Polymer Bulletin 3, 211–217 (1980)

Polymer Bulletin

Optically Active Polychloral[a, b]

L. S. Corley and O. Vogl

Polymer Science and Engineering Department, University of Massachusetts,
Amherst, Massachusetts 01003, USA

INTRODUCTION

Optical activity, defined as the rotation of the plane of plane-polarized light passing through a material, is a property found in molecules and supramolecular structures which lack a plane of symmetry (ORCHIN, JAFFE 1971). The type of optical activity of most frequent concern to chemists derives from a carbon atom or other atom, such as nitrogen, phosphorous or silicon, with four (or in some cases three) different substituents. Optical activity of compounds containing asymmetric carbon atoms is generally measured in solution and expressed as degrees of rotation per unit concentration per unit length. However, many types of crystals also exhibit optical activity in the solid state. These crystals are of two major types. The first type includes crystals of small molecules which are themselves molecularly dissymmetric and show optical activity in solution, such as camphor and sucrose. The second and more interesting type is composed of crystals, not containing optically active small molecules or ions, whose optical activity is produced only by the dissymmetry of the crystal structure itself and which disappears upon destruction of the crystal structure. These crystals include those of ionic sodium chlorate, bromate and quartz, which is polymeric, as well as a number of other mostly inorganic substances (LOWRY 1935).

The silicon and oxygen atoms of alpha-quartz are arranged in helices with the d- and l-form containing helices of opposite chirality. This dense packing of dissymmetric helices in the solid state results in very high optical activity along the optical axes of single crystals of d- and l-alpha-quartz, with the optical rotation ranging from about 20°/mm. to nearly 400°/mm. depending on the wavelength. Optical activity is found in quartz, because left- and right-handed helices are dissymmetric, whereas carbon atoms with four different substituents, the usual causes of optical activity in organic compounds, are asymmetric. Both are chiral, possessing left- or righthandedness.

(a) Haloaldehyde Polymers ,XXI, Part XX: P. Kubisa and O. Vogl, Polymer (London), 21, 525 (1980).

(b) This paper is dedicated to Professor Piero Pino on the occasion of his 60th. birthday, with best wishes.

(c) Present address: Shell Development Co., Houston, Texas.

0170-0839/80/0003/0211/$01.40

Many investigators observed the phenomenon of optical activity associated with asymmetric carbon (or other) atoms in small molecules. The first recorded work to incorporate optical activity into synthetic polymers through an asymmetric carbon atom is that of Walden (WALDEN 1896), who polymerized the bis (-)-2-methylbutyl) ester of methylenesuccinic acid to form a polymer no different in optical rotation from the starting monomer.

Many subsequent attempts to synthesize optically active polymers, however, failed because of uncertainty as to the true definition of an asymmetric carbon atom, particularly in polymers, and as to what structures were capable of producing optical activity. Several attempts were made to produce optically active ordinary vinyl polymers through polymerization of optically active monomers and subsequent removal of the asymmetric side chains (MARVEL, OVERBERGER 1946) (OVERBERGER, PALMER 1967) or by initiation of a monomer such as styrene with an optically active initiator (MARVEL et al. 1943). However, after the optically active side chains or initiator residues were removed, the remaining polymer was not optically active.

The absence of optical activity in these polymers was explained (FRISCH et al. 1953) by showing that asymmetric carbon atoms could not be generated from ordinary vinyl monomers CH_2 CXY in high polymers. The CXY carbon atoms in the polymer in the center of a heterotactic triad, between two CH_2 CXY differing in configuration only, were shown to be not asymmetric but pseudoasymmetric and incapable of contributing to the optical activity. The central carbon atoms in a tactic triad could be regarded as asymmetric only insofar as the two substituents forming the polymer chain were of different lengths, which could contribute to optical activity only in the lowest molecular weight oligomers.

Isotactic polymers were prepared from a number of chiral α-olefins (PINO et al. 1960), such as (+)-(S)-3-methyl-1-pentene, 4-methyl-1-hexene, and 5-methyl-1-heptene, optically active poly (vinyl ethers) (SCHMITT, SCHUERCH 1960), and optically active aldehydes (GOODMAN, ABE 1962). In most cases, optical rotation per monomer unit for the polymer was found to be considerably higher than molar optical rotation for low molecular weight saturated model compounds. The amount of excess rotation for the polymer was found to vary with distance of the asymmetric carbon atom from the chain backbone, reaching a maximum for poly(4-methyl-1-hexene) and becoming quite low as the asymmetric atom was moved several carbons from the chain. The observed excess optical rotation in such polymers was found to increase with decreasing solubility and presumably increasing isotacticity of the polymer (PINO et al. 1960) (PINO, LORENZI 1960) (PINO et al. 1961) (PINO et al. 1963) (PINO et al. 1968). The ratio of molar rotation of polymer to model compound similarly decreased at greater distances of the asymmetric carbon atom from the main chain, and this ratio increased with increased isotacticity of the polymer chain for polymers with asymmetric carbon atoms.

