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Number-average molecular mass determination of polymeric material by pyrolysis–gas chromatography

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Abstract

The number-average molecular mass of a polymeric material has been determined by pyrolysis–gas chromatography (Py–GC) via end-group analysis. The major advantage of this technique is that no sample preparation is required. The sample is not required to be in the dilute solution form, and the amount of sample needed is approximately 0.5 mg. Phenyl group-terminated polybutadiene systems have been studied as an example. The application of Py–GC to obtain the end-group concentration, the number-average molecular mass and the limitations of this method are discussed in detail. The success of this development elevates the role of Py–GC as an important technique for end-group analysis for the determination of number-average molecular mass.

Keywords: Molecular mass; Pyrolysis; Polymers; Polybutadiene

1. Introduction

There are many different approaches to measure the molecular mass of polymeric materials. These approaches can be roughly divided into three categories. The first is the measurement of number-average molecular mass (M_n). Techniques such as end-group analysis [1], membrane osmometry, vapor pressure osmometry [2], reflex index measurement [3], cryoscopy and ebulliometry [2] have been used. The second is the measurement of weight-average molecular mass (M_w) via light scattering [4] and ultracentrifugation [5]. The other is the measurement of molecular mass and its distribution by gel permeation chromatography [6], fractional precipitation [7] and ultracentrifugation [8]. However, in almost all of these techniques, the measurement is performed using dilute solutions of the polymer. In many circumstances, there is a need for a molecular mass determination method that can operate under a solid-phase condition.

In the measurement of M_n, end-group analysis is a widely used method. The key procedure of this M_n determination via end-group analysis is the concentration measurement of the end-group or end-group-containing molecules. There are many methods available to do end-group analysis [9]. These techniques include: (1) titration of a special functional group; (2) elemental analysis of element-specific end-groups; (3) measurement of radioactive-tagged end-groups [10]; and (4) spectroscopic determination of an end-group [11].

The experimental approach for determination of M_n via end-group analysis can differ for condensa-

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tion polymers and addition polymers [12] because of the difference in the types of end-groups usually found. In condensation polymers, the end-groups normally refer to the functional groups in the monomers. The concentration of unreacted functional groups (normally at the end of the chain) can be correlated back to the number of chains in a given amount of polymer. The M_n can be elucidated from that calculation (mass of polymer divided by moles of chains). In addition polymers, the polymeric chain may be end-capped by a molecule with a special functional group. The purpose of this end-capping may be to stabilize the chain to prevent further polymerization reaction [13], to improve a physical property such as chemical resistance [14], or to have this group available for further reaction such as grafting. These end-group molecules are normally introduced in the initiation step of polymerization and/or at the termination step of polymerization. The end-groups are normally different from the repeating units in the polymers. The M_n can be determined by the concentration of end-group or end-group-containing molecules in a given amount of polymer.

Pyrolysis–gas chromatography (Py–GC) [15] is an important technique used for polymer analysis. Py–GC is a technique that uses thermal energy (pyrolysis) to break down a polymeric chain to monomers, oligomers and other fragments, followed by the separation of pyrolysates with GC and detection with appropriate detection methods. Flame ionization detection (FID) is one of the most frequently used detection methods for quantitative analysis of pyrolysates. Mass spectrometry (MS) or mass-selective detection is one of the most commonly used detection methods for identification. The intensities of monomers or monomer-related fragments are commonly used to obtain compositional data [16]. The oligomers or oligomer-related fragments are used to elucidate microstructure information [17].

Py–GC has been used to determine the number-average molecular mass via end-group analysis. The M_n of polyacetylene has been studied through a radiotagging method [10]. In recent years, the M_n of several thermoplastic resin such as polystyrene [18], poly(methyl methylacrylate) [19,20], polycarbonate [21] have also been investigated. The Py–GC approach is similar to other techniques, the only difference is the end-group and monomer concentrations are measured by Py–GC. However, certain thermoplastic resin such as polybutadiene may cross-link after high-temperature processing or long-term radiation aging. If cross-link happened, all traditional approaches (form dilute solution) will become inadequate. The advantage of Py–GC in the M_n determination via end-group analysis has the ability of analyzing cross-linked polymers.

