Use of Laboratory Robotics for Gel Permeation Chromatography Sample Preparation: Automation of High-Temperature Polymer Dissolution

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ABSTRACT: Manual preparation of polymer samples for molecular weight characterization by solution methods such as gel permeation chromatography (GPC) is a time-consuming, labor-intensive, and redundant task. Preparation of samples for high-temperature GPC characterization further complicates the procedure. A typical manual high-temperature sample preparation exposes the analyst to both hot surfaces and solvent vapors. An automated system to prepare samples for high temperature GPC analysis has been developed. The system is based on a Zymark laboratory robotic system, and custom hardware peripherals developed at The Dow Chemical Company. The automated procedure performs all the steps required to prepare samples for high-temperature GPC analysis, including the hot steps. The samples were analyzed using the Waters 150-C GPC in combination with the differential refractive index (DRI) and low-angle laser light scattering (LALLS) detectors to demonstrate the reproducibility and reliability of the automated procedure. The system hardware, software options, and performance are presented in this paper. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **64:** 1613–1623, 1997

Key words: laboratory robotics; GPC; polymer dissolution; automation; high-temp dissolution

INTRODUCTION

Gel permeation chromatography (GPC) is an analytical technique that is used for characterizing the molecular weight of polymers.[1] This technique has become increasingly powerful with the introduction of the low-angle laser light scattering and differential pressure viscometry detectors. These absolute methods require complete dissolution of the polymer sample and an accurate knowledge of the polymer solution concentration. Careful, reproducible, sample preparation has therefore become increasingly important with evolution of the technique.

GPC sample preparation and characterization is performed at ambient conditions or at elevated temperatures, depending on the solubility requirements of the polymer. Although room temperature sample preparation procedures are relatively simple, high-temperature dissolution procedures can expose the analyst to very hot surfaces, solvent, and solvent vapor. Additionally, the sample preparations are both time-consuming and tedious, requiring a significant amount of the ana-

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lyst's time to prepare and analyze the samples. Both safety issues and the redundancy of the preparation procedure make it a suitable candidate for automation.

No commercially available, automated instrument capable of performing high-temperature GPC sample preparations existed. However, a custom system was developed[2] in The Dow Chemical Company, Texas Operations Polyolefins Research Group, for this purpose. This system only performed the initial solvent additions, and not the entire sample preparation process. All hazardous steps were still performed manually. The system is no longer operational because replacement parts are obsolete. The Waters 150-C GPC system offers some built-in automation. During sample dissolution, the 150-C can agitate and later filter the solutions. These steps are performed in the injector oven of the instrument. However, in practice these features are inadequate for samples that are difficult to dissolve or filter. The other major drawback is that one must prepare the solution directly in the Waters stainless steel GPC vial, which is seldom practical for certain types of samples.

Reported here is the development of an automated system to perform high-temperature GPC sample preparation and the experiments performed to test its precision and accuracy. The system is based on a Zymark laboratory robotic system (Zymark Corporation Hopkinton, MA) and custom hardware peripherals developed at Dow Chemical. With the exception of polymer addition to the sample bottles, the system performs all the steps required to completely prepare samples for high-temperature GPC analysis, including the transfer of the hot sample solution to a disposable GPC auto sampler vial.

EXPERIMENTAL

GPC Data Collection

Solutions prepared by the automated system were characterized using a Waters 150-C GPC (Milford, MA) system equipped with four Polymer Labs (Polymer Labs; Amherst, MA), 20-μm PLgel mixed bed columns. The mobile phase was 1,2,4-trichlorobenzene (TCB) at 145°C containing $\sim$ 500 parts per million (ppm) of butylated hydroxytoluene (BHT). The analysis was performed at a flow rate of 1 mL/min yielding a GPC run time of 50 min. The columns were calibrated using 18 polystyrene (PS) standards (with molecular weights ranging from 1,060 to 8,400,000 g/mol; Polymer Labs). A Waters stainless steel, low dead volume 2-μm filter was installed on-line between the injector and the column. This prefilter helps prevent particulate matter from entering the column.