As a result of many of the above observations, Pino and coworkers have proposed that these polymers exist in solution primarily in the helical conformation of one screw sense, with the helicity strongly contributing to the optical rotation (PINO et al. 1968). They (GOODMAN et al. 1967) (ABE 1968) (PINO, NEUENSCHWANDER 1975) considered helicity of the polymer chain in solution as an important contributing factor in causing the excess optical rotations observed for these polymers. However, in contrast to the long and rigid helices observed for polypeptides, the helical regions in these polyolefins and similar polymers were considered as being short-range and constantly coiling and uncoiling, although the total helical content of a polymer solution would remain constant over time at constant conditions. Furthermore, it was thought that the excess optical rotation noted in the polymers was not due primarily to optical rotation by the chiral helices themselves, rather it was felt that the steric effect of the adjacent helix forced the substituents around the asymmetric carbon atoms to assume preferred conformations which in turn increased the observed optical rotation. Indeed, the specific rotation of certain highly crystalline polyolefins was found (BONSIGNORI, LORENZI 1970) (BASSI et al. 1971) to be quite different in solution from that in the crysstalline state, in which crystalline helical forms exist exclusively.

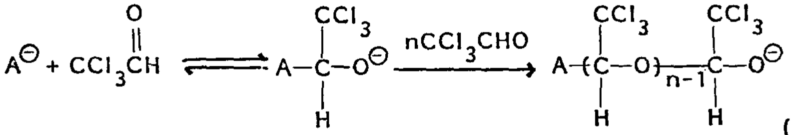
Isotactic polymers, due to energy considerations, crystallize in helical forms (NATTA 1956). However, if these polymers are prepared with optically inactive or racemic initiators, equal amounts of left- and righthanded helices will be formed. The overall effect of this in the crystal structure is crystallization of a 50:50 mixture of the two types of helices in all isotactic polymers (except for certain polymers (BASSI et al. 1971) which contain asymmetric carbon atoms in the side chains); normal isotactic polymers have crystal structures containing equal numbers of left- and righthanded helices in the unit cell. Hence, the crystals do not show optical activity based on helical dissymmetry. Furthermore, even if a helical polymer without asymmetric carbon atoms were initiated asymmetrically to give an excess of one form of helix, the specific rotation in solution could not then be measured, since the optical activity would be destroyed upon dissolution as the dissymmetric helices rearranged to random coils. Hence, for isotactic polymers in solution, optical activity can be demonstrated only when the equilibrium of lefthanded helix: random coil: righthanded helix is shifted by some characteristic of the molecule such that one sense of helix predominates over the other. The standard means of accomplishing this in the past has been by introducing asymmetric groups into the side chains of polymers such that one helical arrangement became more stable than the other because of better packing of the side chains. However, if a polymer could be synthesized having the following criteria, the existence of optical activity due purely to helicity in the polymer would appear possible.

(1) The polymer must have a rigid helical structure. It must be totally isotactic with no helix reversals, or else there must be a significant length of helix between the initiation site and the first reversal, so that the amounts of right- and lefthanded helix formed will not be identical and optical rotation will be caused by the presence of one form of helix predominantly or exclusively, as is the case in quartz.

(2) The optical activity of the polymer must be measured in the solid (crystalline or amorphous) state. If measurement in solution is attempted, the optical activity would be destroyed by uncoiling of the helices and reequilibration to equal proportions of the two helical forms. For the same reason, the solid polymer cannot be contacted with a solvent in which it is soluble before optical activity is measured.

The polymer which would seem best to fit these criteria are polymers containing side groups which are very bulky adjacent to the polymer chain, which could be obtained in the completely isotactic form.

A polymer family with bulky side groups which can be prepared easily is that of the trihaloacetaldehyde polymers, particularly polychloral (VOGL 1969) (VOGL et al. 1972) (KUBISA, VOGL 1977). Only one form of polychloral has been described in the literature; these polymers are best prepared with anionic initiators [Equation 1] by cryotachensic polymerization, are insoluble in all solvents which have been tested and are isotactic as shown by x-ray crystal structure determination (WHITNEY, VOGL 1966) (WASAI et al. 1964). No soluble or atactic forms of polychloral have yet been observed.



$$A^{\ominus} + CCl_3\overset{\overset{O}{\|}}{C}H \rightleftharpoons A-\underset{H}{\overset{CCl_3}{C}}-O^{\ominus} \xrightarrow{nCCl_3CHO} A-(\underset{H}{\overset{CCl_3}{C}}-O)_{n-1}\underset{H}{\overset{CCl_3}{C}}-O^{\ominus} \quad (1)$$

EXPERIMENTAL PART

Optically active initiator salts and polychloral samples were prepared as described in details elsewhere (CORLEY 1978).