In this study, a set of phenyl group-terminated polybutadienes (PBDs) with different M_n has been studied by Py–GC for the development of M_n determination method via end-group analysis. The major advantage of this technique is that no sample preparation is required. The major drawback of this technique is that not every polymeric material contains distinguishable end-groups that can be utilized for M_n determination. The application of Py–GC for determination of M_n and the limitations of this method are discussed in detail. The success of this development elevates the role of Py–GC as an important technique for end-group analysis for the determination of number-average molecular mass.

2. Experimental

2.1. Polymers

All PBD polymers (catalog Nos. 435, 436 and 437) were purchased from Scientific Polymer Products (Ontario, NY, USA). The M_n of PBD polymers have been determined by a size-exclusion chromatography (SEC) method which uses the polystyrene molecular mass standards to obtain the calibration curve. The phenol-terminated polycarbonate was obtained from GE Plastics (Pittsfield, MA, USA). The *tert*.-butylphenol-terminated polycarbonate was obtained from Bayer Plastics (Pittsburgh, PA, USA). All polymer samples were used as received without any further purification.

2.2. Py–GC conditions and Py–GC–MS conditions

Samples of polymer (approximately 0.5 mg) were carefully deposited into a quartz tube. The quartz tube was put into an off-line pyrolysis interface for 4 min at 300°C to evaporate any nonpolymeric materi-

al (water, unreacted reagents). After this cleaning procedure, the quartz tube was equilibrated for 5 min in a 300°C interface connected to the injection port of a Hewlett-Packard (HP) Model 6890 gas chromatograph equipped with a FID system. The samples were pyrolyzed (CDS 2000 Pyroprobe, Pt coil) at a calibrated temperature of 700°C. The coil was heated to the calibrated temperature at 20°C/ms and held at the set temperature for a 20-s interval. The pyrolysis products were split in the 300°C injection port, with 10 p.s.i. head pressure and 250:1 split ratio (1 p.s.i.=6894.76 Pa). All pyrolysates were separated on a fused-silica capillary column (J & W Scientific DB-5, 30 m×0.25 mm I.D., 1.0 μm film) using a linear temperature program (40°C/4 min, 10°C/min, to 320°C/18 min). The GC outlet to the detector was kept at 300°C. For Py–GC–MS experiments, the output from the GC system was connected with an HP 5971 mass-selective detector. An electron ionization mass spectrum was obtained every second over the mass range 15–650 u. The transfer region from GC to MS was kept at 320°C.

2.3. Test of reproducibility

The reproducibility of pyrolysis data for phenyl-terminated PBD was investigated by four consecutive analysis of the sample. The relative standard deviation of all peaks of interest (butadiene, vinyl cyclohexene, toluene and styrene) was below 3%, which demonstrates the reliability of the pyrolysis method.

3. Results and discussion

Fig. 1 shows a typical pyrogram of a phenyl group-terminated PBD polymer. When PBD is pyrolyzed, the major pyrolysates are butadiene monomer and butadiene dimer (vinyl cyclohexene). However, for phenyl-terminated PBD, additional pyrolysates related to this phenyl end-group are detected. All major pyrolysates of phenyl-terminated PBD via mass spectra have been identified and are listed in Table 1.

