Waters Lab Highlights

An Internal Communication of Applications and Techniques

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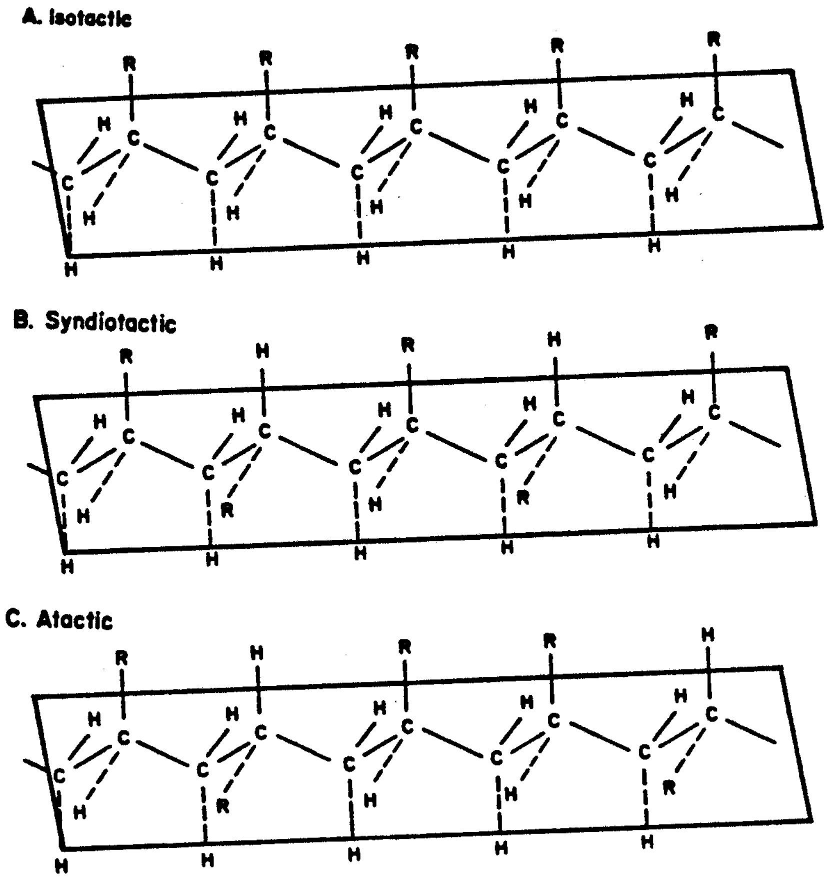
LITERATURE CORNER

HOW POLYMER STEREOCHEMISTRY CAN CAUSE ANOMALIES IN GPC CHARACTERIZATION

In commercial plastics such as polyvinyl chloride (PVC) used in Millipore's Ivex[R] intravenous filter, strength and impact resistance are of paramount importance and are routinely quality controlled.

Molecular weight distribution (MWD) by GPC is often a good indication of impact properties of the molded plastic, but in some cases, polymer aggregates show up as anomalously high molecular weight "tails." These false "tails" have been reported in the literature[1] and have been traced to the stereochemical configuration in the polymer itself. In vinyl polymers, such as PVC, this "tacticity," as it is called, contributes as much to PVC's impact properties as does the correct MWD. Tacticity in an asymmetric polymer such as PVC can be represented by visualizing the polymer chain in its extended zig-zag conformation shown in Figure 1.

FIGURE 1



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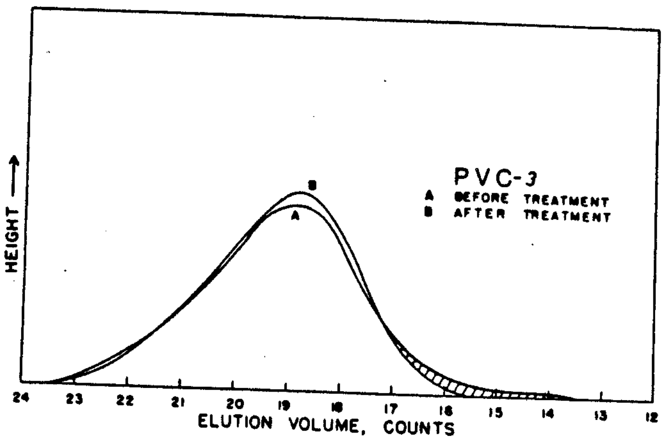
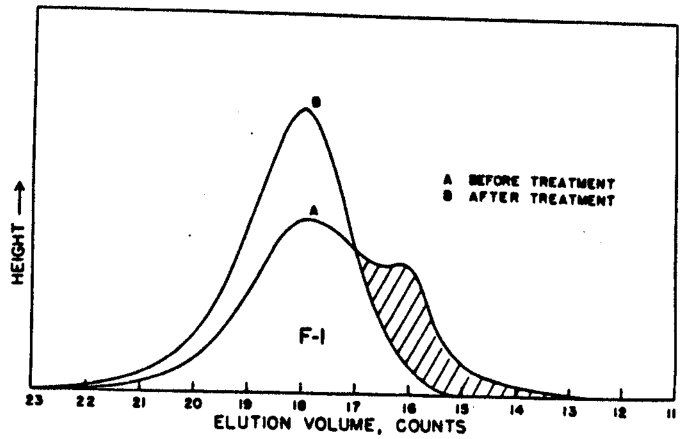
Several different placements of the asymmetric R Group, (Chlorine in PVC on the asymmetric carbon) are possible. When all the Cl groups in PVC lie on the same side of the plane as in "A," the polymer is called "isotactic." If the Cl group alternates from one side to the other as in "B," the PVC is called "syndiotactic." A random placement of the Cl Group as in "C" is called "atactic." Varying combinations of atactic chains in an isotactic or syndiotactic polymer influence the crystal structure by acting as natural plasticizers and affect impact resistance of the plastic. While this is good for the polymer, it is bad for interpreting GPC curves.

In GPC, highly "syndiotactic" chains show up as aggregates and elute anomalously as a tail or a region of high molecular weight in the chromatogram. Two such examples are shown in the figures below.



GPC chromatograms for PVC-3 whole polymer: the effect of dissolving aggregates is to convert Curve A into Curve B.



GPC chromatograms for PVC-3: aggregate peak forms a shoulder on GPC (Curve A) and disappers after heating.

Usually, the aggregates disintegrate into single molecules when heated and the GPC curve looks like the one labelled "after treatment." Chartoff and Lo[1] reported that polymer solutions made up at 0.5% in THF and heated (under N_2) at 85°C for 30 minutes did not show the anomalous second peak. Further experiments ruled out any degradation.

In conclusion, this work proves that not only distribution of monomer units (MWD) is important, but also spatial arrangement (tacticity) influences the shape of a GPC curve. Agglomeration in polymer can prevent one from getting true GPC data, and, if suspected, the sample must be heated to get true size separation by GPC.

1. R. P. Chartoff and S. K. T. Lo, Liquid Chromatography of Polymers and Related Materials, Vol. 8, 135-148, 1980.