

Solid state measurements of optical activity

3. Poly(triphenylmethyl methacrylate) in solution and suspension

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ABSTRACT

Measurements of the optical activity of suspensions of optically active poly(triphenylmethyl methacrylate) (PTrMA) were successfully carried out on THF-soluble and THF-insoluble fractions of the polymer. The values of the optical rotations of $[\alpha]_D^{20}$ were substantially the same and, as expected, depended somewhat on the suspending medium.

INTRODUCTION

Macromolecular conformation can influence optical activity, which in turn can function as a probe for changes in the secondary structure [1,2]. As an example, isotactic polymers often form helices whose handedness follows from the configuration of a chiral center within each monomer unit. In cases like polychloral [3-5] or [poly(triphenylmethyl methacrylate) [6-8], the chiral centers are generated during polymerization via interaction with a chiral initiator and form a rigid helix. In other cases, the chiral center is present in the monomer; this monomer is incorporated into the polymer and the configuration of the monomer unit determines the secondary structure. Examples include poly(S-3-methyl-1-pentene) [9-11], polyaminoacids and polyisocyanides [12].

Optical rotation measurements can provide significant structural information since the rotatory contributions from the secondary structure (i.e. the helix) usually dominate contributions by the chiral center of each monomer unit if the helical conformation is rigid. Even dissymmetric packing of symmetric molecules in molecular or ionic crystals or in cholesteric liquid crystalline states, can generate large optical rotations in the solid state.

In spite of the fact that secondary and higher levels of structure strongly influence optical properties of materials, relating optical properties to molecular conformation

This paper is dedicated to Professor Dragutin Fles on the occasion of his 70th birthday with our warmest wishes.

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and packing has proven very difficult. A second obstacle is that optical measurements are usually done on solutions or on unoriented films where the macromolecular structure is most difficult to determine.

Optical activity of inorganic crystals or organic compounds have been known and measured before [13]. Some measurements of polymers in suspension have also been carried out [9,14]. It was recognized that the matching of the refractive index of the polymer with that of the suspending medium is essential for the accuracy of the measurements. With the more recent discoveries that polymers, which have optical activity based exclusively on macromolecular asymmetry, can be prepared, the importance of reliable measurements of the optical rotation of polymers in the solid state has become more significant.

We have examined optical rotations of suspending materials ranging from sodium chlorate and sodium bromate to macromolecules including polylactides, polysaccharides, polypeptides and RNA [1]. With the eventual goal of using optical-property measurements to characterize dissymmetric macromolecular structures in the solid state, we found good agreement between measurements on suspended crystalline powder and single crystals if the crystals were isotropic, if the refractive index of the suspending medium and the solid could be matched accurately, and if the particle size and the stirring rate during the measurement were appropriate. Under optimum conditions, specific rotations were insensitive to particle concentration and suspending medium.

As mentioned above, optical rotation measurements on suspended solids are complicated by light scattering. Early attempts to overcome this problem were unsuccessful and only about one half of the single crystal value was measured [13]. Optically active polyolefins were measured later but the data were plagued with uncertainties from scattering, mechanical orientation and crystallinity differences [10]; the importance of refractive index matching for suspensions and of minimizing mechanical orientation in films was emphasized [14].

Seven polyolefins were measured and showed substantial differences between suspended solids, thin films and solutions [9-11]. The relative importance of systematic errors and fundamental structural differences between different samples were not evaluated. The principles of measuring specific rotations of crystalline powder suspensions to be equivalent to specific rotations of suspended rotations in single crystals have created some doubts about the structural significance of the few reported measurements. Consequently, the technique of measuring the optical rotation of polymer samples in suspension has not been recognized as general or has not been widely used.

We have measured sodium chlorate and bromate and demonstrated that specific rotations observed for single crystals and powder suspension are identical if proper attention is given to experimental details [1]. Earlier attempts to measure correctly the optical activity were not very successful [15]. For some materials, (e.g.) cellulose acetate, hemocyanine and RNA) we found interesting differences between suspension and solution measurements. These results suggest significant structural differences between the solid state associated molecular aggregates and individual single molecules in solution.

Polymers made from triphenylmethyl methacrylate (TrMA) [16-18] have also been measured in tetrahydrofuran (THF) solutions of soluble polymer fractions that were of lower molecular weight. In addition to the suspension measurements of polyolefins, measurements of optically active polychloral samples [19-23] were made on polymer films.

We had decided to develop a dependable method for measuring the optical rotation of optically active solids, including polymers in powder form and have used poly(triphenylmethyl methacrylate) (PTrMA) as a typical example.

EXPERIMENTAL PART

PTrMA was synthesized from TrMA with a $n\text{-BuLi}:(-)\text{-sparteine}$ initiator [24-26]. The optical rotation of the THF soluble fraction of PTrMA (lot no. 53) measured in THF was $+330^\circ$. The THF-insoluble fraction was lot no. 57. The ash content from initiator residues of the polymer samples was less than 0.1 %.

