

Gel permeation chromatography followed by pyrolysis–gas chromatography–mass spectrometry via a solvent-evaporative interface

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Abstract

The measurement of chemical composition as a function of molecular weight has always been a challenge for analytical chemists. In this paper, we present a unique way to combine gel permeation chromatography (GPC) with pyrolysis–gas chromatography–mass spectrometry (Py–GC–MS) for this purpose. A commercially available solvent-evaporative interface, originally designed for GPC–IR measurements, was used to deposit the eluent of GPC onto aluminum foil. Small strips of aluminum foil were cut and subjected to Py–GC–MS analysis. Compared with the GPC–IR measurements, the proposed technique offers the advantage of being able to distinguish between structurally similar monomers in a complex copolymer. As an example, a copolymer composed of four monomers was analyzed. The results clearly demonstrate that this technique can be applied to complex polymeric systems to yield information regarding chemical heterogeneity versus molecular weight.

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1. Introduction

The properties of a polymeric system depend on its chemical composition and its molecular weight. Furthermore, the properties depend on how the chemical composition is distributed across the molecular weight. The chemical composition versus molecular weight also reflects the history of how the polymer was synthesized. It has been the desire of many analytical chemists to measure the chemical composition as a function of molecular weight. This is sometimes achieved by preparative gel permeation chromatography (GPC) followed by spectroscopic characterization of isolated fractions [1,2]. However, preparative GPC is usually tedious and consumes a large amount of mobile phase. GPC–NMR is an emerging technique that is well-suited for

composition versus molecular weight study. However, in many occasions expensive deuterated mobile phases have to be used and sensitivity is always a concern (see for example [3]). Attempts to use on-line IR detection with flow cells have not been very successful due to IR-opaque mobile phase resulting in limited spectral windows [4–9]. A commercially available solvent-evaporative interface (LC-transform by Lab-connections) offers a much more economical and faster alternative [10–13]. This solvent-evaporative interface collects the eluent of a GPC experiment on a rotating germanium disc or a moving MALDI plate. The germanium disc could be subject to IR analysis while the MALDI plate could be used for TOF mass detection. This GPC–IR coupling or GPC–MALDI TOF requires only one GPC run, thus reducing the experiment time and mobile phase consumption significantly. Since its discovery and commercialization, this solvent-evaporative interface has been used widely to investigate chemical composition as a function of molecular weight.

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MALDI-TOF does not provide compositional information directly—it provides molar mass. GPC-IR experiments do provide information on chemical composition versus molecular weight. One disadvantage of GPC-IR experiments is the difficulty in handling copolymers composed of more than three types of monomers. Another disadvantage of the GPC-IR experiments is the difficulty to distinguish between structurally similar monomers by IR spectroscopy in a copolymer. For example, in a random copolymer of methyl acrylate, methyl methacrylate and methacrylic acid, it is difficult to distinguish methyl acrylate from methyl methacrylate by IR information alone. Yet the properties of polymers made from structurally similar monomers could be dramatically different. Poly(methyl acrylate) has a glass transition temperature that is almost 100 °C lower than that of poly(methyl methacrylate) [14]. Many commercial styrene acrylic copolymers in printing and coating industry are composed of four or five monomers, of which, some are likely to have a high degree of structural similarity. When dealing with these complex copolymers, the two disadvantages of GPC-IR combine to make it unlikely that complete information on composition versus molecular weight can be obtained. We found it necessary to develop an alternative analytical method to enable consistent differentiation between structurally similar monomers in a complex polymer system.

Pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS) has proven to be a powerful tool in the compositional analysis of a copolymer [15–17]. During pyrolysis under inert atmosphere, copolymers often decompose to monomers and other information-rich fragments. These monomers and fragments are then separated by GC, before identification by MS. Compared with IR spectroscopy, Py-GC-MS can differentiate structurally similar monomers. A combination of GPC with Py-GC-MS described here is thus highly desirable because it allows us to monitor the composition of structurally similar monomers as a function of molecular weight.