The detectors used were the differential refractive index (DRI) unit equipped with the 150-C and a Chromatix KMX-6 low angle laser light scattering (LALLS) unit operating with a He–Ne laser at $\lambda_0 = 633$ nm. The LALLS unit was placed on-line between the columns and the DRI detector. The LALLS unit was operated at 145°C using a P_0 setting of 1100 mV (with the 1,3,4 attenuators in the beam path), the 0.15-mm field stop, the 6–7° annulus, and a filter-sec setting of 10. The interdetector delay was 11 s. Literature values[3] were used for the differential index of refraction (dn/dc) of HDPE and LDPE in TCB. For HDPE, $dn/dc = -0.104$ mL/g; for LDPE, $dn/dc = -0.091$ mL/g. These constants were used in the calculation of M_w in light scattering measurements.

Data acquisition software was the Nelson Analytical 2600 LC package. Raw data was smoothed and reduced using the PE Nelson GPC software module (Perkin–Elmer; Cupertino, CA). Polyethylene molecular weights were determined using the universal calibration technique.[4] LALLS data were evaluated with software developed within The Dow Chemical Company.

The sample dissolution time and concentration conditions varied depending upon the sample type, as reported in Tables III–VII.

Hardware Configuration

The system's hardware consisted of a Zymark laboratory robotics system, commercially available peripherals, and custom built equipment. Figure 1 illustrates the robotic hardware used in the system. A Zymark XP robot with a 10-slot System V Controller™ was used in this application. The system was placed on a custom-built table support specially designed to accommodate placement of the robotic system into a fume hood. Parts of the system that could potentially allow the emission of small quantities of solvent vapors were located under the fume hood.

Vials of two different sizes were used in this application; a 30-mL reaction vial and 4-mL WISP

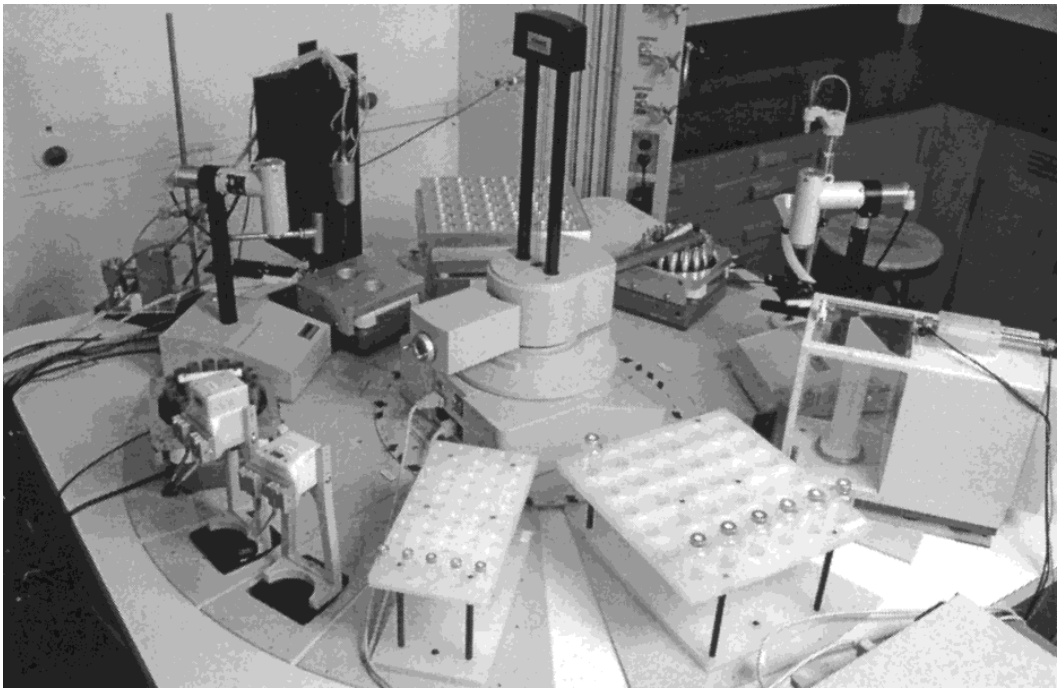

Figure 1 Illustration of the robotic system hardware configuration.

(Waters' autoinjector) style vials (Alltech Associates; Deerfield, IL). A custom polypropylene 36-position rack was built for the 30-mL vial and a Zymark 11-mm 50-position auto sampler rack was modified to house the 4-mL vial. Two Zymark general purpose hands were used to manipulate the vials. The 30-mL vial was used for sample preparation and dissolution. The 4-mL auto sampler vial was used to hold an aliquot of sample removed from the 30-mL vial for analysis. Aluminum seal crimp caps with Teflon™ liners were used to seal both vials (Alltech Associates; Deerfield, IL).

