for 5 min. and kept overnight at 25°, then poured into hydrochloric acid (4·5 ml.) and water (160 ml.). The whole was thrice extracted with light petroleum (b. p. 40—60°), and the extract was thrice washed with 0·5N-sodium hydroxide, then with water, and dried ($MgSO_4$). The product from evaporation of the extract was twice distilled, quinol (0·28 g.) being added on evaporation and before the second distillation, and yielded (+)-1 : 3-*dimethylbutyl methacrylate* (average yield 49%), b. p. 75—78°/20 mm., $n_D^{25}$ 1·4224, $\alpha_{5893}$ 34·77° (Found: C, 70·15; H, 10·75. $C_{10}H_{18}O_2$ requires C, 70·55; H, 10·65%).

Partially active (−)-1 : 3-dimethylbutanol having $\alpha_{5893}$ −10·33° similarly gave (−)-1 : 3-dimethylbutyl methacrylate, b. p. 70—71°/14 mm., $\alpha_{5893}$ −21·69°.

*Polymerisations.*—In each instance the polymer or copolymer was a hard, colourless, glass. The specimen was crushed, and kept at 1 mm., at room temperature for the fully active, and at 75° for the other specimens, until the weight was constant; the losses were small.

(1 and 2) (+)-1 : 3-Dimethylbutyl methacrylate, containing 0·01% of benzoyl peroxide, was heated under nitrogen as follows: (1) at 82°, 30 min.; 45°, 80 hr.; 110°, 5 hr. (2) at 85°, 1 hr.; 79°, 25 hr. For specimen (1) there was found C, 71·1; H, 10·8%. Part of the surface of specimen (2) had become white, opaque, and readily detachable; it was thought that this material might be crystalline: however, it appeared amorphous under the microscope, and an X-ray crystallographic examination (for which we thank Dr. C. W. Bunn, Imperial Chemical Industries Limited, Plastics Division) showed only amorphous polymer to be present; its identity was checked by analysis (Found: C, 70·4; H, 10·9%).

(3) (−)-1 : 3-Dimethylbutyl methacrylate (3·4 g.) containing benzoyl peroxide (0·0068 g.) was heated under nitrogen at 79° for 5 hr.

(4) A similar polymerisation was carried out, but the benzoyl peroxide was replaced by the equimolar quantity of αα′-azoisobutyronitrile (0·0059 g.). Polymers (3) and (4) were lævo-rotatory but, to facilitate comparison of molecular rotations, are recorded as dextrorotatory in Table 1.

(5) (+)-1 : 3-Dimethylbutyl methacrylate (3·41 g.), methyl methacrylate (b. p. 40—41°/100

[6] Heyboer and Staverman, *Rec. Trav. chim.*, 1950, **69**, 787.
[7] Brown, *J. Amer. Chem. Soc.*, 1938, **60**, 1325.

mm.; 4·10 g.), and αα′-azoisobutyronitrile (0·075 g.) were warmed and stirred until homogeneous, the air was then displaced by nitrogen and the whole heated at 76° for 100 min. (Found: C, 64·3; H, 9·25. Calc. for $C_5H_8O_2 : C_{10}H_{18}O_2 = 2·33 : 1$: C, 64·45; H, 9·15%).

(6) Copolymer was similarly prepared from methyl methacrylate (6·00 g.), (+)-1 : 3-dimethylbutyl methacrylate (3·43 g.), and αα′-azoisobutyronitrile (0·093 g.) (Found: C, 63·8; H, 8·85. Calc. for $C_5H_8O_2 : C_{10}H_{18}O_2 = 3·20 : 1$: C, 63·65; H, 8·95%).

The preparation of polymer solutions of known, and relatively high, concentrations presented some difficulty, owing to the time required for dissolution and to the high viscosity of the solutions; the following method was evolved. Polymer (1 g.) and *sym*-tetrachloroethane (20 ml.) were placed in a boiling-tube, which was connected by a ground joint to a vertical tube, surrounded by a water-jacket, through which passed a loosely fitting stirrer. The boiling-tube was placed in a cylindrical recess in a flask, fitted with a reflux condenser, containing boiling butan-1-ol (b. p. 116°). Stirring and heating were continued until dissolution was complete. The density of the solution at 25° was determined. At first, concentration was determined by evaporation of a known weight of solution, followed by heating at 80° to constant weight. Subsequently, and more conveniently, the water-jacket, above, was made a separate unit (a long torus) sliding on to the vertical tube; it was then practicable to weigh accurately the boiling-tube and contents with the vertical tube and stirrer, and so to ascertain the weight of solution containing a known weight of polymer. A comparison of the two methods with the same solution gave *c* 4·96 and 5·03 (g. of polymer in 100 ml. solution) respectively.