In this paper, we employ a Py-GC-MS detection for GPC experiments using only commercially available instruments. The solvent-evaporative interface was used to deposit the eluent of GPC experiments on conventional aluminum foil, leaving a trace of polymer residue resolved by GPC. Small strips of aluminum foil were then cut at selected GPC retention times, corresponding to different molecular weights. The effect is a “micro-preparative GPC”. The aluminum strips, along with the polymer residue, were analyzed directly by Py-GC-MS.

As a test of the proposed technique, we applied such a combination of GPC with Py-GC-MS to the analysis of a styrene-acrylic polymer of known composition. The polymer was prepared from four monomers, two of which are structurally similar. With one GPC run, we derived information on polymer chemical composition as a function of molecular weight. Discussions and suggestions are also included on the potential improvements of this technique.

2. Experimental

2.1. Material

The material studied in this paper was a resin-supported emulsion. For the purpose of this paper, we simply regard it as a polymer emulsion that consists of a high molecular weight latex and a low molecular weight resin. The resin was a random copolymer of styrene, α -methyl styrene and acrylic acid; the latex was a random copolymer of styrene and 2-ethylhexyl acrylate. These polymer subjects were dispersed as an emulsion, with ~40% (wt.) solid and ~60% water.

2.2. GPC experiments

The GPC experiments were performed using a Waters 2690 pump and on two sequentially-connected 10 μ m, 300 mm \times 7.5 mm styrene di-vinylbenzene columns from Polymer Laboratories. The mobile phase was THF flowing at 1.0 cm³/min. The detector for the GPC was a Waters 996 PDA detector. The GPC sample was prepared by dissolving ~0.7 g of co-polymer emulsion in 10 cm³ of THF. The injection volume was 15 μ l.

2.3. GPC eluent collection

We used an LC-transform series 400 (manufactured by Lab-connections, Northborough, MA, USA) to collect the eluent from GPC. In preparation for each GPC experiment, the LC-transform germanium disc was completely covered by a piece of Al foil. The Al foil was wrapped around the disc in a way that firmly secured this foil to the disc, and left a smooth Al surface on the disc. The opaque side of the Al foil was used to collect the polymer residue. It was found that the opaque side provided more adhesion than the glossy side did, possible due to the surface roughness on the opaque side.

The eluent from the PDA detector was introduced into the LC-transform without splitting. The sheath gas was N₂ at a flow rate of 3.4 l/min. The sheath gas temperature was set at 180 °C. The germanium disc was rotating at 10 °/min. After the GPC run, seven aluminum strips with a width of 1 mm and a length of ~5 mm were cut radially across the polymer trace. (An example of how the Al strips were cut is shown in Fig. 2.) The 1 mm width corresponded to an angle of 1.7° and a GPC retention time of 10 s. The centers of the aluminum strips were chosen at GPC retention times of 12, 13, 14, 15, 16, 17 and 18 min.

The GPC-IR experiments were performed using the same GPC and LC-transform devices under the same instrument conditions as described above. The only difference was that in the GPC-IR experiments, the germanium disc was used to collect the GPC eluent directly without Al foil.

2.4. Py-GC-MS experiments

The pyrolyzer used was a CDS PII pyroprobe 2000 (manufactured by CDS Analytical, Oxford, PA) attached to the

GC. The GC–MS system was an HP 5890 II GC with an HP 5965B IRD and an HP 5972 MSD with an ion detection range of 33 Daltons to 450 Daltons. The GC column was a 30 m HP-5 column with He as the eluting gas. The He flow rate was set at constant 1 ml/min. To keep the paper precise, we will present the data from IRD in a separate communication. The IRD data are consistent with the MS data in all aspects.

In preparation for each Py–GC–MS experiment, one Al strip was carefully placed in the quartz tube of the pyrolyzer liner along with some quartz wool. The Al strip was held in position in the tube by the quartz wool in a location that corresponded to the middle of the pyrolyzer coil. The pyrolyzer coil was heated to 710 °C for 10 s at the beginning of the GC run. The GC oven started at 50 °C, ramping to 200 °C at 10 °C/min. The whole GC run took 20 min. Afterward, it was observed that the aluminum strip had been deformed due to melting.