Among the pyrolysates produced from the pyrolysis of phenyl-terminated PBD, all can be used in the end-group analysis to determine the M_n of PBD except the butadiene and vinyl cyclohexene. In this study, the toluene and styrene fragments have been chosen to demonstrate the relationship between M_n and end-group concentration. The major reason toluene and styrene were selected is due to the high pyrolysis yield and good separation efficiencies of those two pyrolysates under the experimental conditions used in this study. In the actual M_n

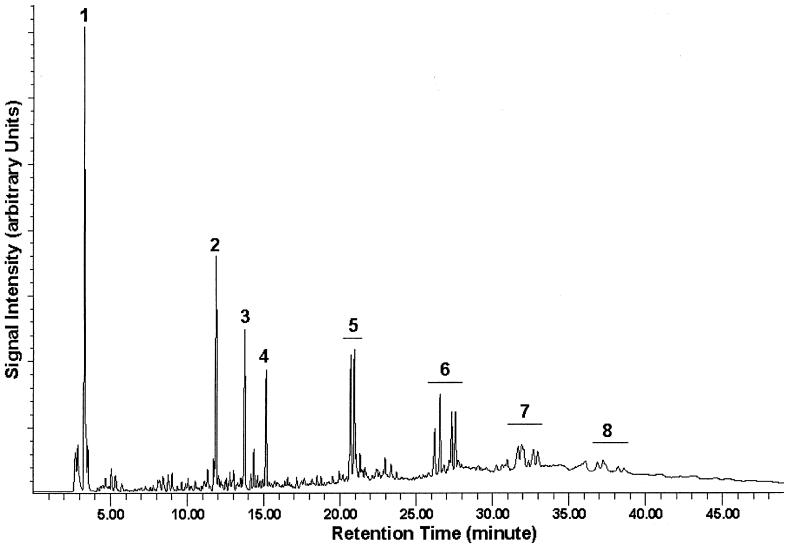

Fig. 1. The pyrogram of a phenyl-terminated PBD.

Table 1
Peak assignments for the pyrogram of phenyl-terminated PBD (Fig. 1)

Peak No.	M_n	Structure
1	54	Butadiene
2	92	Toluene
3	108	Vinylcyclohexene
4	104	Styrene
5	146	Isomers of 1-phenylpentene
6	200	Isomers of 1-phenylnonadiene
7	254	Isomers of 1-phenyltridecatriene
8	308	Isomers of 1-phenylheptadecatetraene

determination experiment, the end-group analysis can be accomplished with only one pyrolysate. The M_n can be calculated by the equation as follows:

$$M_n = \frac{\text{Mass of polymer pyrolyzed}}{\text{Moles of end-group detected}}$$

This is based on the assumption that the relationship between the end-group and polymer chain is well known. For example, each polymer chain contains two end-groups. The moles of end-group detected can be obtained by end-group peak area to calibrate with a known concentration standard.

In the M_n calculation, one important factor is the mass of polymer pyrolyzed. A typical approach is to weigh the polymer before pyrolysis. Because of the small quantity of sample used (typically approximately 0.5 mg), it is easy to introduce errors from operation as well as environment during this process. One way to reduce these operational errors is to change the direct weighing procedure to an indirect weight normalization/equalization. Essentially, it is a procedure to normalize all peaks of interest to a reference peak that correlated to mass of the sample pyrolyzed. In this study, the amount of polymer pyrolyzed was correlated with the quantity of butadiene monomer or butadiene dimer (vinyl cyclohexene) produced. For example, if the butadiene monomer peaks area is 100, all other experimental peaks area can be converted to a normalized peak area based on the relative peak area ratio to the butadiene peak.

Unknown samples may have a different microstructure than the standards. PBDs may have different degrees of saturation, or different mass fractions of *cis*, *trans*, and 1,2 types of repeating units in the polymer chain. These different microstructures will affect the total butadiene and/or butadiene dimer (vinyl cyclohexene) produced during pyrolysis. When the reference peak procedure is used to determine the amount of polymer used, it is necessary to make sure that the standards and the unknown samples have the same microstructure.

Fig. 2 shows the pyrograms of phenyl-terminated PBDs of different M_n. Table 2 lists the normalized peak areas for each phenyl-terminated PBD with different M_n. Fig. 3 shows the plots of toluene and styrene relative peak area versus the 100 000($1/M_n$) of phenyl-terminated PBD. Fig. 3 was created to demonstrate the linear relationship between $1/M_n$ and end-group concentration. Both the toluene and styrene concentrations follow this linear relationship. The vinyl cyclohexene concentration remains constant as a function of M_n indicating that the butadiene monomer-to-dimer ratio remains constant during pyrolysis and is independent of the M_n. This proves that the Py–GC method has been successfully developed to determine the M_n via end-group analysis.