Sample weights were obtained using a Mettler AE160 balance, mounted to a Zymark balance weighing pysection. Solvent addition was performed by a Zymark Master Laboratory Station that pumped solvent to a dispensing post. All TCB additions were weighed on the Mettler balance. Capping and uncapping was performed by Zymark's crimp cappers. Two crimp cappers were needed for this application; a 20-mm (30-mL vial) and a 13-mm (4-mL vial) crimp capper. The 13-mm crimp capper was modified by mounting a nonferric proximity sensor (Omron; HI-WATT Warren, MI) under the cap holder. This provided additional verification during the capping and uncapping steps. A Zymark Power and Event Controller was used to provide contact closures and to monitor digital states from peripheral verification devices.

The 30-mL vials were heated on a custom built heated rack. The heater consisted of a 36-position aluminum plate mounted on top of a Thermolyne Hot plate (Fisher Scientific; Pittsburgh, PA). The 4-mL vial was preheated and remained heated after sample transfer to prevent precipitation. A custom built heated rack was fabricated for the 4-mL vial. The heater consisted of an aluminum plate machined to house the Waters' 16-position auto sampler carousel. The aluminum plate was mounted on top of a Corning Glass Works hot plate (Fisher Scientific; Pittsburgh, PA).

A custom transfer station was built to transfer the hot solution from the 30-mL reaction vial to the 4-mL auto sampler vial. This station consisted of a heated reservoir that can hold an aliquot of solution prior to dispensing into the auto sampler vial. It was found that a 4-mL reservoir volume offered high performance of the station and provided reproducible sample aliquots during sample holding. Tubing connections from the heated reservoir to two syringes on the Zymark Master Laboratory Station allowed solutions to be aspirated into the reservoir and clean solvent to be pushed through it between samples.

All hot plates and heater devices were con-

trolled with custom temperature controlling units (HI-WATT; Warren MI). These controlling units were comprised of a temperature controller, a high temperature limit control, and an 0–2-V output for remote temperature readings.

MANUAL VERSUS AUTOMATED PROCEDURE

Manual Procedure

The analyst first collected the bottle and cap tare weights. The 2-oz, screw-cap bottles were loaded with the sample and reweighed. A set volume (usually 20 mL) of TCB was added to the bottles using a Brinkman Dispensette™ hand pump designed for 4-L reagent bottles. The solvent mass was then determined. Although the sample concentrations were accurately known, they varied between samples because of variations in both sample and solvent mass. Because of the high temperature and lengthy time required for analysis, the TCB was fortified with BHT as a stabilizer. This was required to prevent sample degradation. The tightly capped bottles were placed upright in a convection oven at ~160°C. During the dissolution time, the samples were periodically inverted to ensure that all of the sample was dissolved. A Waters 150-C GPC carousel was loaded with Waters stainless steel vials and placed in the oven. The Waters Teflon™ prefilter units that accompany the vials were assembled. With gloved hands, the analyst uncapped the bottles and transferred a ~6-mL aliquot into the vials by pouring. A filter unit was immediately placed over the top of the vial. These steps occurred inside of the oven. After a few minutes in the closed oven to reestablish temperature, the filter units were manually pushed into the vials with a plunger. The filtered sample resided in the Teflon™ unit which was "sealed" by crimping a sheath of aluminum foil around the opening of the filter holder. The samples were then placed into the GPC for analysis.

When several dozen vials and filter units were used, they were collected and cleaned by immersing in hot TCB for several hours. The TCB was decanted while still hot and the parts dried in a convection oven.

Automated Procedure

Where possible and practical, the automated procedure was designed to mimic some of the manual steps. Other steps were eliminated or replaced with a different method when an opportunity to improve the procedure was identified. The system was designed to prepare up to 32 samples (two fully loaded, Waters' 150-C GPC carousels).

The analyst first initialized the system via menu selections, which were written in Easylab™ (Zymark Corporation Hopkinton, MA). The initialization routines reset software flags and variables and check hardware peripherals. After the initialization, the analyst entered run information, such as number of samples, sample identification, desired solution concentration, and the dissolution time. Other parameters, such as desired system mode of operation and peripheral options, were also selected via menus. The analyst may also provide additional information, such as GPC method name and name of data file to store each GPC analysis, and for downloading to the GPC data acquisition interface box. These data were written to a file, by the System V controller, which was compatible with the data acquisition software.