The refractive index of all liquids was determined on an Abbe Refractometer (ERMA, Japan).

The optical rotations were measured on a Perkin-Elmer 241 Polarimeter at a temperature of $20 \pm 1^\circ\text{C}$ at 589 nm. For solution measurements glass cells with a path length of 2 - 100 mm were used. Suspension measurements were carried out in 10 mm glass cells with magnetic stirring. All suspensions were prepared from polymer powders with particle sizes of less than 45 microns.

RESULTS AND DISCUSSION

Solution Measurements: The optical rotation of the THF-soluble fraction of PTrMA prepared with a $n\text{-butyllithium}/(-)\text{-sparteine}$ initiating system was measured in THF solution and in a mixture of carbon disulfide:carbon tetrachloride 4:1 (Figure 1). As expected, the values of the optical rotation depended on the type of solvent used and did not depend on the polymer concentration. We also found that the THF-insoluble PTrMA fraction was soluble in dibromomethane. Viscosity measurements in dibromomethane gave for the THF-soluble fraction an η_{inh} of 0.08 dL/g and for the THF-insoluble

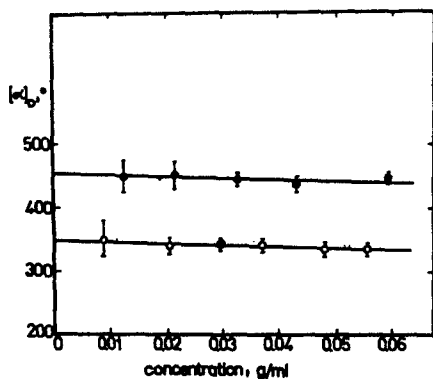


Figure 1.
Optical Rotation of the Tetrahydrofuran Soluble Fraction of PTrMA as a Function of Concentration Solvents: o Tetrahydrofuran, ● Carbon disulfide: Carbon tetrachloride 4:1

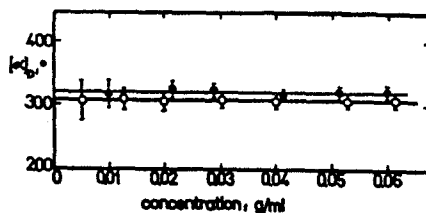


Figure 2.
Optical Rotation of the Tetrahydrofuran Soluble ● and Tetrahydrofuran Insoluble o Fraction of PTrMA in Dibromomethane Solution as a Function of Concentration

fraction an η_{inh} of 0.11 dL/g. Both THF-soluble and THF-insoluble polymers had essentially the same optical rotation in dibromomethane (Figure 2), demonstrating again that the same type of polymer gives the same (or similar) value of optical rotation when the same solvent (or suspending media) was used. The values of optical rotation of PTrMA in various solvents and suspending media are shown in the Table.

Measurement of Optical Rotation of
Poly(Triphenylmethyl Methacrylate)

Measurement Method	Solvents or Suspending Media	Refractive Index	Optical Rotation of PTrMA $[\alpha]_D$	
			Soluble	Insoluble in THF
Solution	THF	1.408	345°	-
	CH ₂ Br ₂	1.538	325°	310°
	CCl ₄ - CS ₂	1.587	445°	-
Suspension	CCl ₄ - CS ₂	1.549	425°	405°
	C ₆ H ₅ OH - CS ₂	1.557	450°	420°
	CCl ₄ - C ₆ H ₅ Br ₂	1.595	450°	430°

Suspension Measurements: It had been demonstrated that the optical rotation of polymer samples in powder form could be measured under the conditions indicated earlier [27]. For the optical activity measurements of PTrMA in suspension accurate values could be obtained. The refractive index of the powder to be measured should be identical or very similar to that of the suspending media. The refractive index of the suspending media was best matched by using a mixture of

two liquids of different refractive index, one being higher and one being lower than the refractive index of the powder that was measured. It was also preferable that the density of the polymer and the suspending media was also similar. For accurate results, the measurements were carried out with mechanical stirring at a constant stirring rate between 300 and 1 000 rpm. When the refractive index difference between the suspending media and the sample was too large to obtain meaningful measurements, the suspension appeared opaque and the photocell current became too low. In order to obtain reliable results of measurements of the optical rotation, the suspension measurements were observed as a function of concentration. The dependence of optical rotation as a function of concentration is a sensitive measure for the determination of correct values. The optical rotation had to be either independent of the optical rotation or had to have only a minimal slope. The optical rotation was then extrapolated to zero concentration.