Consistent with other end-group analysis techniques, there is an upper limit of M_n that can be determined by Py–GC. It is based on the detection limit for the end-group-containing pyrolysates. The typical approach is to check the key peak intensity with a known M_n standard then estimate the detection limit of that peak to judge the upper limit of M_n that can be determined. For example, in this study, the key peak can be either toluene or styrene. Based on the peak area obtained for the $M_n = 2600$ sample (as in Fig. 2), one can estimate that if the peak area was reduced to 10% of the current intensity, that peak could still be detected and measured with the standard detection criterion of a 3:1 signal-to-noise ratio. Therefore the upper limit of M_n that can be determined is $2600/0.1 = 26\,000$.

How valid is this estimate? If the curves in Fig. 3 are extrapolated to the baseline, when the 100 000($1/M_n$) reaches zero (M_n approaching infinity), the relative peak area of toluene and styrene will approach zero. The actual toluene and styrene peak areas are not only affected by the M_n, but also affected by the separation and detection efficiency of the Py–GC instrument. If one estimate the upper

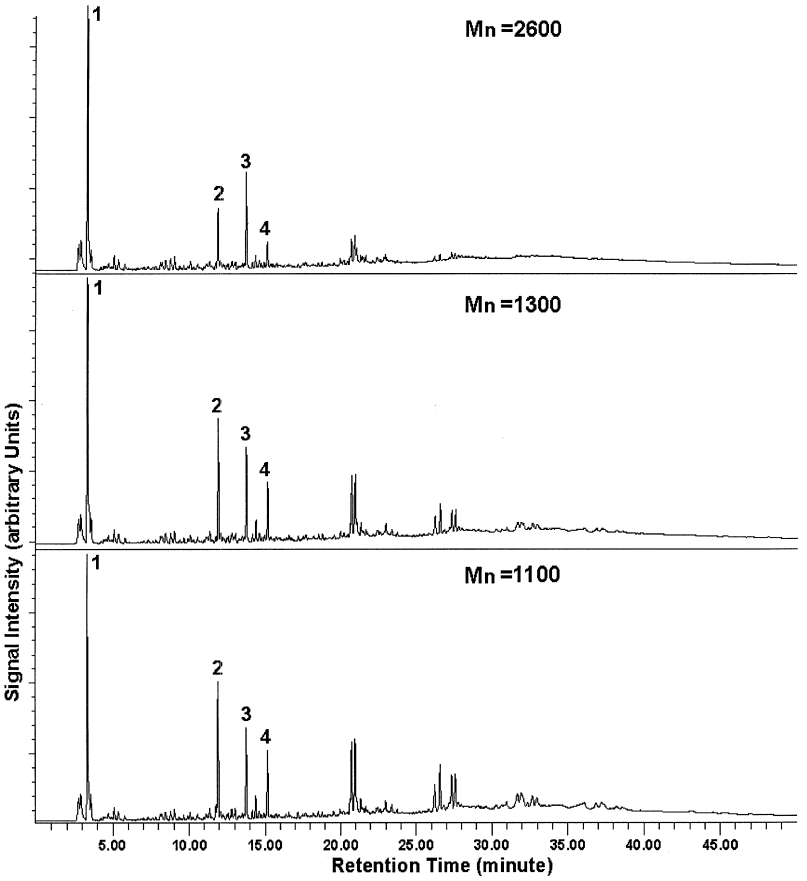

Fig. 2. The pyrogram of a phenyl-terminated PBD with different M_n.

