*Stereoregular Polymers. IX. Polymerization of Optically Active α-Olefins**

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In their previous work[1], the authors polymerized styrene with anionic catalysts containing the optically active alkyl group such as optically active amylsodium or triamylaluminum combined with titanium trichloride. The purpose was to obtain optically active polystyrene, in which one helical configuration (either right- or left-handed screw helix) presumably induced by the active group might be predominantly present. However, the attempt was not successful.

X-Ray analyses of various isotactic polymers have shown that the crystalline structure of the polymer, and accordingly the crystallinity and the melting temperature are largely dependent on the side group of the chain[2]. In other words, the type of helix, i. e. the number of monomeric units or of turns in the identity period, may be decided definitely by the shape and size of the substituent group of the chain.

The present work was carried out as one of the programs of attempting to regulate the direction of helical configuration of polymer chain in its screw sense. Two optically active α-olefins, *l*-4-methyl-1-hexene and *d*-3-methyl-1-pentene, were polymerized by the Ziegler catalyst and the nature of the polymer was examined in anticipation that the asymmetric substituent might induce the helical configuration, which exists with only one (right- or left-handed) screw sense, in the polymer chain.

Experimental

Preparation of Monomers.—*l-2-Methyl-1-butanol.*—Commercial fusel oil was fractionally distilled by Stedman type column (about seventy theoretical plates) repeatedly. *l*-2-Methyl-1-butanol thus obtained showed b. p. 128°C and α_D^{28} $-9.36°$ ($l=20$ cm.) (optical purity 98.7%)[3].

d-1-Chloro-2-methylbutane.—The alcohol was converted to the chloride by thionyl chloride. Yield 78.7%, b. p. 99°C, $[\alpha]_D^{30}$ $+1.63°$ (optical purity 97%)[4].

Optically Active 1-Bromo-2-ethoxy-4-methylhexane.— 2-Methylbutylmagnesium chloride derived from optically active *d*-1-chloro-2-mehthylbutane was made to react with α, β-dibromo ethyl ether[5] to give 1-bromo-2-ethoxy-4-methylhexane[6]. Yield 60.3%, b. p. 91∼93°C/15 mmHg.

l-4-Methyl-1-hexene[7].—The ethoxyheptyl bromide gave *l*-4-methylhexene in 61% yield by refluxing an alcoholic solution with zine powder for 10 hr.

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* This paper is based upon a portion of a thesis submitted by S. Takeuchi in partial fulfillment of the requirements for the Degree of Master of Science in Osaka University, March, 1960.

[1] S. Murahashi, S. Nozakura and S. Takeuchi, This Bulletin, 33, 658 (1960).

[2] G. Natta, *Angew. Chem.*, 68, 393 (1956).

[3] R. M. Ideda, R. E. Kepner and A. D. Webb, *Anal. Chem.*, 28, 1335 (1956).

[4] A. Mackenzie and G. W. Clough, *J. Chem. Soc.*, 103, 698 (1913).

[5] L. S. Swallen and C. E. Boord, *J. Am. Chem. Soc.*, 52, 651 (1930); H. B. Dykstra, J. F. Lewis and C. E. Boord, ibid., 52, 3396 (1930).

[6] D. C. Rowland, K. W. Greenlee, J. M. Derfer and C. E. Boord, *J. Org. Chem.*, 17, 807 (1952).

[7] F. J. Soday and C. E. Boord, *J. Am. Chem. Soc.*, 55, 3293 (1933).