The system was programmed to check all peripherals for proper operation prior to starting the run. The robotic arm retrieved a capped vial from the designated reference weight position of the 30-mL vial rack and placed it on the analytical balance. The reference weight was stored with the run data and was used to track balance performance. The sample preparation process starts by collecting the tare weights for a given number of reaction vials with crimp caps. The sample was added manually to the vials. This was the only step that was not automated. The automated preparation procedure can run free of analyst intervention from this point.

The robot reweighed each vial to determine the amount of added sample. The sample weight was used to calculate the volume of TCB needed to achieve the desired solution concentration at 145°C. Unlike the manual procedure, this step provided the analyst with nearly identical sample concentrations, simplifying later data comparisons. The analyst had the option of screening the sample weights prior to TCB addition. The 30-mL vial was then uncapped and filled with the appropriate volume of TCB. The actual volume of TCB dispensed was determined gravimetrically. The cap was restored on the vial, crimped at the large crimp capping station, and reweighed to verify that the vial was capped. Like the manual preparation, the TCB used was fortified with BHT. The

Table I TCB Evaporation Test for 4-mL and 30-mL Vials

	Initial Mass (g)	Mass (g) at 1.5 h	Mass (g) at 6 h	Mass (g) at 23 h	Difference at 23 h	Difference (%) at 23 h
4-mL vial						
1	10.4205	10.4149	10.4063	10.3748	0.0457	0.439
2	8.8123	8.8099	8.8005	8.7665	0.0458	0.520
3	9.0449	9.0435	9.0356	9.0045	0.0404	0.447
4	7.0964	7.0936	7.0878	7.0738	0.0226	0.318
5	8.5391	8.5366	8.5311	8.5151	0.0241	0.281
30-mL vial						
1	74.8385	—	74.8253	74.7981	0.0404	0.054
2	63.1908	—	63.1794	63.1645	0.0263	0.042
3	52.1067	—	52.1026	52.0883	0.0184	0.035

sample was placed in the heater for a specified amount of time. At specified intervals, the robotic arm removed the 30-mL vial from the rack and shook the contents by rapid rotary movement and wrist rotation.

Approximately 2 min before the dissolution time expired, the robotic arm retrieves a 4-mL auto sampler vial and placed it in the carousel heater for preheating prior to sample transfer. These vials were disposable, eliminating the manual vial cleaning step. The 30-mL vial was removed from the heater and placed in the transfer station. The transfer station aspirated a 3.5-mL aliquot of solution and dispensed it in the hot 4-mL auto sampler vial. The auto sampler vial was crimp capped and placed in the carousel heater. The transfer station was then purged with clean TCB. These steps were repeated until all samples were prepared. Successful crimping at the small crimper was verified by moving the crimped vial in front of the nonferrous sensor. The sensor was necessary because gravimetric capping verification was not performed to minimized polymer precipitation due to cooling. Error recovery steps were initiated should the sensor fail to detect a cap. Sample preparation data generated by the system was stored on floppy disk. The data file format was readable by the GPC data acquisition software, a feature which minimized transcription errors.

Filtering of the solution prior to transfer into the auto sampler vial was desirable for some samples but was not necessary for this system. Automated filtration, using the Waters filtration cup, was incorporated on subsequent systems developed at Dow Chemical. In this sample preparation procedure, filtering was performed in the GPC prior to analysis with a filter installed on-line between the injector assembly and the GPC columns. However, provisions were to made to include the automated filtration in the event it becomes necessary.

When the run was completed the carousel rack was manually moved to the GPC oven for analysis. The floppy disk, containing the run data written by the robotic system, was manually loaded into the GPC data acquisition system.

Other Software Features

In addition to the procedure described above, the automated system was programmed to perform the tasks listed below:

1. Software and hardware versatility made it possible to automate other lab procedures. For example, room temperature GPC preparations and preparations with solvents other than TCB could be performed with the system.
2. The system was programmed to prepare calibration standard solutions directly into the 4-mL vials.
3. The analyst had the option of selecting a "serial" or "batch" mode of sample preparation. In the serial mode, the events of the preparation were timed so that each sample resided in the dissolution rack for the user specified dissolution time. The batch mode was analyst interactive. The analyst sent commands to the robotic controller when sample shaking and transferring were desired.
4. Completed samples were disposed of di-