3. Results and discussion

The molecular weight distribution of the material studied is shown in Fig. 1. The GPC chromatogram gives a bimodal distribution—a peak and a shoulder. The early eluting peak has a retention time of 14.4 min at the peak maximum, corresponding to the latex. When calibrated against polystyrene standards, the peak molecular weight is about 22,600 Da. The shoulder does not show a clear peak maximum due to overlapping with the earlier eluting peak. If we assign a peak maximum retention time of 17.0 min, this would correspond to a molecular weight of 10,000 Da if calibrated against polystyrene standards. The small peaks from 19.5 to 24 min are oligomers and other low molecular weight materials present in the emulsion.

The GPC effluent of the above material was directed into the solvent-evaporative device (LC-transform) where it was

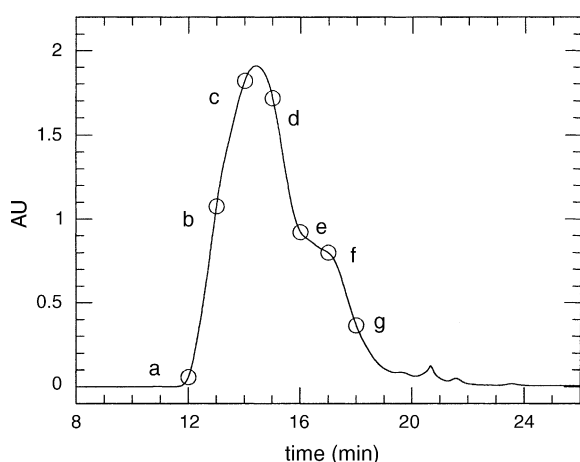


Fig. 1. GPC chromatogram of the polymer emulsion sample from the UV detector. The chromatogram was obtained at a UV wavelength of 254 nm. Circles indicate the positions where Py–GC–MS experiments were performed. AU stands for absorption units.



Fig. 2. An example of an Al foil covered collecting disc. In this example, six strips of Al foil were cut at 20°, 30°, 40°, 50°, 60° and 70° for Py–GC–MS analysis. The width of the Al strips is 1 mm.

deposited onto the Al foil covered germanium disc. Shown in Fig. 2 is an example of an Al foil covered germanium disc. By close-examination of the picture one can see a white trace parallel to the edge of the disc. This trace is the polymer residue, resulting from the separation by GPC. Using a razor blade, seven equal-width strips (a–g in Fig. 1) across the polymer residue trace were cut from the Al foil and were subjected to Py–GC–MS experiments. Each of the seven strips carried polymer residues corresponding to a specific retention time range.

We first attempted to combine GPC with Py–GC–MS by using the solvent-evaporative device (LC-transform) without the Al foil. At the advice of the LC-transform manufacturer, we tried to scrape selected sections of the polymer residue off the germanium plate with a razor blade. But often the polymer residue shattered into small pieces or the whole trace of the polymer residue was torn off. We also tried to wash off selected sections of polymer residue from the germanium plate. A micro-syringe was used to dispense a small drop of solvent onto a targeted section of the polymer trace. After allowing time for solubilization, the resulting solution was withdrawn into the micro-syringe. But, it was difficult to ensure complete removal of polymer in selected regions and it was almost impossible to control the size of the wash-off spot. The use of Al foil solved all the above problems, allowing complete isolation of small selected sections of the polymer trace with ease.

The Py–GC–MS analysis of individual Al strips reveals monomer composition present at various retention times. As an example, we present in Fig. 3 the Py–GC–MS results of point c in Fig. 1. The top trace of Fig. 3 is the total ion count chromatogram. The peaks in the top trace were identified by their MS spectra. As an example, shown in the bottom trace of Fig. 3 is the mass spectrum of peak 2. This mass spectrum is consistent with a library spectrum of styrene. A small peak at ~3 min in the top trace did not give a good