The optical rotation of the THF-soluble fraction of PTRMA was measured in three suspending media: a) n-butanol: carbon disulfide, b) carbon tetrachloride: carbon disulfide and carbon tetrachloride: dibromobenzene (Figure 3). The optical rotation varied from $+425^\circ$ to $+450^\circ$. The slightly different values reflected the interaction of the powdered sample with the suspending media. The suspending media in the mixture which had the higher refractive index (carbon disulfide and dibromobenzene) played a predominant role and apparently interacted more strongly with the surface of the suspended solid. At lower concentrations the suspension measure-

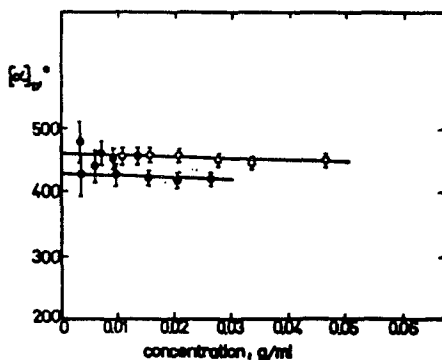


Figure 3.
Optical Rotation of the Tetrahydrofuran Soluble Fraction of PTRMA in Suspension (3 Suspending Media) as a Function of Concentration

- n-butanol : carbon disulfide
- carbon tetrachloride : dibromobenzene
- carbon tetrachloride : carbon disulfide

ments of the optical rotation become less accurate. It was very probable that some of the polymer particles deposited on the surface of the measuring cell gave an apparently lower concentration of the powder for the measurement.

Similar data for the optical rotation measurements were obtained on THF-insoluble samples of PTRMA. The values ranged from $+405^\circ$ to $+430^\circ$ (Figure 4). For the optical rotation of the THF-insoluble fraction of PTRMA a very accurate study of the optical rotation as a function of the refractive index was carried out. At the same time the comparison with sodium chlorate was performed (Figure 5).

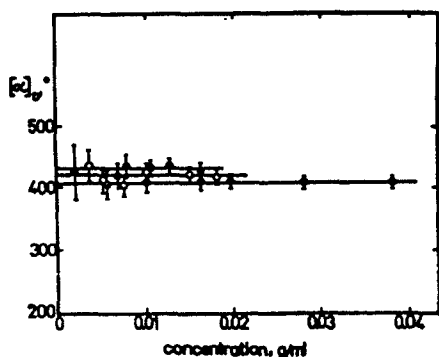


Figure 4.
Optical Rotation of the Tetrahydrofuran Insoluble Fraction of PTrMA in Suspension (3 Suspending Media) as a Function of Concentration

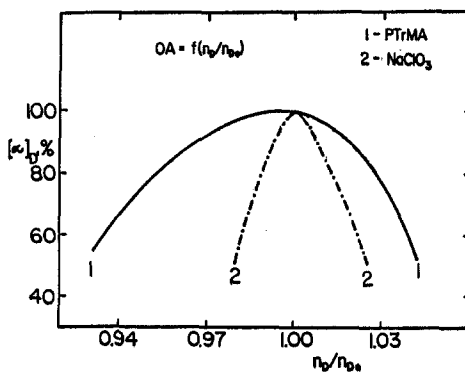


Figure 5.
Comparison of relative specific rotation ($[\alpha]_D^{20}$) as a function of relative refractive index (n_D/n_{D_0}) for NaClO_3 and PTrMA

For the first time we had established the identity of specific rotations determined from powdered suspensions and solutions of macromolecules, in our case PTrMA. The demonstration that diverse macromolecules show a similar dependence of optical rotation as a function of refractive index, particle size and concentration provided the first direct evidence that optical rotation measurements on powdered suspensions can relate to molecular structure rather than artifacts from light-scattering or sample birefringence.

We have continued to pursue in this work the possibility that suspension measurements of optical activity can provide a tool for characterizing details of macromolecular conformation in powders and the morphology of films. Of particular interest to us are those solid state properties which are lost or altered when the material is brought into solution or dissociated into its components.

In our case of the measurement of the optical activity of PTrMA, the values from the solution and the solid state measurements are substantially the same. This seems to indicate that no particular macromolecular interaction between the polymer chains takes place and for the lack of light scattering that the polymer samples are substantially non-crystalline. It can also be concluded that the polymer samples are rigid rods, probably in solution and in the solid state, which does not allow them to crystallize in the fashion that has been established for the very flexible polyethylene. Viscosity measurements in dibromomethane gave for the THF-soluble fraction an η_{inh} of 0.08 dL/g and for the THF-insoluble fraction an η_{inh} of 0.11 dL/g.

In conclusion, we were able to develop a technique to measure accurately the optical rotation of PTrMA in suspension. The obtained values are comparable with those from

solution measurements. This technique of measuring the optical activity in the solid state, in powder form, is being investigated for its possible general use in inorganic and organic crystals and for other optically active polymers.

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