Table II Manual Weighing Versus Automated System Weighing

	AE200 (manual) (g)	AE160 (robot) (g)	Difference (%)
Sample Wt	0.0395	0.0392	0.7595
	0.0350	0.0347	0.8571
	0.0341	0.0342	−0.2933
	0.0377	0.0379	−0.5305
	0.0375	0.0376	−0.2667
	0.0339	0.0340	−0.2950
	0.0287	0.0289	−0.6969
	0.0308	0.0307	0.3247
	0.0341	0.0340	0.2933
	0.0367	0.0373	−1.6349
TCB Wt	28.3792	28.3792	0.0000
	25.0949	25.0952	−0.0012
	24.7076	24.7080	−0.0016
	27.3931	27.3936	−0.0018
	27.2114	27.2112	0.0007
	24.5820	24.5814	0.0024
	20.8140	20.8142	−0.0010
	22.1965	22.1966	−0.0005
	24.5747	24.5750	−0.0012
	27.0078	27.0077	0.0004
Concentration	(mg/mL)	(mg/mL)	
	1.8192	1.8054	0.7595
	1.8229	1.8072	0.8583
	1.8038	1.8091	−0.2916
	1.7988	1.8083	−0.5287
	1.8012	1.8060	−0.2674
	1.8024	1.8078	−0.2974
	1.8022	1.8147	−0.6959
	1.8136	1.8077	0.3251
	1.8136	1.8083	0.2945
	1.7760	1.8051	−1.6353

rectly into a waste bucket by the robotic arm or moved back to the 30-mL vial rack for later reuse.

5. Menu selections were available for testing and configuring hardware for a run. Selections such as toggling the temperature controlling units ON/OFF, aligning rack positions, aligning robotics fingers, exercising the robotics arm, and choosing specific types of sample preparation procedures were all available in the software.
6. A magnetic switch mounted to the hood door detected whether the door was clear of the robotic arm prior to the start of a run.
7. The system could recover from most errors due to extensive run status checking by the software during operation.
8. Dissolution parameters such as temperature, time, and shaking frequency can be specified by the analyst prior to a run.

RESULTS AND DISCUSSION

Several experiments were conducted to determine the viability of the automated preparation procedure. Parameters investigated are listed below:

1. Determine if evaporation losses occurred when the vials were in the dissolution and auto sampler carousel heaters.
2. Determine the performance stability of the analytical balance located near an operating fume hood.
3. Determine if polymer degradation occurred in the dissolution heater and auto sampler carousel racks.
4. Compare data between well characterized manually prepared samples and samples prepared by the robot.
5. Determine dissolution reproducibility and reliability on relatively insoluble and thermally sensitive samples.
6. Determine the extent of cross-contamination between samples.
7. Evaluate the robotically prepared samples with the LALLS absolute molecular weight detector.

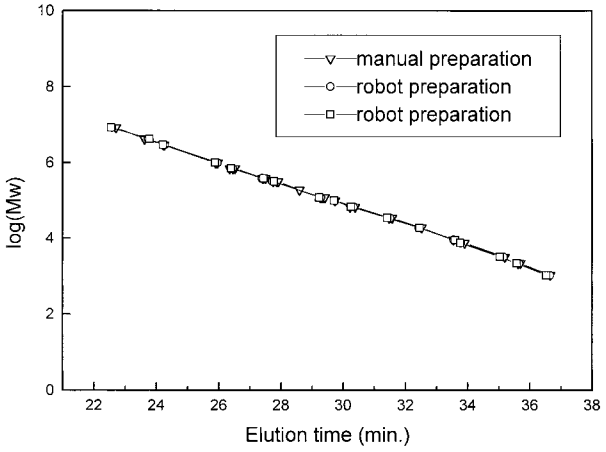

Figure 2 Comparison of GPC calibration curves plotted using manually prepared and robotically prepared narrow MWD polystyrene standards.

Table III GPC Data for High Density Polyethylene

$n = 9$	Concentration (g/mL)	Smoothed Area/1E4	Normalized Area/1E6	M_w (g/mol)	M_n (g/mol)	M_w/M_n
Mean	0.0020	978	4,869	271,126	6,389	42.491
SD	2.54E-6	24	123	7,268	302	1.515
RSD	0.25	4.98	5.07	5.36	9.45	7.13

Dissolution heating time is 480 min for all samples. RSD, relative standard deviation at 2 σ.