TABLE 1. *Rotatory powers of polymers and copolymers of* (+)-1 : 3-*dimethylbutyl methacrylate and of* (+)-1 : 3-*dimethylbutyl pivalate in* sym-*tetrachloroethane at* 25°.

| Compound | Solution no. | c | Rotation | Rotation * at λ (Å) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 6438 | 5893 | 5461 | 5086 | 4358 |
| Fully active polymer (1) ... | i | 4·79 | [α] | 14·2° | 18·0° | 20·2° | 24·2° | — |
| | ii | 5·01 | [α] | 14·4 | 17·7 | 20·2 | 24·3 | 33·4° |
| | iii | 6·63 | [α] | 13·9 | 18·3 | — | 25·2 | 34·7 |
| | iv | 7·19 | [α] | 15·0 | 17·3 | 21·4 | 25·3 | 34·9 |
| | | | [M] | 24·3 | 30·3 | 34·4 | 41·3 | 56·8 |
| Fully active polymer (2) ... | i | 4·96 | [α] | 14·5 | 18·0 | 21·1 | 24·8 | 33·2 |
| | ii | 4·88 | [α] | 14·8 | 18·2 | 20·8 | 24·8 | 33·5 |
| | | | [M] | 24·9 | 30·9 | 35·6 | 42·2 | 56·7 |
| Pivalate .................. | i | 4·71 | [α] | 20·5 | 23·4 | 26·8 | 31·3 | 44·0 |
| | ii | 4·74 | [α] | 20·2 | 23·3 | 26·8 | 31·0 | 44·3 |
| | | | [M] | 37·9 | 43·5 | 49·8 | 58·0 | 82·3 |
| | | | [M]ₛ | −13·0 | −12·6 | −14·2 | −15·8 | −25·6 |
| Partially active polymer (3) | i | 4·93 | [α] | 9·6 | 11·1 | 12·7 | 14·8 | 20·5 |
| | ii | 4·85 | [α] | 9·4 | 10·8 | 12·5 | 14·9 | 20·7 |
| Partially active polymer (4) | i | 4·87 | [α] | 9·0 | 11·1 | 13·3 | 15·3 | 20·9 |
| | ii | 4·81 | [α] | 9·2 | 11·2 | 13·0 | 15·5 | 20·3 |
| | | | [M]ₛₙ | 1·3 | −0·5 | −0·4 | −0·5 | 0·4 |
| Copolymer (5) ............ | i | 5·27 | [α] | 6·3 | 8·8 | 10·1 | 11·9 | 16·6 |
| | ii | 5·17 | [α] | 7·0 | 8·7 | 10·3 | 11·7 | 15·5 |
| | | | [M]ₛₙ | 1·1 | 2·2 | 3·0 | 2·8 | 3·5 |
| Copolymer (6) ............ | i | 5·33 | [α] | 5·0 | 6·8 | 8·3 | 9·6 | 12·5 |
| | ii | 5·14 | [α] | 6·0 | 7·0 | 8·1 | 9·8 | 12·4 |
| | | | [M]ₛₙ | 0·8 | 1·0 | 1·7 | 1·8 | 1·1 |

* Positive unless otherwise stated.

TABLE 2.

| Polymer or copolymer no. ...... | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| c ........................ | 0·657 | 0·345 | 0·621 | 0·614 | 0·674 | 0·682 |
| [η]c ...................... | 0·99 | 2·21 | 0·95 | 0·51 | 0·29 | 0·26 |

In Table 1, the molecular rotations are calculated from the average of the specific rotation (at *c* 5); the values for polymers (3) and (4) have been combined.

The intrinsic viscosity, $[\eta]_c = (1/c) \ln (\eta_{\text{soln.}}/\eta_{\text{solv.}})$, of a solution of the polymer or copolymer in *sym*-tetrachloroethane was determined at 25°.