Table 2
The normalized relative peak areas for each phenyl-terminated PBD with different M_n

M_n	Peak area			
	Butadiene	Vinyl cyclohexene	Toluene	Styrene
1100	100	37	57	29
1300	100	38	49	26
2600	100	38	25	13

limit of M_n that can be determined via this approach, it is important to use more than one standard. More than one data point can illustrate both the pyrolysis and instrument efficiencies of the key components (end-group) detected, as well as the trend of signal change with M_n.

The other factor that influences the upper limit of

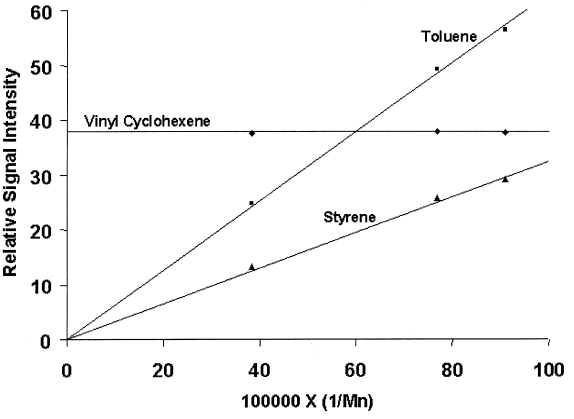

Fig. 3. The plots of toluene and styrene relative peak area versus the M_n of phenyl-terminated PBD.

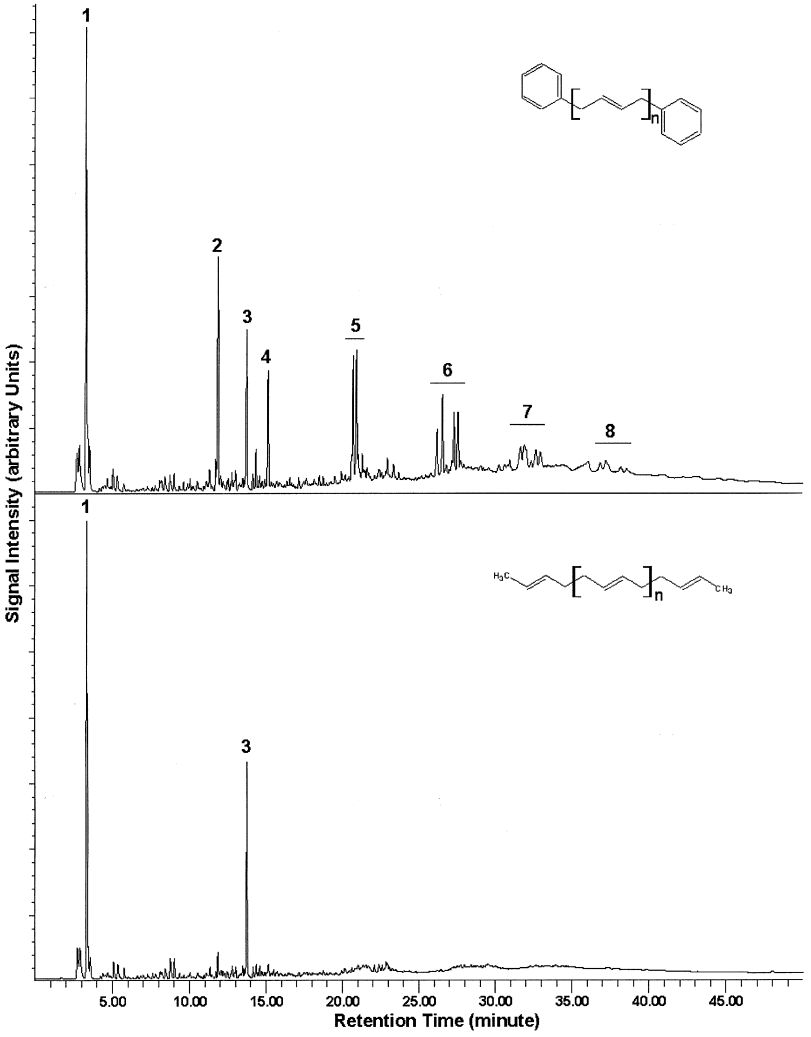

Fig. 4. The pyrograms of PBD with and without phenyl termination.