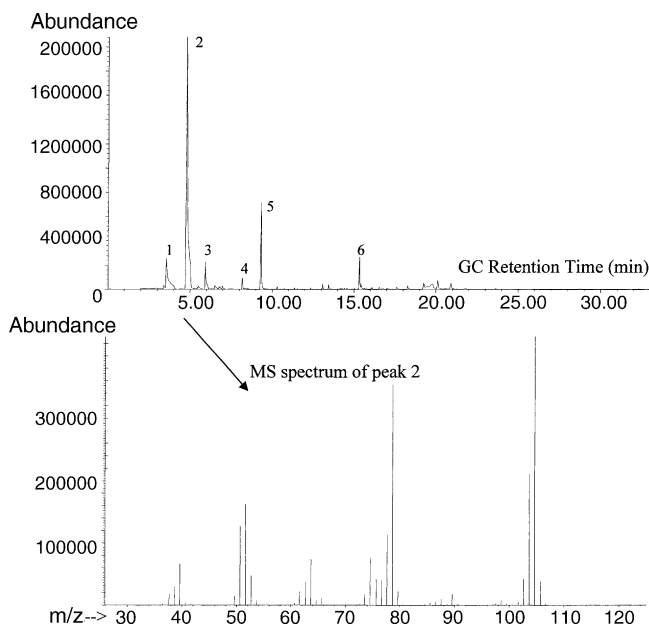


Fig. 3. The Py-GC-MS results on point c in Fig. 1. *Top trace*: The total ion count chromatogram of point c in Fig. 1. *Peak identities*: (1) 2-ethyl-1-hexene; (2) styrene; (3) α -methyl styrene; (4) 2-ethylhexyl acetate; (5) 2-ethylhexyl acrylate; (6) styrene dimer. *Bottom trace*: The MS spectrum obtained on peak #2 in the top trace.

quality mass spectrum. But this small peak showed 55 ion and 72 ion-indications of acrylic acid. The other monomers we identified at point c in Fig. 1, according to the MS spectra, are α -methyl styrene and 2-ethylhexyl acrylate. In addition to these monomers, we also observed 2-ethyl-1-hexene and 2-ethylhexyl acetate, which are pyrolysis products of 2-ethylhexyl acrylate. Styrene dimer is also present, providing further indication that the composition at point c in Fig. 1 contains styrene.

We further examined the Py-GC-MS results across all seven points in Fig. 1. Point c in Fig. 1 comes before the peak maximum of the latex peak. It is the resin not the latex which was prepared from α -methyl styrene. Yet we observed α -methyl styrene as one of the monomers at point c. This suggests that there is a certain amount of resin present even at point c in Fig. 1, showing that the molecular weight distribution of the resin is quite broad. The same broad molecular weight distribution is also true for the latex. We observed the monomers from both the resin and the latex at all seven Al strips.

In order to compare the proposed GPC Py-GC-MS experiment with the conventional GPC-IR experiment, we also performed the GPC-IR experiment using LC-transform on the same polymer emulsion. Shown in Fig. 4 is the IR spectrum at point c in Fig. 1. Fig. 4 shows aromatic C-H stretching between 3000 to 3200 cm^{-1} and aliphatic C-H stretching from 2700 to 3000 cm^{-1} . Also in Fig. 4 there is a C=O peak at $\sim 1700 \text{ cm}^{-1}$. Around 700–800 cm^{-1} there are two peaks from mono-substituted aromatic C-H bending. It could be derived from Fig. 4 that the composition at point c is

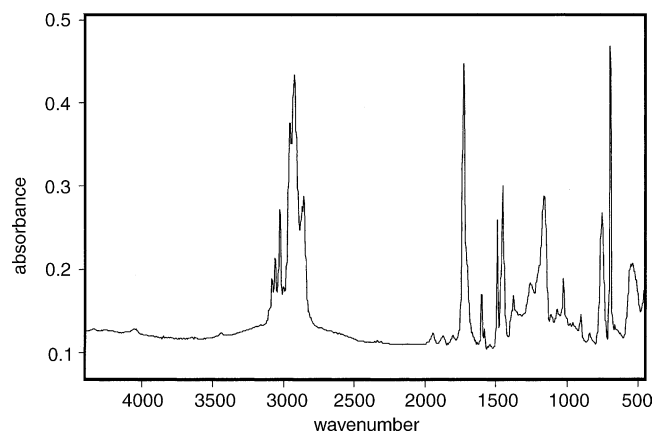


Fig. 4. The IR spectrum of point c in Fig. 1 (obtained from GPC-IR experiment).

styrene-acrylic in nature. However, it is difficult to identify the monomer composition from Fig. 4 alone.