TABLE I

	Polymerization[a]				Polymer			
	Monomer g.	$AlEt_3$ g.	$TiCl_4$ g.	Yield %	M. p. °C	$[\alpha]_D$(in toluene)	$[\eta]$[b]	d_4^{13}
l-4-Methyl-1-hexene	3.6	0.56	0.38	19	180～182	+251°(27.5°)	0.86	0.862[c]
〃	5.7	0.75	0.50	7	171～174	+249 (21)	0.79	0.86
5-Methyl-1-hexene	3.1	0.38	0.25	25	112～114	+ 54 (22)	—	—[d]
〃	2.1	0.38	0.25	58	102～104	+ 52 (22)	—	—
〃	1.6	0.38	0.25	46	96	+ 54 (22)	—	—
d-3-Methyl-1-pentene	4.4	0.75	0.50	20	260～264	+255 (24)[g]	—	0.831[e]
dl-3-Methyl-1-pentene	1.3	0.38	0.25	8	200～205	— —	—	0.832[f]

a, Solvent: 20 ml. *n*-heptane. b, Toluene solution at 29.9°. c, Found: C, 84.94; H, 14.29. d, Found: C, 85.26; H, 14.10; Ash, 0.26. e, Found: C, 84.60; H, 14.09; Ash, 0.89. f, Unfractionated. Found: C, 85.38; H, 14.12; Ash, trace. All the samples contained traces of ash. Calcd. for $[C_nH_{2n}]_p$: C, 85.63; H, 14.37%. g, in petrolatum liquid.

B. p. 87～88°C, $[\alpha]_D^{31}$ $-2.50°$ (optical purity 94%)[8] n_D^{31} 1.3970, d_4^{31} 0.692.

5-Methyl-1-hexene.— It was synthesized similarly from commercial isoamyl alcohol via isoamyl chloride in 16% yield based on the chloride. B. p. 83～85°C. The isoamyl chloride showed an optical activity ($[\alpha]_D^{22}$ +0.33°), which corresponded to that calculated for a mixture of 81% pure isoamyl chloride and 19% *d*-1-chloro-2-methylbutane[9].

d-3-Methyl-1-pentanol.—Optically active 3-methyl-1-pentanol was synthesized from formaldehyde and 2-methylbutylmagnesium chloride derived from *d*-1-chloro-2-methylbutane (b. p. 99～100°C, $[\alpha]_D^{10}$ +1.71°, optical purity ca. 100%), which was obtained from optically pure *l*-2-methyl-1-butanol, b. p. 127.5～128.5°C, $[\alpha]_D^{11}$ $-9.55°$ (l=20 cm.). Gaseous formaldehyde was bubbled through the ethereal solution of the Grignard reagent with dry nitrogen. The subsequent decomposition and steam-distillation of the product gave *d*-3-methyl-1-pentanol in 38.3% yield, b. p. 147～149°, $[\alpha]_D^{10}$ +8.41° (literature[8]: $[\alpha]_D^{19.5}$ +8.53°).

d-3-Methylpentyl Acetate.— The acetate was obtained from the alcohol by using *p*-toluenesulfonic acid as a condensing catalyst, yield 69%, b.p. 156～158°C, $[\alpha]_D^{8}$ +8.53° (literature[8]: $[\alpha]_D^{19}$ +8.30°).

d-3-Methyl-1-pentene. — The methylpentyl acetate was dropped with a stream of nitrogen through a quartz tube packed with glass pieces at 500°C. The pyrolysis gave *d*-3-methyl-1-pentene in 36% yield. b. p. 54～55°C, $[\alpha]_D^{12}$ +32.95° (literature[8]: $[\alpha]_D^{17}$ +32.86°).

dl-3-Methyl-1-pentanol.—Ethylene oxide was bubbled through an ethereal solution of *sec*-butylmagnesium chloride using nitrogen as a carrier gas. The product was decomposed by saturated aqueous ammonium chloride and steam-distilled to give *dl*-3-methyl-1-pentanol. Yield 52%, b. p. 148～150°C.

dl-3-Methyl-1-pentene. — The racemic 3-methyl-1-pentene was obtained from the racemic methylpentanol via its acetate similarly as described on the optically active methylpentene. Yield 35% based on the alcohol, b. p. 54～56°C.