M_n that can be determined is the analytical dynamic range of Py–GC. If the amount of sample being pyrolyzed increases 10 times, with the same detection limit, the upper limit of M_n that can be determined will extend 10 times. However, every pyrolyzer has its sample quantity limit to obtain uniform/reproducible pyrolysis results and every GC system has its column-loading limit to obtain linear response of separation and detection.

The Py–GC end-group analysis cannot be applied to every polymeric system to obtain M_n information. The conditions necessary for the M_n determination are that the end-group must be detectable, distinguishable and all end-groups must be known. For example, if a polymer chain was terminated with a carboxylic acid group, the end-group will not be detected by Py–GC. The carboxylic acid under pyrolysis conditions will decompose to carbon dioxide and its correlated alkane fragment. However, this may be overcome by pre-pyrolysis derivatization to convert acid functional group to alkyl ester. Most of ester-containing pyrolysates can be detected by the Py–GC. Sometimes, the end-groups are detectable, but are difficult to distinguish from the end-groups of other pyrolysates. One example is PBD terminated with its monomer unit. Fig. 4 shows two pyrograms of PBD, one with and one without phenyl group termination. The end-group of butadiene cannot be

distinguished from the other monomer units in the chain when the phenyl groups are not present. There is no way that the M_n can be determined for this polymer.

Another example is end-group-terminated bisphenol-A polycarbonate [21]. Fig. 5 shows the pyrograms of phenol and *tert*.-butylphenol-terminated bisphenol-A polycarbonate. All pyrolysates labeled in the figure have been identified by their mass spectra and listed in the Table 3. Because phenol is one of the pyrolysis fragments from bisphenol-A polycarbonate, the phenol group from the end of the chain cannot be distinguished from the

Table 3
Peak assignments for the pyrograms of phenol and *tert*.-butylphenol-terminated polycarbonate (Fig. 5)

Peak No.	M_n	Structure
1	94	Phenol
2	108	4-Methylphenol
3	122	4-Ethylphenol
4	136	4-Isopropylphenol
5	150	4-*tert*.-Butylphenol
6	134	4-Isopropylenephenol
7	212	4-(1-Methyl-1-phenylethylphenol
8	210	3-Hydroxy-9,9′-dimethylfluorene
9	228	Bisphenol-A