RESULTS AND DISCUSSION

Since little is known of the optical rotatory properties of solutions of polymers bearing optically active groups, the effect on rotation of change of concentration, initiator, and molecular weight has been investigated.
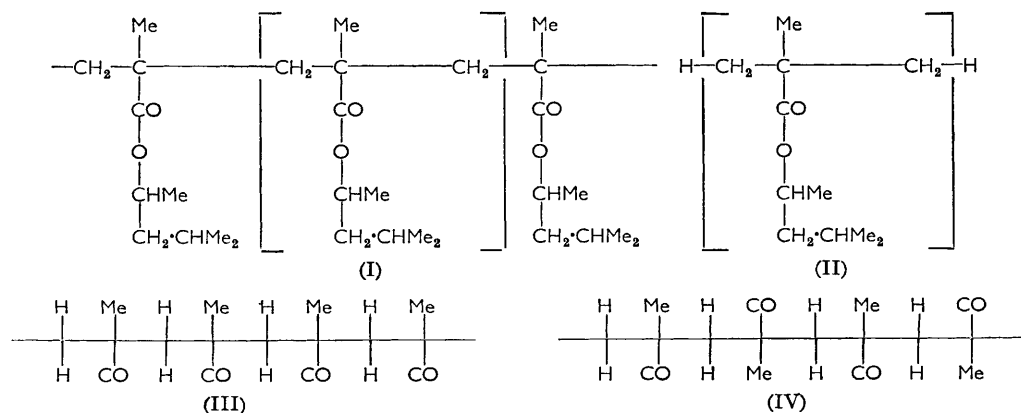
With respect to fully active poly[(+)-1 : 3-dimethylbutyl methacrylate] [polymer (1), Table 1], variation of $c$ from 4·79 to 7·19, the last value approaching the limit of solubility of the polymer, resulted in no significant change in the specific rotations.

A specimen of (+)-1 : 3-dimethylbutyl methacrylate (61·5% optically pure) was polymerised by initiation with benzoyl peroxide and with $\alpha\alpha'$-azoisobutyronitrile. The rotatory powers of the two polymers [(3) and (4), Table 1] are seen to be substantially the same, indicating that the steric course of polymerisation is unaffected by the nature of the radicals initiating the reaction. Further, the change in molecular weight corresponding to a doubling in intrinsic viscosity does not significantly alter the specific rotations [polymers (1) and (2), and (3) and (4), Tables 2 and 1].

It is necessary, in the present discussion, to use the distinction which has been made [8] between the primary and the secondary structure of a macromolecule. The former is the covalent structure of the polymer considered apart from the chain-coiling due to steric or other non-covalent interactions of the side groups, and for the present polymers is exemplified in formula (I). The secondary structure is the form of helical coiling which the polymer chain takes up in any given circumstance; it is a conformation, not a configuration.

The following treatment, which is provisional, provides an analysis of the rotatory power of the polymers in terms of various aspects of their structure. There are potentially three contributions to the rotatory power: (*a*) that due to the (+)-1 : 3-dimethylbutyl groups, together with the groups to which they are immediately covalently bonded in the polymer, and that due to possible dissymmetry in (*b*) the primary, (*c*) the secondary, chain structure.

It is considered that the contribution of the asymmetric side groups, together with their immediate environment in the molecule, is substantially equal to the molecular rotation of (+)-1 : 3-dimethylbutyl pivalate, since the structures within the square brackets of (I) and (II) are identical. It is seen (Table 1) that the algebraic difference between the



(I)    (II)

(III)    (IV)

molecular rotation of fully active poly[(+)-1 : 3-dimethylbutyl methacrylate] and that of the pivalate is a series of negative rotations of about one-third the magnitude of those of the pivalate. This rotatory power ($[M]_s$) is to be ascribed to structural features other than the individual ester units.

[8] Kendrew, Bodo, Dintzis, Parrish, Wyckoff, and Phillips, *Nature*, 1958, **181**, 662; Bernal, *Discuss. Faraday Soc.*, 1958, **25**, 7.

The present polymers all contain the polymethacryloyl main chain, the isotactic and the syndiotactic structure for which are represented by the Fischer projection formulæ (III) and (IV). As discussed earlier in relation to the literature, each of these structures has numerous " local " planes of symmetry, the first at every carbon atom, the second at every methylated carbon atom, whence it is inferred that neither configuration, nor random sequences of short sections of (III) and (IV) alternately, can give rise to optical activity, a conclusion supported by the experimental evidence.[1,9] Poly(methyl methacrylate) chains terminate largely by disproportionation at 60°,[10] and entirely so at 90°;[11] probably, therefore, the present polymethacrylates terminate by disproportionation and possess the symmetry associated with simple terminations.[1,2] It is concluded that the primary chain structure exhibits an overall symmetry, and therefore does not contribute to the rotatory power of the polymer.

