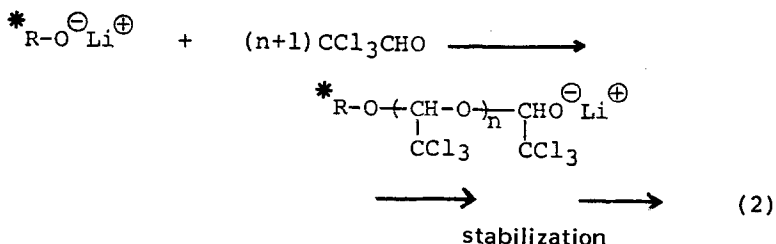




Lithium alkoxide of cholesterol was prepared from cholesterol (Aldrich Chemical Company,  $[\alpha]_D^{25} = 30.86^\circ$ ,  $\text{CHCl}_3$ ) and equimolar amounts of butyllithium in *n*-hexane at room temperature. The specific rotations of the resultant alkoxide  $[\alpha]_D$ , at  $23^\circ\text{C}$  and  $60^\circ\text{C}$  were  $-29.49^\circ$  and  $-29.08^\circ$ , respectively.

The polymerization of chloral was carried out with the lithium alkoxide of cholesterol as the initiator in *n*-hexane at  $0^\circ\text{C}$  similarly to a method described previously (VOGL 1969) (VOGL et al. 1972). The mole percentage of the initiator used relative to chloral was 0.2 mole %. The polychloral plug was grated and the polymer



powder was stabilized by successive treatment with 10% HCl in methanol and a 0.5M solution of  $\text{PCl}_5$  in carbon tetrachloride (CORLEY 1979) (CORLEY, VOGL 1980b) (CORLEY, VOGL 1980c). The polymer was extracted with acetone for 3 days in a Soxhlet apparatus and dried at 0.1 mm Hg. The stabilized, optically active polychloral was used for chromatographic separations.

Isotactic polymers of R-(+)- and S-(-)- $\alpha$ -methylbenzyl methacrylates were prepared by the polymerization of each monomer with cyclohexylmagnesium chloride in toluene at  $-78^\circ\text{C}$  (OHTA 1979); the number average molecular weights were measured to be 79,300 and 53,800, respectively by gel permeation chromatography. The isotacticity of either polymer were determined to be nearly 100% judged by triad analysis of the polymer.  $^1\text{H}$  NMR spectra were taken in nitrobenzene- $d_5$  at  $100^\circ\text{C}$ . The optical rotation of the poly( $\alpha$ -methylbenzyl methacrylate) was measured by a JASCO DIP-181 polarimeter at 365 nm and  $25^\circ\text{C}$  as a 1.3-15 mg/ml solution in chloroform using a cell with a pathlength of 2.0 cm. The specific rotations of the polymers were  $+377^\circ$  and  $-351^\circ$ , respectively, in chloroform at 365 nm and  $25^\circ\text{C}$ .

Polychloral with a grain size of 30 ~ 150 mesh (43 g) was packed into a column, 15 mm in diameter and 550 mm in length. Tetrahydrofuran was used as the eluant for the partial resolution of the isotactic polymers of R-(+)- and S-(-)- $\alpha$ -methylbenzyl methacrylates. The resolution was carried out at room temperature and at a flow rate of 0.62 ml/min. The eluate was collected every 5.5 min (3.4 ml) and evaporated to dryness at 0.1 mm Hg. The residue of each fraction was weighed and redissolved in chloroform for the measurement of the optical rotation.

## RESULTS AND DISCUSSION

When polychloral prepared with the lithium alkoxide of cholesterol was used as the column packing for the separation of a racemic mixture of the isotactic polymers of R-(+)- and S-(-)- $\alpha$ -methylbenzyl methacrylates, a partial resolution of the polymer was achieved (Figure 1). This result strongly implies that polychloral prepared with this optically active initiator has a helix conformation preferential in one screw sense (i.e. it is optically active). Figure 1 shows the weight of the polymer per unit volume of each fraction and its specific rotation plotted against the elution volume. The polymer fractions eluted at the early stages showed a positive optical rotation and those at later stages showed negative optical rotation. This means that the polymer from R-monomer is eluted preferentially from the column. Although the polymer mixture showed a broad single elution peak in the chromatogram, the retention volume for the polymer of R-monomer (37.7 ml) was found to be slightly less than that for the polymer of S-monomer (39.1 ml). This was determined in a separate experiment where optically pure polymer was injected separately. The separation factor,  $\alpha$ , was calculated to be 1.1. The optical purity of the fractionated polymer was at most 17% for the fraction rich in R-polymer and 15% for the S-polymer rich fraction. Chromatographic experiments with toluene and chloroform as eluants gave similar results.