The first set of experiments evaluated the evaporative losses from the vials in the heaters. Significant evaporative losses can result in an unknown solution concentration and yield erroneous final results when detectors such as on-line light scattering units or viscometers, which require accurately measured sample concentration, are used. To determine if the vials were being crimp "sealed" sufficiently, the 4- and 30-mL vials were filled with varying volumes of TCB and checked gravimetrically for evaporation losses. The evaporation results are listed in Table I. After 23 h of heating at 150°C, a marginal total weight loss of 0.5% occurred in the 4-mL vials, indicating the seal was comparable to the seal obtained manually. The weight loss from the 30-mL vials was much smaller. Samples were rarely maintained at elevated temperatures for 23 h prior to analysis.

Next, the precision and accuracy of the system's analytical balance was investigated. The balance was positioned in close proximity to an open fume hood door. Vibrations and air currents generated by the fume hood could contribute to poor balance performance. Inaccurate gravimetric data generated by the balance would affect both system performance and the accuracy of the sample concentrations. To minimize instability errors the system took multiple balance readings and used an average weight value. Also, tare commands were not used to zero the balance. The software obtained all weight data by subtraction of the balance reading prior to loading. To evaluate balance performance, several polymer samples were prepared by the robot. The sample weights were compared to those obtained manually on another analytical balance (Mettler AE200). The data in Table II demonstrate the agreement between both procedures. This suggested that the automated system balance was weighing reliably in front of the operating fume hood.

The robot's ability to reproducibly prepare calibration standards was evaluated. Standard preparation involved manually adding the polymer standard(s) to the 4-mL vial followed by automated TCB addition, crimp capping, and placement into the heated carousel rack. The calibration curve generated for robotically prepared standards was compared to the calibration curve obtained from manually prepared standards. The calibration curves shown in Figure 2 were superimposable. The automated system did not degrade the standards during the preparation steps.

Experiments were also conducted to determine if the robotic system could dissolve intractable samples (i.e., high molecular weight, highly crystalline polymers) or prepare samples that have a tendency to degrade. A variety of different types of polymer samples were chosen for these studies. All samples were analyzed using the GPC conditions outlined in the Experimental Section. To assess system performance for relatively insoluble samples, a high density polyethylene (HDPE, Asahi Chemical) film grade resin was used. This polymer had a bimodal molecular weight distribu-

Table IV GPC Data for Chlorinated Polyethylene, 25% CI

$n = 10$	Concentration (g/mL)	Smoothed Area/1E4	Normalized Area/1E6	M_w (g/mol)	M_n (g/mol)	M_w/M_n
Mean	0.0027	521	1,923	133,010	19,720	6.759
SD	4.31E-6	20	72	3,240	1,083	0.320
RSD	0.32	0.32	7.50	4.87	10.98	9.46

Dissolution heating time is 240 min for all samples. RSD, relative standard deviation at 2 σ.

Table V GPC Data for Linear Low Density Polyethylene

$n = 10$	Concentration (g/mL)	Smoothed Area/1E4	Normalized Area/1E6	M_w (g/mol)	M_n (g/mol)	M_w/M_n
Mean	0.0030	2,366	7,859	119,680	30,470	3.932
SD	2.83E-6	62	208	1,451	1,158	0.127
RSD	0.19	0.19	5.30	2.43	7.60	6.44

Dissolution heating time is 270 min for all samples. RSD, relative standard deviation at 2 σ.

tion with a large fraction of very high molecular weight material. The high molecular weight and high crystallinity made this sample one of the more difficult types of polyethylene to dissolve. Table III shows the results obtained for this sample repetitively prepared and characterized.

Table IV lists the results obtained for a typical chlorinated polyethylene (CPE, Tyrin™ 25% chlorine The Dow Chemical Company) sample. The CPE polymer represented a sample with low refractive index detector signal and one that could degrade with extensive heating. For example, 25% CPE had a dn/dc value < 0.05 mL/g at 633 nm in TCB at 145°C. (at $\sim$ 40% chlorine, CPE/TCB solutions and the TCB mobile phase are isorefractive). In addition, the CPE polymer verified if adequate mixing occurred during the shaking routine. CPE had a tendency to stick on the upper part of the dissolution vial, especially above the solvent level. Shaking was crucial to ensure complete dissolution. The reproducibility of the molecular weight moments and the detector area counts demonstrated that the CPE was not degraded by the automated sample preparation. Also, reproducible detector area counts for both samples indicated that the sample concentrations were reproducible. It should be noted that polymer dissolution is governed by the temperature, time, and degree of shaking. All of these parameters were defined by the analyst via the software interface prior to the start of a run.

