Optically Active Polymers. III.* Polymers of 1, 3-Dimethylbutyl Methacrylate

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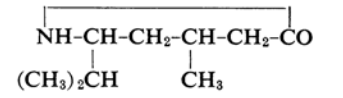
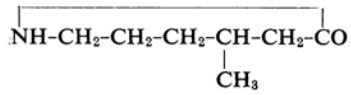
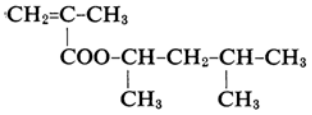
In an earlier study, Imoto and Sakurai[1] synthesized a polymer of (−)-*l*-4-methyl-7-isopropyl-2-oxohexamethyleneimine (I) and found that its optical rotation increased with the molecular weight. Recently Overberger and Jabloner[2] obtained a polymer of D-(−)-β-methyl-ε-caprolactam (II), measured its rotatory dispersion, and concluded that the polymer showed no definite proof for the assignment of a helical structure. However, if we can assume that the longer the molecule, the greater is the portion of molecular-structural (helical) asymmetry, an increase in molecular rotation with molecular weight is understandable.



(I)

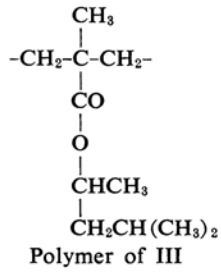


(II)

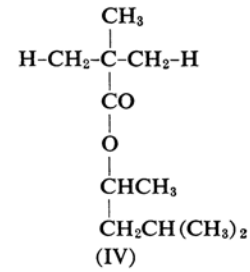


(III)

Arcus and West[3] synthesized (+)-1, 3-dimethylbutyl methacrylate (III) and carried out its polymerization in the presence of benzoyl peroxide or azobisisobutyronitrile. The molecular rotation [M] of the polymer and (+)-1, 3-dimethylbutyl pivalate (IV) was determined for five wavelengths at 25°C in tetrachloroethane. Compound IV could be recognized as the unit of the polymer of compound III.



Polymer of III



(IV)

Moreover, the difference between the values of [M] of IV and the polymer of III was considered to be that part of the [M] which was due to structural features other than the individual ester units. For example, at 4358 Å, the values of [M] were determined as follows: IV, +82°; Polymer of III, +60°, and the difference, −22°. It was concluded that the contribution of the difference was due to disymmetric coiling of the main chain.

This paper will deal with the preparation of three kinds of polymers of (+)-1, 3-dimethylbutyl methacrylate (III), polymers which were assumed to be isotactic, syndiotactic and atactic, as well as with the determination of the optical rotatory dispersion of the polymers. Moreover, the polymerization of optically impure (−)-1, 3-dimethylbutyl methacrylate and the optical rotatory dispersion of the polymers will be investigated.

* Part II: M. Imoto and S. Kimura, *Makromol. Chem.*, 53, 210 (1962).

1) M. Imoto, H. Sakurai and T. Kono, *J. Polymer Sci.*, 50, 467 (1961).

2) C. G. Overberger and J. Jabloner, *J. Am. Chem. Soc.*, 85, 3431 (1963).

3) C. L. Arcus and D. West, *J. Chem. Soc.*, 1959, 2699.

It is known that methyl methacrylate can be polymerized with *n*-BuLi at −78°C to give an isotactic polymer, while with azobisisobutyronitril (AIBN) at a higher temperature it gives an atactic polymer, and at about −40°C, a syndiotactic polymer. Granting that these specific polymerizations of methyl methacrylate could also be applied to 1,3-dimethylbutyl methacrylate, isotactic, syndiotactic and atactic polymers of optically active 1,3-dimethylbutyl methacrylate may be obtained.[4] It seemed an interesting problem to investigate the relationship between the change in the optical rotatory power of a polymer, with its molecular weight, and the stereospecific configuration of the polymer molecule. However, no definite result could be obtained.