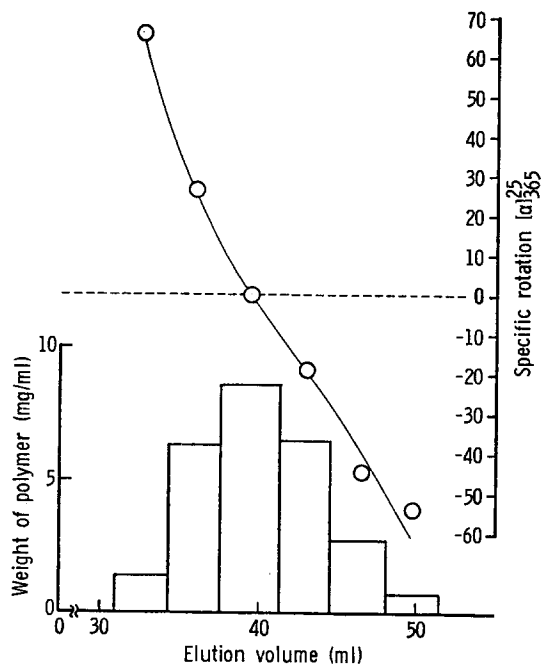


Figure 1. Resolution of a mixture of equal amounts of poly[R-(+)- $\alpha$ -methylbenzyl methacrylate] and poly[S-(-)- $\alpha$ -methylbenzyl methacrylate] with optically active and isotactic polychloral as the column packing.

This was determined in a separate experiment where optically pure polymer was injected separately. The separation factor,  $\alpha$ , was calculated to be 1.1. The optical purity of the fractionated polymer was at most 17% for the fraction rich in R-polymer and 15% for the S-polymer rich fraction. Chromatographic experiments with toluene and chloroform as eluants gave similar results.

To confirm that the partial resolution of the racemic mixture is due to the optical activity of the adsorbent, optically inactive polychloral was prepared with lithium tert-butoxide and stabilized (CORLEY 1979) (CORLEY, VOGL 1980b) (CORLEY, VOGL 1980c). When this polymer was used for the attempted resolution of

isotactic R-(+)- and S-(-)- $\alpha$ -methylbenzyl methacrylate polymer, the optical rotation of the major fractions was zero. However, the first two and the last two fractions showed small positive and negative optical rotations, (Figure 2). This separation is believed to

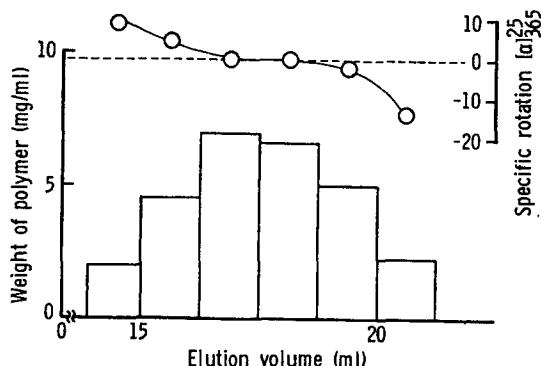


Figure 2. Attempted resolution of an equal amount mixture of poly[R-(+)- $\alpha$ -methylbenzyl methacrylate] by using polychloral prepared with lithium tert-butoxide. (polychloral 25g, eluant: tetrahydrofuran, flow rate 0.23 ml/min.)

be caused by a direct chromatographic effect, common in GPC, since the molecular weight of the R-polymer is larger than that of the S-polymer. Extent of resolution is greatly enhanced by using the polychloral prepared with optically active initiator.

Isotactic polychloral prepared with an optically active lithium alkoxide has an optically active fragment from the anion of the initiator as an endgroup and this chiral endgroup

induces the formation, or at least the predominance of formation, of one of a helical chain over the other. Because the polychloral is insoluble, the chiral helix is retained in the solid state. The resolution of isotactic poly[R-(+)- $\alpha$ -methylbenzyl methacrylate] from poly[S-(-)- $\alpha$ -methylbenzyl methacrylate] is a strong indication of the existence of optically active polychloral prepared with the lithium alkoxide of cholesterol as the initiator and resolution of the R-(+) and S-(-) polymers results from the specific interaction between the polychloral helix (VOGL, HATADA 1975) and the two poly( $\alpha$ -methylbenzyl methacrylates). The isotactic polymer of R-(+)- $\alpha$ -methylbenzyl methacrylate apparently interacts less effectively with the isotactic polychloral helix and consequently is eluted faster than the S-polymer.

This method of resolution of enantiomers with optically active polychloral prepared with optically active initiator, may develop into a useful technique for the resolution of racemic mixtures of low and high molecular weight substances. Optically active polychloral may have use as column packing for several types of chromatographic separations. Further investigations are in progress.

#### ACKNOWLEDGEMENTS

This paper is communication XXII of Haloaldehyde Polymers. The work was supported in part by a grant from the National Science Foundation.

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*Received January 21, 1981*