Polymerization. — The heptene monomers, *l*-4-methyl-1-hexene and 5-methyl-1-hexene, were polymerized in a five-necked flask described previously[10]. The vessel was flushed with dry nitrogen, and charged with *n*-heptane, titanium tetrachloride and aluminum triethyl (*n*-heptane solution), and the monomer was injected by a hypodermic syringe through a rubber cap fitted on the vessel. The mixture was heated for 10 hr. at 70°C. All procedures were done in a stream of dry nitrogen. The reaction mixture was then poured into a large volume of methanol containing a small amount of hydrochloric acid to decompose the catalyst. After being allowed to stand overnight the precipitated polymer was collected by centrifugation, washed with methanol, and dried.

The hexene monomers, *d*- and *dl*-3-methyl-1-pentene, were polymerized by analogous procedures but using a sealed tube as the reaction vessel and at 50°C for longer periods, 40 hr. for racemic and 144 hr. for *d*-monomer.

The results of polymerization were summarized in Table I.

The polyheptenes were soluble in chloroform, carbon tetrachloride, toluene, benzene, decalin, carbon disulfide, and hot *n*-heptane, and insoluble in ether, alcohol and acetone.

Poly-*d*-3-methyl-1-pentene was almost insoluble in usual organic solvents. This was slightly soluble above its melting point in petrolatum liquid, dibutyl phthalate and dioctyl phthalate. The solution in petrolatum liquid was maintained clear and stable even after it had cooled to room temperature, but the polymer precipitated from the phthalate solutions below about 290°C and no appreciable amount of polymer appeared from the liquid phases by adding methanol.

On the other hand, the polymeric product of *dl*-3-methyl-1-pentene was found to be largely contaminated with polyethylene produced from the Ziegler catalyst itself and was fractionated successively by boiling toluene and by boiling decalin. The toluene-soluble fraction (68%) containing a considerable amount of polyethylene melted between 130 and 190°C. The decalin-soluble fraction (17%) and the remaining insoluble fraction (15%) melted at 225～226°C and 245～247°C, respectively. The solubility of decalin-insoluble fraction seemed

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[8] P. Pino and L. Lardicci, *Chem. & Ind.*, **1959**, 483.

[9] F. C. Witmore and J. H. Olewine, *J. Am. Chem. Soc.*, **60**, 2570 (1938).

[10] S. Murahashi, S. Nozakura, M. Sumi and K. Hatada, This Bulletin, **32**, 1094 (1959).

to be slightly greater than that of poly-*d*-3-methyl-1-pentene but was about the same.

Optical Rotation.— For the determinations of optical rotatory dispersion and optical purity a Rudolph high-precision photoelectric spectropolarimeter model 200S-80 was used.

The observed optical rotation of a solution of poly-*d*-3-methyl-1-pentene in petrolatum liquid was α^{24}_{D} +4.68° (l=20 cm.) at c=0.0745. The petrolatum liquid, however, had an optical rotation α^{24}_{D} +2.15° (l=10 cm.), and the specific rotation of the polymer, $[\alpha]^{24}_{\text{D}}$ +255°, was calculated from the difference of rotations of the solution and the solvent.

Density.—Determination of polymer density was carried out by a density gradient tube using methanol and water as media.

Melting Point.—The polymer sample was placed on a metal block under the microscope. The metal block was heated by a hot plate and the melting point of the sample was measured.

Results

The dependence of the optical rotation on the concentration of poly-*l*-4-methyl-1-hexene was examined in four solvents, toluene, decalin, carbon tetrachloride and carbon disulfide. The results are shown in Fig. 1. The linear ralationships between the rotation and the polymer concentration were obtained in each solvent. These led to the values of specific rotation $[\alpha]^{27.5}_{\text{D}}$ +251° (toluene), $[\alpha]^{24}_{\text{D}}$ +268° (decalin), $[\alpha]^{25}_{\text{D}}$ +236° (carbon tetrachloride) and $[\alpha]^{13}_{\text{D}}$ +290° (carbon disufide).