Experimental

Syntheses of Optically Active Monomers. — 1) The resolution of *dl*-1,3-dimethylbutanol was carried out through the salt of 1,3-dimethylbutyl hydrogen phthalate with brucine, according to the method of Kenyon et al.[5] In recrystallization from acetone, the salt of *d*-ester crystallized out first. accordingly, optically pure *d*-1,3-dimethylbutanol could be obtained. However, the *l*-isomer was recovered in a less optically pure state. The specific rotations observed were as follows:

d-1,3-dimethyl butanol $[\alpha]_D^{14}$ +20.41°

l-1,3-dimethyl butanol $[\alpha]_D^{17}$ −7.53°

2) 1,3-Dimethylbutyl methacrylate was prepared by the reaction of the alcohol with methacrylic chloride, according to the method of Arcus et al.[3] *d*-, *l*- and *dl*-1,3-Dimethylbutyl methacrylate (DBMA) were purified by repeated distillation in the stream of nitrogen and in the presence of picric acid (an inhibitor for polymerization). Their boiling points were 75—78°C/20 mmHg and 65°C/15 mmHg.

d-DBMA	$[\alpha]_D^{20}$ +58.1°	n_D^{24} 1.4232[a]
l-DBMA	$[\alpha]_D^{20}$ −21.8°	n_D^{24} 1.4229
dl-DBMA	d_4^{25} 0.8698[b]	n_D^{24} 1.4237

a) n_D^{24} 1.4224 (Arcus, West[3]).
b) d_4^{20} 0.8714 (Crawford[6]).

Hydrogenation of the *d*-Monomer to *d*-1,3-Dimethylbutyl Pivalate. — Three milliliters of the *d*-monomer in *n*-hexane was hydrogenated in the presence of 0.3 g. of the palladium charcoal catalyst with shaking. After the absorption of hydrogen had stopped, the content was filtered and fractionated. The yield was 1.8 g. B. p. 75°C/21.5 mmHg; n_D^{23} 1.4053; $[\alpha]_D^{23}$ ±1 (lit.[3]: b. p. 78°C/22 mmHg, n_D^{23} 1.4070). The structure was identified from its infrared spectrum.

Polymerization.—*Isotactic Polymerization.*—To a solution of 5 ml. of DBMA in 10 ml. of purified toluene, 0.2 ml. of a 4 N *n*-butyl lithium solution in heptane was added at −78°C. After it had stood for 2 hr., the mixtue was poured into mixture of a large amount of methanonl and a small quantity of hydrogen chloride. What was assumed to be isotactic polymer was precipitated out.

Atactic Polymerization.—To 0.005 g. of azobisisobutyronitrile in a hard glass tube, 5 ml. of DBMA was added. The tube was then deaerated, sealed and heated at 60°C for 5.5 hr. while being shaken. The contents were dissolved in benzene and then poured into methanol to isolate the atactic poly-DBMA.

Syndiotactic Polymerization.—A solution of 0.02 g. of azobisisobutyronitrile in 5 ml. of DBMA was placed in a tube. The tube was deaerated, sealed, cooled at −35°C—−50°C, and irradiated for 30—36 hr. The light was obtained from a high-voltage mercury lamp of the Mazda SHL-100 type and filtered through UVD_1-filter. The contents were dissolved in a mixture of benzene and a small quantity of hydroquinone, and then poured into methanol. What was assumed to be syndiotactic poly-DBMA was isolated. These poly-DBMA's were then purified by the reprecipitation method using benzene and methanol.

Fraction of the Polymer of DBMA.—One gram of the polymer was dissolved in 50 ml. of benzene. When, to this solution, methanol was added portion-by-portion, 4—7 fractions were obtained.

Measurement of the Softening Temperature (Ts). — The Ts was measured by the deck-glass method, using an electroheating melting point apparatus and raising the temperature by one degree per minute.

Optical Rotation and Dispersion.—The apparatuses used were a Lippich-type polarimeter, a dispersion polarimeter (the Rudolf 260/655/850/810 type) and a spectrophotometer equipped with a polarimetric attachment (the Shimadzu QR-50 type). The two types of dispersion polarimeters gave the same results.