To test the system's accuracy, multiple solutions were prepared from two different lab standards. The standards were a linear low density polyethylene (LLDPE, Dowlex™ The Dow Chemical Company) and polystyrene (Dow 1683). Tables V and VI list the GPC results obtained for these polymers. Dow 1683 has an accepted weight average molecular weight (M_w) of 250,000 g/mol. The generally accepted M_w for the LLDPE within Dow Chemical is 120,000 g/mol. Excellent agreement was obtained for both polymers. The precision in M_w (1.3% RSD for Dow 1683 and 2.4% RSD for LLDPE) demonstrated the data reproducibility.

Table VII shows typical results after a manual preparation of the LLDPE sample. Note the variation in the sample concentrations. This variation reflected mainly differences in sample pellet mass. Of course, the analyst could prepare the samples with nearly identical concentrations but it is very impractical in a lab where hundreds to thousands of samples are analyzed regularly. For example, sample pellets could be cut, but this may compromise the sampling procedure. Alternatively, solvent volumes could be manually adjusted, making the process more time consuming. Comparison of the data in Tables III–VI, and especially Table V, with the data in Table VII demonstrate that the automated preparation meets or exceeds the reproducibility of the manual preparation.

It should be noted here that error in the molecular weight moments, particularly M_n and M_z, are

Table VI GPC Data for Polystyrene Standard Dow 1683

$n = 14$	Concentration (g/mL)	Smoothed Area/1E4	Normalized Area/1E6	M_w (g/mol)	M_n (g/mol)	M_w/M_n
Mean	0.0050	573	1,140	250,521	99,893	2.508
SD	1.05E-5	11	21	1,683	1,099	0.030
RSD	0.42	3.82	3.66	1.34	2.20	2.38

Dissolution heating time is 1 h for all samples. RSD, relative standard deviation at 2 σ.

Table VII GPC Data for Linear Low Density Polyethylene, Manually Prepared Samples

n = 10	Concentration (g/mL)	Smoothed Area/1E4	Normalized Area/1E6	M_w (g/mol)	M_n (g/mol)	M_w/M_n
Mean	0.00162	1,272	7,851	124,680	31,220	3.998
SD	2.49E-4	203	318	3,147	1,207	0.155
RSD	30.74	31.93	8.11	5.05	7.73	7.74

Dissolution heating time is 270 min for all samples. RSD, relative standard deviation at 2 σ.

somewhat sample dependent regardless of the sample preparation method. Data in Tables III–VII illustrate this point, with a higher uncertainty in M_w for the CPE sample than for the LLDPE sample. This occurred in part because of differences in detector response for a given polymer–solvent combination. Also, the M_n and M_z moments were very baseline selection dependent.[5] Samples with a broad MWD (HDPE film resin) or a poor detector response (CPE due to a low dn/dc value in TCB) had a higher error associated with the molecular weight moments.

Sample cross-contamination was also addressed. During a run, an aliquot of a solution was pulled into the holding reservoir at the transfer station, prior to dispensing into the 4-mL auto sampler vial. Failure to flush the reservoir before transferring the next sample could lead to contamination of the sample. The primary concern was that residual solution left in the reservoir could evaporate and leave a residue of polymer and/or additives adhering to the wall. Also, the transfer station could become plugged, making the station inoperable. The holding reservoir was therefore purged with fresh TCB between samples. To ensure effective purging between solutions, several samples with large differences in composition, molecular weight, and molecular weight distribution were prepared in sequence. The samples were different enough that significant contamination would be easily discernible in the detector response. For example, Figure 3 shows an overlay of the refractive index detector responses for HDPE (very broad MWD polyethylene), PS 1683 (broad MWD polystyrene), and NBS 1483 (narrow MWD polyethylene). No deleterious cross-contamination was detected in the samples.

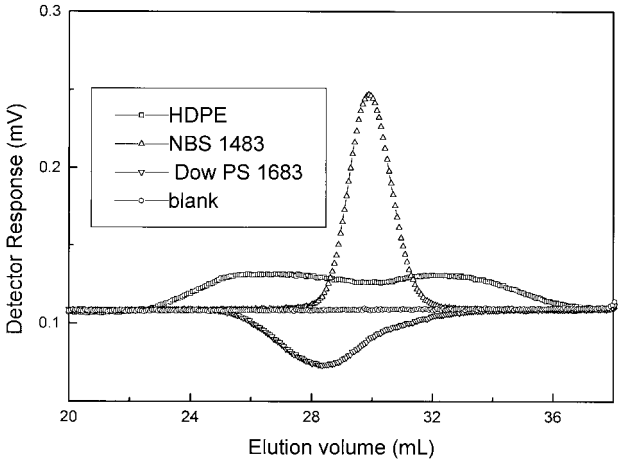

Figure 3 Detector overlays of samples prepared in sequence by the robotic procedure. These traces show that no detectable cross-contamination occurred during the preparation.