Polarimetric measurements were made with a Perkin-Elmer 141MC or 241MC Polarimeter (electronic) or a Carl Zeiss 369415 visual polarimeter. Optical rotations of soluble materials were measured on solutions in appropriate solvents; rotations of insoluble polymers were measured on swollen films between glass plates. For the latter measurements, a cell was constructed of two circular pieces, 27 mm in diameter, of 1/8" aluminum sheet. The cell could be screwed to the mounting platform in the Perkin-Elmer 141 MC polarimeter so that optical rotation could be measured at angles of orientation of the cell differing by 120°. The empty cell (with a drop of liquid between the plates) showed zero optical rotation.

RESULTS AND DISCUSSION

We have succeeded in preparing samples of polychloral initiated by anionic polymerization initiators where the optical activity is either in the anion or in the cation. Polymers of opposite optical rotation were synthesized. We do not claim at this time that the optical activity induced in the samples of isotactic polychloral is at a maximum. The optical activity is, however, not the result of initiator residue, which was carefully extracted (and even when left in the polymer would contribute to about 1% of the optical activity because of the low initiator concentration used); even if the optical activity in the polymer came from a high contribution of optically active endgroups, it would have to be extraordinarily large to account for the extent of optical activity that we measured in our polychloral samples with optical activity.

Polychloral films were cut into a number of discs of 12 mm. diameter and annealed in diphenyl ether at 50°C. for from two days to one week. The discs were then laminated (with diphenyl ether) within the polarimeter film cell and the thickness of the cell was measured at three points along its perimeter, with an average value taken. The thickness of the laminated film sandwiches used was generally 0.5 to 1.5 mm.; in all cases the transparency of the films laminated with diphenyl ether was good. The thickness of the individual films used was generally on the order of 0.05 mm.

Polarimeter measurements on the cell containing the laminated films were then performed at three orientations at 0°, 120° and 240°. Average rotations for the films, and average absolute rotations, were determined, together with average specific rotations per millimeter (Table 1).

TABLE 1

Optical Rotation Data for Polychloral Films (a)

Initiator (b)	Thickness of laminated films in mm.	Average rotation values at cell angles of			Average rotation (per mm.)
		0°	120°	240°	
Ph_3P	0.83	+ 0.17	+ 0.05	+ 0.26	+0.16°
	1.50	- 0.41	- 0.22	- 0.89	-0.58°
$PhCH_2\overset{\oplus}{P}Ph_3Br^{\ominus}$	1.04	+ 0.35	- 0.62	- 0.75	-0.34°
Brucine	0.26	- 0.96	+ 1.68	- 0.80	-0.03°
$(CH_3)_4\overset{\oplus}{N}$ $Ket^{\ominus}$(c)	0.59	+ 0.18	- 1.45	- 0.59	-0.62°
$(CH_3)_4\overset{\oplus}{N}$ $Ket^{\ominus}$(c,d)	0.65	+ 62.4	+ 42.4	+ 32.8	+45.9°
$(+)-(CH_3)(n-C_3H_7)(C_6H_5)(C_6H_5CH_2)\overset{\oplus}{P}Cl^{\ominus}$	1.47	- 50.1	- 55.5	- 48.8	-51.5°

(a) Films CH_3OH extracted, then annealed for 2-6 days in diphenyl ether at 50°C.; optical rotation measured as laminates moistened with diphenyl ether.

(b) 0.4 mole % (with respect to chloral) of initiator used as 0.4M solutions in $CHCl_3$.

(c) $Ket^{\ominus}$= (+)-Ketopinate. (2-oxo-7, 7-dimethylbicyclo(2.2.1)heptane-1-carboxylate)

(d) Sulfolane used as initiator solvent.