Results and Discussion

Polymerization of DBMA.—The results obtained are shown in Table I. All the polymers were colorless and soluble in petroleum ether, acetone, benzene, toluene, dioxane, chloroform and dichloroethane, while they were insoluble in methanol and swelled in ethanol. The tacticities of the polymers could be observed from their softening temperatures (Ts) and from their infrared spectra. Ts's of the isotactic, atactic and syndiotactic polymers fell in the ranges of the Ts's of the isotactic, atactic and syndiotactic polymethyl methacrylates which have previously been described by Fox, Stroupe et al.[7]

4) T. Tsuruta and H. Kanai (XII Annual Meeting of the Polymer Society of Japan, Preliminary Issue, [A17], p. 26 (1963)) stated that ethyl-, isopropyl- and *t*-butylesters of methacrylic acid could be polymerized to polymers having the same tacticity as methyl methacrylate, by the methods applied to methyl methacrylate.
5) J. Kenyon and H. E. Strauss, *J. Chem. Soc.*, **1949**, 2153.
6) J. W. C. Crawford, *J. Soc. Chem. Ind.*, **68**, 201 (1949).
7) T. G. Fox, B. S. Garrett, W. E. Goode, S. Gratch, J. F. Kincaid, A. Spell and J. D. Stroupe, *J. Am. Chem. Soc.*, **80**, 1769 (1958); J. D. Stroupe and R. E. Hughes, ibid., 2341.

TABLE I. RESULTS OF POLYMERIZATION OF DBMA AND SOME PROPERTIES OF THE POLYMER

No.*1	Monmer ml.	Initiator mol./l.	Temp. °C	Time hr.	Yield %	$[\eta]$*2 dl./g.	Ts °C	$[\alpha]_D$, in dioxane
RI	*dl*-, 5	*n*-Bu-Li, 0.08	−78	2.5	86.2	(0.79)	—	—
DI	*d*-, 5	0.08	−78	2	81.7	0.31	83—87	+9°
LI	*l*-, 4	0.09	−78	2.5	73.9	0.43	86—95	−15°
RA	*dl*-, 5	AIBN, 0.0055	60	4.5	66.0	(2.32)	—	—
DA	*d*-, 5	0.0080	60	4	87.5	2.81	98—104	+17°
LA	*l*-, 4	0.0061	60	5.5	95.5	2.06*3	90—119*3	−18°*3
RS	*dl*-, 5	AIBN, 0.0291	−35——40	30	73.7	(1.03)	—	—
DS	*d*-, 5	0.0294	−40——50	33	56.6	1.93	118—126	+14.5°
LS	*l*-, 4	0.0282	−35——40	36	71.5	2.08	128—135	−17°

*1 R, D and L mean racemic, dextro and laevo, respectively. I, A and S mean isotactic, atactic and syndiotactic polymer.
*2 At 30°C in $CHCl_3$. $[\eta]$ in parentheses were measured at 30°C in toluene.
*3 Soluble part in dioxane.

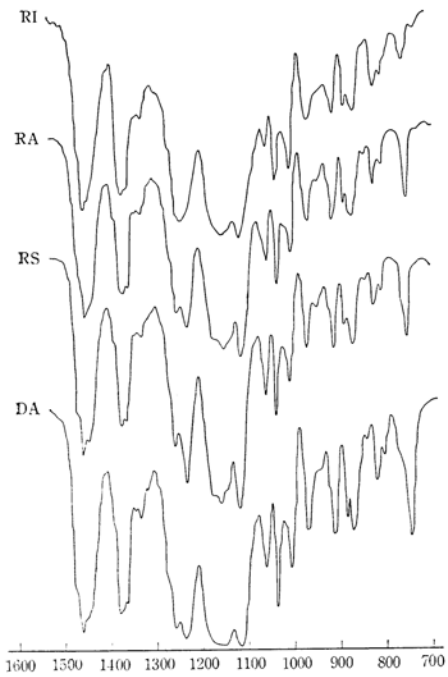


Fig. 1. IR-spectra of poly-DBMA.