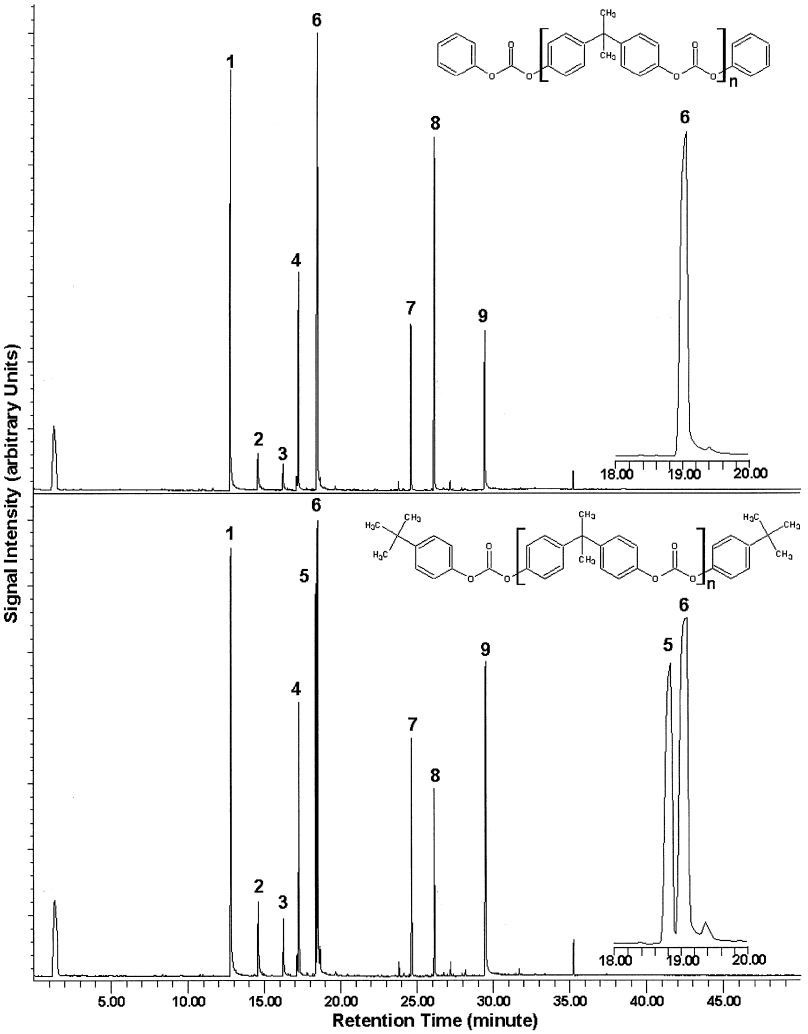

Fig. 5. The pyrograms of bisphenol-A polycarbonate with phenol termination and with *tert*.-butylphenol termination. All peaks labeled have been identified and listed in Table 3.

phenol fragment of bisphenol-A polycarbonate. On the other hand, the pyrogram of *tert*.-butylphenol-terminated bisphenol-A polycarbonate shows that the end-group of *tert*.-butylphenol can be clearly distinguished as a separate peak. Certainly, in the *tert*.-butylphenol-terminated polycarbonate case, the end-group concentration can be calculated, and the M_n can be elucidated.

End group analysis by Py–GC relies on detection of the end-group or end-group-containing pyrolysates. Because different functional groups have different pyrolysis efficiencies as well as GC detection efficiencies, polymers containing certain functional groups will be more amenable to this technique. For example, aromatic functional groups such as a phenyl group have a very high sensitivity in Py–GC experiments. In contrast, polar groups such as amine functional groups are not a favorable functional group for the Py–GC experiments.

The curve interpolation/extrapolation method is the favorite approach for the Py–GC end-group analysis to determine M_n. This approach will greatly reduce the errors introduced by weighing the samples as well as the efficiency of pyrolysis from the pyrolyzer and separation/detection from the GC system. Statistical considerations for calculation of M_n are similar to those for other end-group analysis techniques. The relationship between end-group and polymeric chain is very important. If a polymer chain is linear, and the end-group is capped on both sides of the chain, the number of end-groups detected will be twice the number of polymer chains. If each end-group is different, the number of specific end-groups detected will be the same as the number of polymer chains. If the polymer chain is not linear, then the number of branches must be known before the correlation between the number of end-groups and the number of polymer chains can be determined. Finally, end-group analysis can only obtain the number ''average'' molecular mass. There is no information related to the molecular mass ''distribution''.

4. Conclusions

A method has been developed to utilize Py–GC to determine the M_n via end-group analysis. The major advantage of this technique is that no sample preparation is required. The major drawback of this technique is that not every polymeric material contains distinguishable end-groups that can be utilized for M_n determination. Similar to all other Py–GC experiments, this is a quantitative measurement of end-groups or end-group-containing compounds within a given amount polymer pyrolyzed. The key process in this method is utilizing the calibration curve from standards to relate the end-group concentration to the M_n. Based on this concept, the capability and the efficiency of detecting end-groups are critical in successful application of the Py–GC technique. Py–GC can be successfully applied to polymers with end-groups such as aromatic groups, methacrylate groups, etc. Groups such as carboxylic acid, amine, hydroxyl, etc., are not well suited to Py–GC. In this study, phenyl-terminated PBDs were analyzed as a general example. The application of Py–GC to determine the M_n and the limitation of this method were discussed in detail. This development offers Py–GC as a complementary tool for the determination of number-average molecular mass.

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