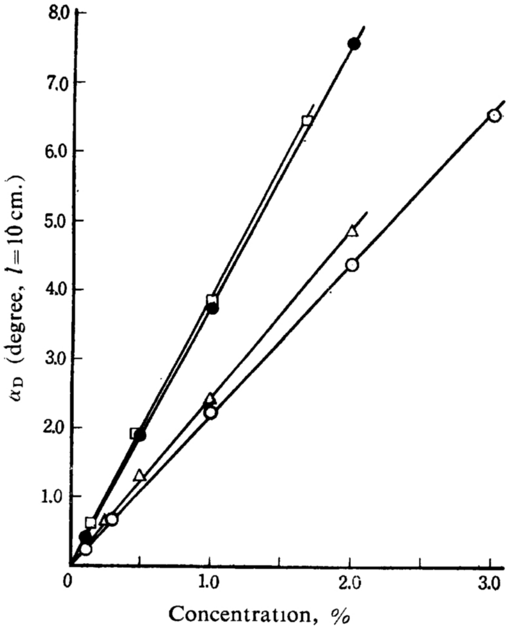

Fig. 1. Optical rotation vs. concentration of poly-*l*-4-methyl-1-hexene in various solvents: ○ in toluene at 27.5°C; △ in decalin at 24°C; □ in carbon tetrachloride at 25°C; ● in carbon disulfide at 13°C.

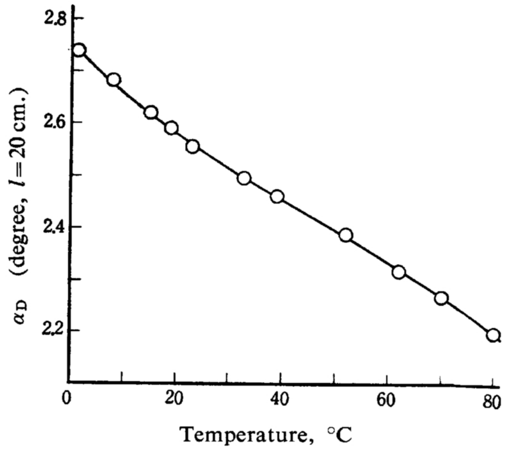

Fig. 2. Temperature dependence of optical rotation of 0.5% poly-*l*-4-methyl-1-hexene solution in decalin.

The plots of the optical rotation of 0.5% poly-*l*-4-methyl-1-hexene solution in decalin vs. temperature are shown in Fig. 2. The rotation decreased almost linearly with the elevation of temperature from 2 to 80°C.

To the toluene solution of the polymer (concentration 1.05%) *n*-heptane, a poor solvent for the polymer, was added successively and the change of optical rotation of the solution was followed. Similarly *n*-butanol, a precipitant against the polymer, was added in another series of this experiment. The results showed that the rotation was rather strictly linear to the concentration of the polymer alone (Fig. 3). In these experiments the ageing of the

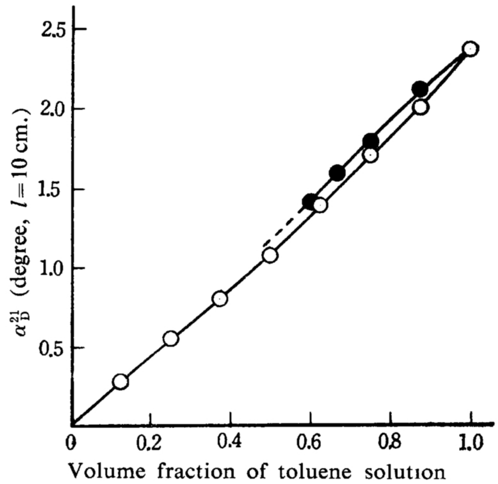

Fig. 3. Changes in optical rotation with the addition of *n*-heptane (○) and *n*-butanol (●) to 1.05% solution of poly-*l*-4-methyl-1-hexene in toluene. Dotted line, precipitation occurred.

solution caused no change in the optical rotation after adding the poor or the bad solvent.