RI: racemic-isotactic RA: racemic-atactic
RS: racemic-syndiotactic DA: dextro-atactic

The infrared spectra of the polymers are shown in Fig. 1. From the figure, the relative intensities of the absorption bands for the three kinds of poly-DBMA's (RS, RA and RI) were tabulated as in Table II.

The orders of the intensities in this table coincide with those for polymethylmethacrylates which were described Baumann et al.[8] From

8) U. Baumann, H. Schreiber and K. Tessmar, *Makromol. Chem.*, **36**, 81 (1959).

TABLE II. THE RELATIVE INTENSITIES OF THE INFRARED ABSORPTION BANDS OF POLY-DBMA

cm^{-1}	752	806	825	915	1060	1238
μ	13.38	12.40	12.12	11.00	9.45	8.08
RS	4+	+	2+	4+	4+	3+
RA	4+	+	2+	4+	3+	2+
RI	2+	+	+	2+	1+	0

the order of the Ts's and from the comparison of the intensities of the absorptions with the data obtained by Baumann et al., it was concluded that the polymers obtained in the present work consisted principally of isotactic, atactic and syndiotactic poly-DBMA's) respectively. Furthermore, Fig. 1 shows that the spectra of DA (atactic (+)-polymer) and RA (atactic (±) polymer) were almost exactly the same. This means that the presence of asymmetric carbon in the side chain had no effect on the stereospecific polymerization.

Optical Rotation of Poly-DBMA.—The values of specific rotation ($[\alpha]_D$ (20°C, in chloroform)) given in Table III were measured at the concentrations of 1.0—1.5 g./dl. In other measurement, it was confirmed that $[\alpha]_D$ was constant over such a range of concentrations.

From the data in Table III, the relationships between specific rotations and molecular weights may be illustrated as in Fig. 2. It seems that, in the cases of DI(isotactic (+)-polymer) and DA, the specific rotation increases with the molecular weight, while in the cases of DS (syndiotactic (+)-polymer), LS (syndiotactic (−)-polymer) and LA (atactic (−)-polymer), the specific rotation remains constant during the change in molecular weight. It may be assumed that the difference between isotactic (DI) and syndiotactic polymers (DS) suggests a difference in the molecular conformation.

TABLE III. RESULTS OF FRACTIONATIONS OF POLYMERS AND SPECIFIC ROTATIONS OF EACH FRACTIONATES

No. of fraction	DI			DA			DS		
	Yield %	$[\eta]$	$[\alpha]_D$	Yield %	$[\eta]$	$[\alpha]_D$	Yield %	$[\eta]$	$[\alpha]_D$
1	13	0.59	+23.5	12	4.50	+27.3	5	3.76	+19.6
2	33	0.37	+14.3	16	3.11	+15.1	25	2.87	+16.8
3	13	0.33	+14.0	26	2.26	+15.8	28	0.78	+17.2
4	35	0.15	+13.4	20	1.63	+12.6	23	0.75	+16.3
5	3	—	—	9	1.53	+10.9			
6				7	1.51	+19.2			
7				5	—	—			
Total	97			95			81		

No. of fraction	LI			LA			LS		
	Yield %	$[\eta]$	$[\alpha]_D$	Yield %	$[\eta]$	$[\alpha]_D$	Yield %	$[\eta]$	$[\alpha]_D$
1	—	0.62	−17.8 −16.9	2	—	—	25	3.30	−8.0
2	—	0.55	−8.8	37	5.35	−6.0 −4.4	25	2.21	−9.0
3	—	0.51	−8.3	20	3.46	−5.9			
4	—	0.17	−8.5	9	2.32	−5.9	20	0.98	−8.0
5				25	2.03	−7.8 −8.6	26	0.27	−4.7
6									
7				5	1.53	−8.4			
Total	—			88			96		