Since a regular left- or right-hand helix is dissymmetric, the secondary structure can, in principle, contribute, and the rotations $[M]_s$ are ascribed to this source. Dissymmetric coiling of the main chain, conforming more to a right- than to a left-hand helix (or *vice versa*) may have arisen during polymerisation; alternatively it may be the most stable conformation of the chain molecule in solution, in each instance dissymmetric coiling being imposed by the steric requirements for the minimum-energy accommodation of the asymmetric side-groups.

Inspection of a C.R.L.-Catalin model of the syndiotactic polymer shows that the main chain conforms to a planar zig-zag only if the chain methyl groups and the carbonyl groups of the ester units are closely packed; a conformation providing maximum relaxation of packing requires rotation about links of the main chain such that the latter takes on a helical form, and since the conformation is to accommodate 1 : 3-dimethylbutyl groups which are asymmetric and all of the same configuration, a preference is to be expected for either a right- or a left-hand helix. For the isotactic configuration of the main chain, also, the closeness of packing renders a helical conformation probable.

From the stability of the rotatory power to change in molecular size, and in end groups, and to alteration in the larger-scale coiling associated with change in concentration, it is inferred that the secondary coiling, for a given temperature and solvent, is a stable, and, if averaged over more than a minimum number of units, a constant feature of the polymer chain.

The partially active polymers can be considered as copolymers of the optically pure (+)-methacrylate with the (±)methacrylate, and, with respect to these polymers, and the copolymers of the (+)-methacrylate and methyl methacrylate, it is of use to calculate the molecular secondary rotation due to units other than those of optically pure monomer. Evaluation of this quantity, $[M]_{sn}$, requires subtraction of a molecular-rotation component equivalent to the proportion of optically pure monomer present; it can be shown to be given by:

$$[M]_{sn} = m([\alpha] - [\alpha]'x)/100(1 - x)$$

where $x$ is the weight-fraction of optically pure 1 : 3-dimethylbutyl methacrylate units present in the copolymer, $[\alpha]$ and $[\alpha]'$ are the specific rotation of the given polymer and of fully active poly[(+)-1 : 3-dimethylbutyl methacrylate], and $m$ is the molecular weight of the second monomer. The assumption is made that, in its situation in the copolymer, the (+)-monomer unit contributes the same rotatory power as in the fully active (+)-polymer: that is, not only the component (*a*), above, but also that due to secondary coiling.

For the partially active polymer, the contribution, $[M]_{sn}$, from the (±)-units is found to be a series of small quantities of variable sign: it is inferred that these units are essentially optically inert, *d*-contributions of whatever kind being cancelled by the corresponding

[9] Beredjick and Schuerch, *J. Amer. Chem. Soc.*, 1958, **80**, 1933.
[10] Bevington, Melville, and Taylor, *J. Polymer Sci.*, 1954, **14**, 463.
[11] Bamford and Jenkins, *Nature*, 1955, **176**, 78.

$l$-contributions; the optically pure units contribute, proportionally, the same rotatory power as in the fully-active polymer.

With respect to the copolymers of fully active $(+)$-1 : 3-dimethylbutyl methacrylate with methyl methacrylate in molar ratio 1 : 2·33 and 1 : 3·20, the rotations deduced for the secondary structure of the methyl methacrylate units ($[M]_{sn}$, Table 1) are quantities of $(+)$-sign, opposite to that found for the secondary structure of the 1 : 3-dimethylbutyl methacrylate units. Further, the polymer richer in the latter possesses the larger values of $[M]_{sn}$. No explanation of the sign-difference is put forward; with respect to the difference in magnitude, it is possible that a left- rather than a right-hand helical form (or *vice versa*) of the methyl methacrylate sequences conforms better to adjacent $(+)$-1 : 3-dimethylbutyl methacrylate units, whence a greater proportion of the latter will increase the dissymmetry in coiling of the methyl methacrylate sequences, giving rise to a larger value of $[M]_{sn}$.