The optical rotatory dispersion was measured with the polymer in two solvents, decalin ($c=0.4\%$, $l=10$ cm.) and toluene-*n*-heptane mixture (1 : 1 vol./vol., $c=0.6\%$, $l=10$ cm.). The results are shown in Figs. 4 and 5. The plots $\alpha_\lambda\lambda^2$ vs. α_λ, where α_λ is the optical rotation at a wavelength λ, were linear as shown in Fig. 5, and no abnormal dispersion was observed.

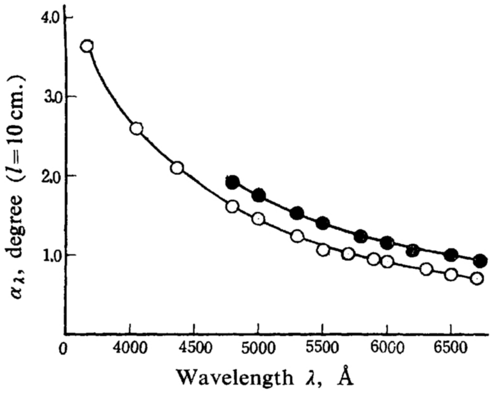

Fig. 4. Optical rotatory dispersion of poly-*l*-4-methyl-1-hexene : ○ in decalin ($c=0.4$) at 21°C ; ● in toluene-*n*-heptane mixture (1 : 1 vol./vol., $c=0.6$) at 19°C.

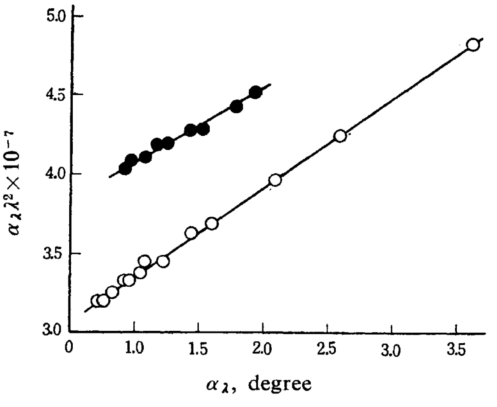

Fig. 5. $\alpha_\lambda\lambda^2$ vs. α_λ in the optical rotatory dispersion of poly-*l*-4-methyl-1-hexene : ○ in decalin ; ● in toluene-*n*-heptane mixture.

All the polymers obtained here gave sharp crystalline X-ray patterns except the toluene-soluble fraction of poly-*dl*-3-methyl-1-pentene. The patterns given by poly-*d*-3-methyl-1-pentene and the decalin-insoluble fraction of poly-*dl*-3-methyl-1-pentene were completely different. The spacings obtained from the powder X-ray diagrams are summarized in Table II.

TABLE II. SPACINGS FOR POLY-*d*-3-METHYL-1-PENTENE AND POLY-*dl*-3-METHYL-1-PENTENE

Poly-*d*-3-methyl -1-pentene	Poly-*dl*-3-methyl-1-pentene[a]
9.60 Å (vs)	9.26 (s)
6.92 (vw)	8.65 (s)
6.18 (m)	5.38 (s)
5.55 (vw)	4.74 (mw)
5.09 (vw)	4.20 (m)
4.66 (s)	3.91 (m)
4.23 (vw)	
4.05 (w)	
3.26 (w)	
3.07 (vw)	
2.75 (vw broad)	
2.53 (vw)	
2.39 (vw)	

a Decalin-insoluble fraction.