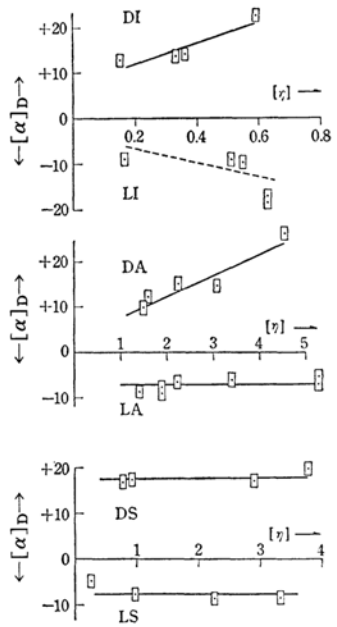


Fig. 2. Relation between specific rotation of poly-DBMA and their molecular weights.

DI: dextro-isotactic LI: laevo-isotactic
LA: laevo-isotactic DS: dextro-syndiotactic

Optical Rotatory Dispersion of the Polymer.—The optical rotatory dispersions of the polymers are illustrated in Fig. 3. The dispersion curves of the polymers from the *d*-monomer could not be compared with those of the polymers from the *l*-monomer because of the optical impurity of the *l*-monomer. If $[\alpha]$ comes only from asymmetric carbon, the relation between $[\alpha]$ and the wavelength, λ, may be given by the simple Drude equation (1):

$$[\alpha]=\frac{k\lambda_c^2}{\lambda^2-\lambda_c^2} \qquad (1)$$

where λ_c is the dispersion constant and k is the rotatory constant. The results are illustrated in Figs. 4 and 5. As the figures shows, the results of poly-DBMA did not fit the equation, while the *d*-monomer and its hydrogenated compound obeyed the equation.

Recently, Klabunovskii et al.[9] obtained poly-(+)-2-methylbutyl methacrylate and investigated its structure spectro-polarimetrically. Their polymerization was carried out with radical and ionic catalysts (benzoyl peroxide and phenyl magnesium bromide). The optical dispersion curves in the 302—589 mμ range

9) E. I. Klabunovskii, M. I. Shwarzman and Y. I. Petrov, *Vysokomolec. Soed.*, **6**, 1579 (1964).

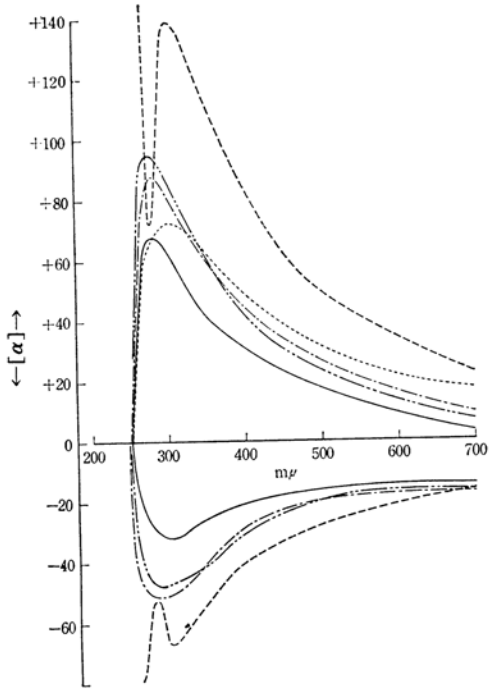


Fig. 3. Optical rotatory dispersion of DBMA, 1,3-dimethylbutyl pivalate and poly-DBMA.

------ Monomer (DBMA)
..... Pivalate
—·—· Isotactic polymer
—··— Atactic polymer
——— Syndiotactic polymer

were determined and could be described by Drude's single term equation. The value of λ_c for the monomer was close to that of both polymers (173 m$\mu\pm$14).

