Performance PerSPECtives

Waters® Alliance® GPC/V 2000 System:
Challenges of Polypropylene Analysis

Introduction: Polypropylene (PP) differs from polyethylene (PE) by a simple methyl group that is present on each repeating unit (See Figure 1) .

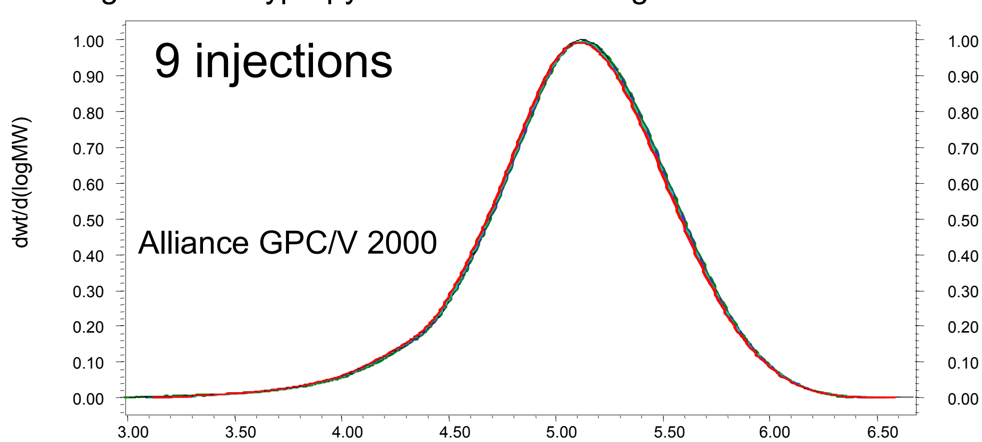
Figure 1: Structure of Polyethylene (PE) and Polypropylene (PP)

PE: $-(CH_2-CH_2)-_n$ **PP:** $-(CH_2-\underset{}{\overset{CH_3}{\overset{|}{CH}}})-_n$

The orientation of the methyl group for each repeating PP unit determines the crystallinity of the polymer. If all of the methyl groups occur at the top of the chain, the polymer is said to be isotactic. If the methyl group alternates between top and bottom of the chain for each repeat unit, it is syndiotactic, and if the methyl group occurs randomly for each repeat unit, then the polymer is atactic. This Performance PerSPECtive describes the sample preparation conditions necessary to ensure complete dissolution of polypropylene, along with the outstanding molecular weight reproducibility that may be obtained using the Alliance® GPC/V 2000.

High Temperature GPC Analysis of Polypropylene: Atactic PP may be run at ~90 °C in xylene. The more crystalline syndiotactic and isotactic PPs require higher temperature, 140 °C to 150 °C, and 1,2,4 trichlorobenzene as solvent. The crystalline forms of PP need to be dissolved at temperatures between 155 °C – 170 °C for 2 – 3 hours. It is imperative that the polymer solution contain an antioxidant to protect the PP from degradation during the sample preparation procedure. Following the proper dissolution protocol, very reproducible GPC analysis of PP may be obtained with the GPC/V2000 system. Figure 2 shows an overlay of nine molecular weight distributions of an isotactic PP that was dissolved at 170 °C for 2 hours, then run at an analysis temperature of 145 °C. The system contained a Styragel® HT 3-column set, using 1,2,4 TCB at 1.0 mL/minute flow rate. The concentration was 0.080%.

Figure 2: Polypropylene Molecular Weight Distributions



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Polypropylene Analysis Reproducibility: Table 1 shows the superb molecular weight average reproducibility obtained on Waters Alliance GPC/V 2000 System for nine Injections of an Isotactic Polypropylene Sample. (MWDs from the three injections from three different vials shown in Figure 2). Note that Mn, Mw, Mv and even Mz have RSD's of < 1.0%. There is no evidence of any degradation of the polypropylene sample, as the MW averages are virtually unchanged throughout the 10 hours in the sample management compartment. The combination of the RI and viscometer detectors allows the determination pf Mv (viscosity average molecular weight), alpha, (slope of the viscosity law plot), and the intrinsic viscosity.

Table 1: Molecular Weight Average Reproducibility of an Isotactic Polypropylene

	SampleName	Vial	Injection	Mn	Mw	Mz	Mv	alpha	Intrinsic Viscosity
1	PP_1	1	1	68403	202041	420760	176370	0.671	1.027
2	PP_1	1	2	68891	200527	430077	174789	0.674	1.032
3	PP_1	1	3	68623	200845	426057	175704	0.679	1.029
4	PP_1	2	1	68827	200945	429981	175228	0.675	1.030
5	PP_1	2	2	68563	199850	430889	174693	0.681	1.030
6	PP_1	2	3	68782	198546	432850	172944	0.675	1.033
7	PP_1	3	1	68595	199515	434953	173809	0.676	1.032
8	PP_1	3	2	68127	198318	429704	172395	0.670	1.047
9	PP_1	3	3	68049	197501	427125	171702	0.671	1.039
Mean				68540	199788	429155	174181	0.675	1.032
% RSD				0.433	0.732	0.962	0.904	0.543	0.572

Summary:

- The crystallinity of a polypropylene sample determines the necessary sample preparation procedure and the GPC analysis conditions.
- Highly crystalline PP requires dissolution at ~170 °C for a at least 2 hours.
- Once in solution, the sample may be analyzed at 140 °C – 150 °C.
- Antioxidants should be present during the sample preparation to protect the PP from oxidative degradation.
- The combination of the RI and viscometer detectors allows calculation of Mv, the Mark-Houwink constants (K and alpha), and the whole polymer intrinsic viscosity.
- Waters Alliance® GPC/V 2000 System provides exceptional reproducibility for the analysis of polypropylene samples.