Discussion

Both of the optically active polymers, poly-*l*-4-methyl-1-hexene and poly-*d*-3-methyl-1-pentene, showed enormously large optical rotations compared with those of the monomers. The large optical rotations seemed to be contributed not only by the neighboring groups around the asymmetric carbon atom of the side group but also by the molecular asymmetry of the helical configuration of the main chain, more practically by a predominant concentration of either right- or left-handed helix in the solution.

It is doubtful that the isotactic polymer such as poly-α-olefin still maintains its helical structure in the solution. However, Takeda and his collaborators[11) recently stated from their infrared absorption study that in carbon disulfide isotactic polystyrene retained its helical structure[12) even in the solution state. This encouraged us to investigate the optical rotation of poly-*l*-4-methyl-1-hexene in solution by varying the conditions in order to learn its exact nature.

The concentration of the helix might vary with the concentration of the polymer, if it remained in the solution in any extent. The temperature might also affect the concentration of the helix. The concentration of the helix would be considered to be related to the interaction between the molecules of polymer and solvent. A good solvent may release the helical configuration of the polymer to transform it into a randomly coiled structure and, on the other hand, poor solvent might probably coil up the chain to a helix as shown by

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11) M. Takeda, K. Iimura, A. Yamada and Y. Imamura, ibid., 32, 1150 (1959).

12) H. Tadokoro et al., ibid., 32, 313, 534 (1959); *J. Polymer Sci.*, 36, 553 (1959).

Doty and his coworkers[13] for poly(γ-benzyl L-glutamate).

However, the concentration, the temperature and the addition of bad solvent gave no distinct change in the specific rotation of the polymer in solution, compared with the large change observed in the helix-coil transformation of poly (γ-benzyl L-glutamate). In addition, the plots of optical rotatory dispersion fitted the equation $\alpha_\lambda\lambda^2=\lambda_c^2\alpha_\lambda+A'$[13] derived from the simple one-term Drude equation $[\alpha_\lambda]=A/(\lambda^2-\lambda_c^2)$, where λ_c, A and A' are the constants, respectively, and no complex dispersion was found. These facts strongly suggest that the optical rotation of this polymer is attributed to only one species, the asymmetric carbon atom of the substituent group, at least in solution.

The polymer formed from the 5-methyl-1-hexene monomer had a specific rotation $[\alpha]^{22}_{D}$ $+54°$ in toluene. Obviously this was caused by *l*-4-methyl-1-hexene units in the polymer which had been contained in the monomer used. Reding[14] has reported that the polymer produced from a mixture of 4-methyl-1-pentene and 3-methyl-1-butene was a copolymer but not a mixture of the homopolymers of each monomer. Therefore, it may be preferable to consider the polymer obtained here as being also the copolymer of 5-methyl-1-hexene and *l*-4-methyl-1-hexene. It must be noted that the specific rotation of this polymer was about 20% of that of poly-*l*-4-methyl-1-hexene and the percentage was coincident with the content of *d*-1-chloro-2-methylbutane in amyl chloride mixture used as the starting material of the monomer, although many steps had been taken in the way from the chloride to the polymer.

The optical rotatory behavior of poly-*l*-4-methyl-1-hexene gave no positive evidence either for the existence of helical configuration in solution or, if any, for a predominant existence of right- or left-handed helices. This might be caused by the absence of strong intramolecular attraction such as hydrogen bond to coil up the chain to a helix in solution. Even if the helix was maintained in solution, the one carbon atom inserted between the main chain and the asymmetric carbon atom would weaken the steric influence of the neighboring groups around the asymmetric carbon atom. This might result in no regulation of the direction of helical configuration in a single screw sense.

The density of poly-*l*-4-methyl-1-hexene was coincident with the value reported for poly-*dl*-4-methyl-1-hexene by Natta[2]. The melting point was also approximately the same as those observed by Natta (188°C)[2] and Campbell (157~160°C)[15] with the polymer formed from the racemic monomer. These facts seem to suggest that there is almost no difference in the crystalline structure of either the optically active or the racemic polymer even in the solid state.