As is known from the studies of polypeptides, if the optical activity comes from assymmetric carbon and the molecular helical structure, $[\alpha]$ may obey Moffitt's equation (2):

$$\frac{3}{n^2+2}\cdot\frac{M}{100}[\alpha]=\frac{a\lambda_0^2}{\lambda^2-\lambda_0^2}+\frac{b\lambda^4}{(\lambda^2-\lambda_0^2)^2} \quad (2)$$

where n is the refractive index of the solvent; M is the molecular weight of the structural unit of the polymer; a is a term for the helix and the residue, and b is a constant for the helical structure. As Fig. 6 shows, if a value of 212 was adopted for λ_0, a straight line was obtained in the case of the atactic *d*-polymer (DA). (In the case of polypeptides, a value of 212 is also suitable.) From the inclination of the straight line, it was deduced that b was -64.3. This value of b would correspond to about 10% of the right-hand helical structure if we were dealing with polypeptide. However, the polymer which we have dealt with is not a polypeptide. Therefore, no definite

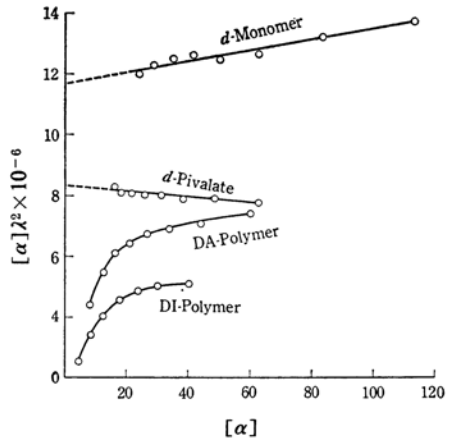


Fig. 4. Adaptability of the Drude equation for *d*-monomer and *d*-polymers.

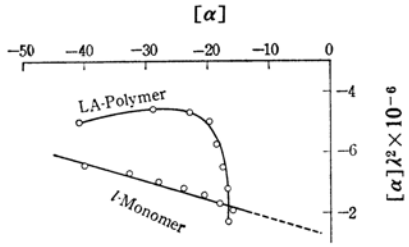


Fig. 5. Adaptability of the Drude equation for *l*-monomer and *l*-polymer.

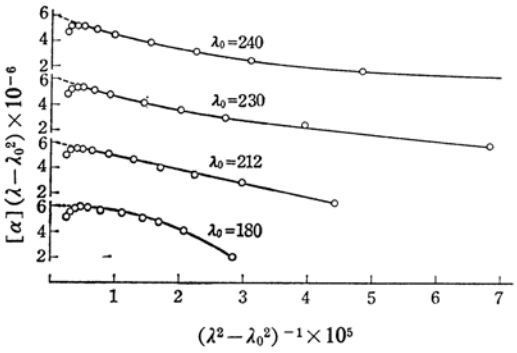


Fig. 6. Adaptability of the Moffit equation for DA.

conclusion as to its molecular asymmetry can be made. In the cases of isotactic and syndiotactic *d*-polymers (DI and SI), a straight line could not be obtained by using a value of 212 for λ_0. However, it could be concluded qualitatively that the b constant for DI was negative, and for those for LA, LI and LS, positive.

Summary

The polymerization of (+)-1,3-dimethylbutyl methacrylate and its optically impure

(−)-isomer have been carried out through different three initiations:

(1) *n*-BuLi in toluene at −78°C gave isotactic polymers (DI and LI). (2) Azobisisobutyronitrile at 60°C gave atactic polymers (DA and LA). (3) Photopolymerization in the presence of azobisisobutyronitrile at −35—−50°C gave syndiotactic polymers (DS and LS). The tacticities of the resulting polymers have been deduced from their softening temperatures and their infrared spectra. Optically active polymers have been fractionated from a benzene solution by adding methanol. In the cases of DI and DA, the specific rotation $[\alpha]_D$ increased with the molecular weight, while in the cases of DS, LS and LA, $[\alpha]_D$ remained constant during the change in molecular weight. The optical rotatory dispersion of the polymers has been measured. Drude's equation does not hold. In the case of DA, however, a straight line was obtained by Moffitt's equation, giving −64.3 as the *b*-values.

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