One advantage of our GPC Py-GC-MS combination over the original GPC-IR is illustrated by a comparison of Figs. 3 and 4. In Fig. 3, all four monomers were effectively separated by Py-GC before the MS detector unambiguously identified them. In the contrast, Fig. 4 does not provide adequate information for the identification of all the monomers. We will further attempt to measure the ratio change of these monomers as a function of molecular weight with the GPC Py-GC-MS combination.

The chemical composition of a copolymer is determined by the monomer percentages. To monitor the chemical composition change versus molecular weight, we look at the change of monomer ratios versus GPC retention time. From the top trace of Fig. 3, we could obtain peak area of the individual monomers, except acrylic acid. Due to the poor signal to noise ratio, acrylic acid did not always give a peak in the TIC chromatograms. We thus constructed single ion chromatograms using the acrylic acid parent ion ($m/z = 72$). From the 72 ion chromatogram we extracted the peak areas and use them to represent acrylic acid. Table 1 lists the peak areas of the four monomers and 2-ethyl-1-hexene. The ratios of peak area were then calculated at all seven points in Fig. 1, using the numbers in Table 1. Shown in Fig. 5 is the ratio of 2-ethylhexyl acrylate to styrene, as a function of GPC retention time. The ratio decreases with the GPC retention time. The ratios of 2-ethylhexyl acrylate to α -methyl styrene and 2-ethylhexyl acrylate to acrylic acid also decrease with the GPC retention time. Ratios of 2-ethyl-1-hexene to other monomers show the same trend. All of these indicate that 2-ethylhexyl acrylate is more abundant at higher molecular weight than at lower molecular weight, consistent with the fact that 2-ethylhexyl acrylate was included in the preparation of the high molecular weight latex but not the low molecular weight resin.

Among the four monomers in this copolymer, styrene and α -methyl styrene are structurally similar. The separation of these two monomers by Py-GC allowed us to study the ratio

Table 1
Peak areas of pyrolysis products from MS chromatograms

	Corresponding position in Fig. 1						
	a	b	c	d	e	f	g
Acrylic acid parent ion	BDL	2.9 E3	8.3 E3	1.7 E4	1.0 E4	1.2 E4	6.8 E3
2-Ethyl-1-hexene	1.3 E6	8.9 E6	2.2 E7	3.9 E7	7.8 E6	1.4 E6	1.5 E5
Styrene	9.9 E6	6.2 E7	1.4 E8	2.7 E8	5.9 E7	2.0 E7	6.3 E6
α -Methyl styrene	8.8 E5	4.3 E6	9.6 E6	1.9 E7	1.2 E7	1.6 E7	7.1 E6
2-Ethylhexyl acrylate	1.6 E6	1.3 E7	2.6 E7	5.1 E7	1.1 E7	1.7 E6	1.8 E5

BDL stands for "below detection limit".

of these two monomers as a function of molecular weight. The results are presented in Fig. 6. To obtain the ratio of α -methyl styrene to styrene from the GPC-IR experiments, one needs to distinguish styrene from α -methyl styrene in IR spectra, such as shown in Fig. 4. This is difficult if not impossible. Being able to differentiate structurally similar monomers is another advantage of GPC Py-GC-MS combination over GPC-IR.

According to Fig. 6, the ratio of α -methyl styrene to styrene increases as a function of GPC retention time. The

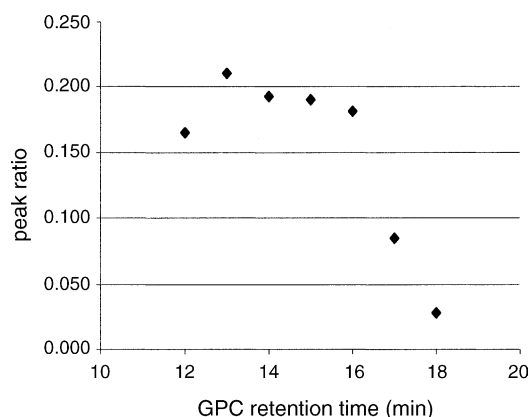


Fig. 5. The peak area ratio of 2-ethylhexyl acrylate to styrene vs. GPC retention time. Ratios were obtained from MS chromatogram peak areas in Table 1.