On the contrary, the melting point of poly-*d*-3-methyl-1-pentene is distinctly higher than that of the decalin-insoluble fraction of poly-*dl*-3-methyl-1-pentene, which seemed to have almost the same crystallinity and stereoregularity as those of the former polymer from its solubility behavior. Furthermore, the X-ray diffraction patterns of these two polymers are so different that the polymers appeared to be constituted with completely different monomeric units from each other.

The low conversion and also the very low stereospecificity in the polymerization of *dl*-3-methyl-1-pentene suggest the difficulty of isotactic propagation of this monomer. This may be caused by the copolymerization of the *d*- and *l*-monomers, in which the asymmetric tertiary carbon atoms are adjacent to the vinyl groups.

In the polymerization of racemic monomer three types are probable in the formation of its polymer: a mixture of homopolymers of *d*- and *l*-monomer each, a random copolymer and a block-copolymer of these. Furthermore, each type of these is able to form isotactic, atactic and stereo-block polymers in regard to the main chain of the polymer.

For the polymer of *dl*-3-methyl-1-pentene the authors obtained three fractions according to the solubility difference. The problem as to which of the above mentioned types correspond to the respective fractions is very interesting, although this is not certain at the present stage of this work.

In poly-3-methyl-1-pentene the asymmetric carbon atom of side chain is adjacent and so close to the main chain of the polymer that it may affect the configuration of the chain, contrary to the case of poly-4-methyl-1-hexene. Therefore, the predominant or exclusive formation of either the right- or left-handed helix may be expected in much more probability for poly-*d*-3-methyl-1-pentene than for poly-*l*-4-methyl-1-hexene. Unfortunately, the detailed investigation on the optical rotation of poly-*d*-3-methyl-1-pentene could not be done due to the extremely low solubility of the polymer, although the polymer showed a

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[13] P. Doty and J. T. Yang, *J. Am. Chem. Soc.*, **78**, 498 (1956); **79**, 761 (1957).

[14] F. P. Reding, *J. Polymer Sci.*, **37**, 555 (1959).

[15] T. W. Campbell and A. C. Haven, Jr., *J. Appl. Polymer Sci.*, **1**, 73 (1959).

very large specific rotation, $[\alpha]_D^{24}$ +255°, in petrolatum liquid.

After the completion of this work, papers by Pino and Lorenzi$^{16)}$, and Bailey and Yates$^{17)}$ appeared, which described the same subject independently. Bailey and Yates reported that the specific rotation of poly-*d*-3-methyl-1-pentene $[\alpha]_D^{25}$ was $-257°$ in 1, 1-ditolylethane. The present sample of the same polymer showed distinctly dextro rotation also in 1, 1-ditolylethane, but the exact value could not be obtained, because the concentration of the solution was too small to be measured, due to the extremely low solubility of the polymer in 1, 1-ditolylethane at room temperature. Pino and Lorenzi reported that the various soluble fractions of poly-*d*-3-methyl-1-pentene, which seemed to be atactic or stereoblock, had dextro rotations.

Pino and Lorenzi concluded in their paper that in dilute solution and in the molten state the isotactic and stereo-block polymers of optically active α-olefins may be at least in part spiralized and that helices of a single screw sense may largely prevail, because of the remarkable dependence of the optical rotation on stereoregularity and temperature. However, the temperature coefficient of optical rotation must also be dependent on the magnitude of specific rotation itself and in this respect the temperature coefficients of the optical rotation of optically active poly-α-olefins may be considered to be not so large. Other considerations seem to be necessary to explain the large optical rotations of these isotactic polymers formed from optically active α-olefins.

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16) P. Pino and G. P. Lorenzi, *J. Am. Chem. Soc.*, **82**, 4745 (1960).

17) W. J. Bailey and E. T. Yates, *J. Org. Chem.*, **25**, 1800 (1960).