The characterization of polymer solutions requires complete dissolution and often *how* the solution was prepared and treated is important when interpreting the experimental results. This is particularly true for polyethylene solutions which are notorious for yielding spurious results in GPC, GPC-LALLS and traditional light scattering experiments, depending upon how the solution was treated prior to analysis. Kratochvil[6] made clear the need for molecular dissolution in light scattering characterization and pointed out the difficulties encounted with polyethylene samples. One example[7] involved the dissolution of NBS LDPE standard 1476, where light scattering molecular weight results were dependent upon sample treatment. Sometimes conventional concentration sensitive detectors can miss the differences that are introduced by the sample preparation procedure. The LALLS photometer, being an absolute molecular weight detector (for the M_w moment), was a good tool to use for evaluation the automated sample preparation. Some researchers[8,9] even use it to determine when molecular dissolution has occurred prior to characterization by observing the absence of "spiking" due to polyethylene "super aggregates" or "microgels."

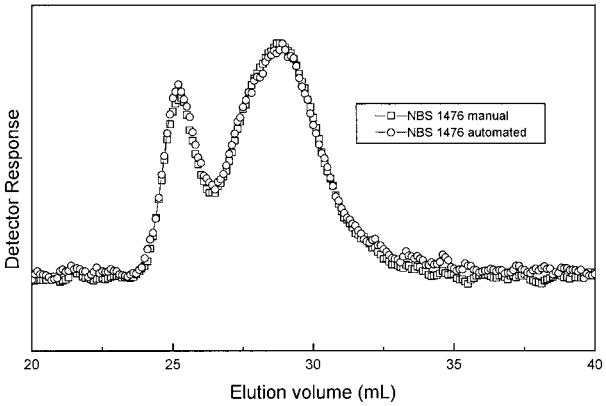

Figure 4 LALLS detector overlays of manually vs automated prepared samples. Sample is NBS 1476 LDPE prepared at ca. 4.2 mg/mL. LALLS M_w, manual; 140,600 g/mol. LALLS M_w, automated; 146,900 g/mol.

For our purposes, it was most important to have good reproducibility in the sample preparation, so that data could be confidently compared over long periods of time. Identical samples prepared manually and by the automated system at the same concentration should give identical peak areas under the LALLS response if the sample preparation procedures do not introduce artifacts (the most likely one being that the samples were not fully dissolved). Figure 4 shows an unsmoothed LALLS overlay of the data and the absolute M_w. The detector responses were nearly identical as were the M_w values calculated from the LALLS responses. This indicated that the automated sample preparation did not add an "artifact" to the data. In our experiences since system implementation, other data collected using the LALLS photometer have been consistent with this result.

ADDITIONAL HARDWARE MODULES

Several robotic polymer sample preparation systems have been developed at Dow Chemical based on the robotic system described in this manuscript. Those systems have included similar functionality plus additional capabilities. These capabilities included room temperature filtration using disposable membrane disk filters, centrifugation, and linear shaking at elevated temperatures. Other enhancements included run information and automated data transfer from the robotic system to an Excel v. 4.0 spreadsheet utilizing Windows' v.3.1 (Microsoft Corporation) dynamic data exchange (DDE) capabilities. These capabilities can be installed in the system reported here as needed.

CONCLUSIONS

Using a Zymate XP robotic arm, various Zymark peripherals, and peripherals designed in-house, a system has been assembled to automate all steps of the high-temperature GPC sample preparation.

The system was capable of handling a variety of different polymers. The agitation of the samples was sufficient to dissolve high-molecular-weight polymers. The ability to accurately control the temperature and dissolution time was sufficient to prevent degradation of the thermally unstable polymers. Excellent reproducibility was obtained for sample concentrations and molecular weight moments of the samples used to evaluate the robotic preparation. Data reproducibility obtained from samples prepared by the automated procedure was comparable or better than data obtained from manually prepared samples.

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