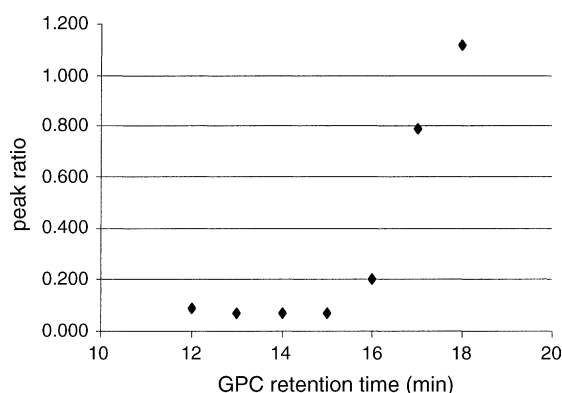


Fig. 6. The peak area ratio of α -methyl styrene to styrene vs. GPC retention time. Ratios were obtained from MS chromatogram peak areas in Table 1.

ratio of α -methyl styrene to 2-ethylhexyl acrylate was also found to increase as a function of GPC retention time, while the ratio of α -methyl styrene to styrene was unchanged versus GPC retention time. Analysis of these three peak ratios lead us to conclude that α -methyl styrene was more abundant at lower molecular weight than at higher molecular weight. This is understandable and is expected as α -methyl styrene was present only in the preparation of the low molecular weight resin.

As illustrated above, all the possible monomer area ratios were generated from Table 1. This accounts to six possible monomer/monomer area ratios. In addition, area ratios of 2-ethyl-1-hexene to monomer area were taken into account. We considered how these ratios changed as a function of GPC retention time. The analysis showed that acrylic acid is more abundant at lower molecular weight than at higher molecular weight. Styrene seems to exist significantly both at lower and higher molecular weight. Overall, the information on chemical composition versus molecular weight obtained from the analysis agrees well with the fact that the copolymer was made of a latex and a resin with previously mentioned compositions. This validates the combination of GPC with Py-GC-MS as a convenient tool in the study of chemical heterogeneity versus molecular weight.

Our intention was to demonstrate the technique on an uncomplicated model of known composition. Although shown on a four-monomer copolymer, this GPC Py-GC-MS combination will also be applicable to more complex systems since GC is capable of resolving many monomers with one run. All monomers can be resolved using various GC conditions, including different GC columns and different oven temperature programs. The potential of Py-GC has been explored and is well-established for other polymers such as polyimides, epoxy and polydienes [15,17,18]. It is foreseeable that this GPC Py-GC-MS combination can also be applied to non-styrene-acrylic polymers. Recently Py-GC-MS has been applied to large bio-molecules [19]. The combination of HPLC and Py-GC-MS with application on bio-molecules is also worth exploring.

This technique could be further improved with more efforts. We have only been able to monitor the trend in polymer composition versus molecular weight. However, the weight percentages of monomers versus molecular weight could be available based on suitably obtained detector response which can be derived from Py-GC analysis of standard materials.

Also, other pyrolysis instruments such as Curie-point pyrolyzers might offer some advantages over the heat resistance pyrolyzer used in this paper. This is because a Curie-point pyrolyzer operates at designated Curie temperatures and with consistent pyrolysis temperature, we expect better quantitative information.

4. Conclusions

The combination of GPC and Py–GC–MS above can be viewed as a two dimensional chromatography with an identification detector. Each experiment generates one set of 4-D data. The four dimensions are GPC retention time, GC retention time, m/z ratio and ion count. Like virtually all experimentally generated 4-D data, one dimension is discrete, which helps to reduce the data size and the time required to generate the data. This brings up one disadvantage of the GPC Py–GC–MS combination when compared to the traditional GPC–IR. In traditional GPC–IR, chemical composition can be studied as a continuous function of molecular weight. In the GPC Py–GC–MS combination, the GPC retention time dimension is discrete. Nevertheless, we can selectively focus on any retention times that are more interesting than others.

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