Films initiated with optically inactive initiators such as triphenylphosphine and benzyltriphenylphosphonium bromide showed small apparent optical rotations which were due to birefringence. However, two of the optically active initiators, tetramethylammonium (+)-ketopinate where the optical activity is in the anion (Equation 2) and (+)-methyl-n-propylphenylbenzylphosphonium chloride

$$\overset{*}{A}{}^{\ominus}\ cat^{\oplus} \xrightarrow{n\ CCl_3CHO} \overset{*}{A}\text{-}[CH(CCl_3)O]_{n-1}CH(CCl_3)\text{-}O^{\ominus}\ cat^{\oplus} \qquad (2)$$

where the optical activity is in the cation (Equation 3) have been used as anionic initiators in chloral polymerization and have given

$$A^{\ominus}\ \overset{*}{cat}{}^{\oplus} \xrightarrow{n\ CCl_3CHO} A\text{-}[CH(CCl_3)O]_{n-1}CH(CCl_3)\text{-}O^{\ominus}\ \overset{*}{cat}{}^{\oplus} \qquad (3)$$

films with very high optical activity of the same sign (though differing somewhat in magnitude) at all three rotation angles of the cell. Because of the strong optical rotation of the same sign at all three cell angles in cells containing from 10 to 30 laminated film discs, we believe we have demonstrated that optically active polychloral has been formed.

ACKNOWLEDGEMENTS: Exploratory experiments to prepare optically active polychloral were conducted at the University of Massachusetts by K. Hatada. We would like to thank J. Michalski and Z. Skrzypczynski of the Centre of Molecular and Macromolecular Studies of the Polish Academy of Sciences in Lodz, Poland, for providing us with a sample of (+)-methyl-n-propylphenylbenzylphosphonium chloride. This work was written when O.V. was a Visiting Professor at Kyoto University, Japan, as recipient of the Senior Scientist Fellowship Award by the Japan Society for the Promotion of Science.

REFERENCES

1. A. ABE, J. Am. Chem. Soc., 90(9), 2205 (1968).
2. I.W. BASSI, O. BONSIGNORI, G.P. LORENZI and P. PINO, J. Polym. Sci., Polym. Phys. Ed., 9, 193 (1971)
3. O. BONSIGNORI and G.P. LORENZI, J. Polym. Sci., Polym. Phys. Ed., 8, 1639 (1970)
4. L.S. CORLEY, Ph.D. Dissertation, Univ. of Massachusetts, 1978
5. H.L. FRISCH, C. SCHUERCH and M. SZWARC, J. Polym. Sci., 11, 559 (1953)
6. M. GOODMAN and A. ABE, J. Polym. Sci., 59, S37 (1962)
7. M. GOODMAN, A. ABE and Y.-L. FAN, Macromol. Revs., 1, 1 (1967)
8. P. KUBISA and O. VOGL, Macromol. Synth., 6, 49 (1977).
9. T.M. LOWRY, Optical Rotatory Power, Longmans, Green & Co., London, 1935
10. C.S. MARVEL, R.L. FRANK and E. PRILL, J. Am. Chem. Soc., 65, 1647 (1943)
11. C.S. MARVEL and C.G. OVERBERGER, J. Am. Chem. Soc., 68, 2106 (1946)

12. M. ORCHIN and H.H. JAFFE, *Symmetry, Orbitals, and Spectra*, John Wiley & Sons, Inc., New York, 1971, pp. 99-103
13. C.G. OVERBERGER and L.C. PALMER, J. Am. Chem. Soc., **78**, 666 (1956)
14. P. PINO, F. CIARDELLI, G.P. LORENZI and G. MONTAGNOLI, Makromol. Chem., **61**, 707 (1963)
15. P. PINO and G.P. LORENZI, J. Am. Chem. Soc., **82**, 4745 (1960)
16. P. PINO, G.P. LORENZI and L. LARDICCI, Chim. Ind. (Milan), **42**, 712 (1960)
17. P. PINO, G.P. LORENZI, L. LARDICCI and F. CIARDELLI, Vysokomol. Soedin. Ser. A, **3**, 1597 (1961)
18. P. PINO and P. NEUENSCHWANDER, J. Polym. Sci., Polym. Symp. Ed., **51**, 171 (1975)
19. P. PINO, P. SALVADORI, E. CHIELLINI and P.L. LUISI, Pure Appl. Chem., **16**, 469 (1968)
20. G. SCHMITT and C. SCHUERCH, J. Polym. Sci., **45**, 313 (1960)
21. O. VOGL, U.S. Pat. 3,454,527 (1969)
22. O. VOGL, H.C. MILLER and W.H. SHARKEY, Macromolecules, **5**, 658 (1972)
23. P. WALDEN, Z. Physik. Chem. (Leipzig), **20**, 383 (1896)
24. G. WASAI, T. IWATA, K. HIRONO, M. SURAGANO, T. SAEGUSA and J. FURUKAWA, Kogyo-Kagaku Zasshi, **67**, 1970 (1964)
25. J. WHITNEY and O. VOGL, unpublished data, 1966

Received and accepted September 1, 1980