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Rubber, raw synthetic — Determination of the molecular-mass distribution of solution polymers by gel permeation chromatography

Caoutchouc synthétique brut — Détermination de la répartition de la masse moléculaire pour les caoutchoucs polymérisés en solution par chromatographie par perméation de gel

Reference number
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Contents

Page

Foreword

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For an explanation on the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the WTO principles in the Technical Barriers to Trade (TBT), see the following URL: Foreword - Supplementary information

The committee responsible for this document is ISO/TC 45, *Rubber and rubber products*, Subcommittee SC 2, *Testing and analysis*.

This second edition cancels and replaces the first edition (ISO 11344:2004), which has been technically revised by replacing the hazardous *o*-dichlorobenzene with BHT (butylated hydroxy toluene) in the procedure. It also incorporates the Technical Corrigendum ISO 11344:2004/Cor.1:2008.

Rubber, raw synthetic — Determination of the molecular-mass distribution of solution polymers by gel permeation chromatography

WARNING 1 — Persons using this International Standard should be familiar with normal laboratory practice. This International Standard does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to ensure compliance with any national regulatory conditions.

WARNING 2 — Certain procedures specified in this International Standard might involve the use or generation of substances, or the generation of waste, that could constitute a local environmental hazard. Reference should be made to appropriate documentation on safe handling and disposal after use.

1 Scope

This International Standard describes a method for the determination of the molecular mass, expressed as polystyrene, and the molecular-mass distribution of polymers produced in solution which are completely soluble in tetrahydrofuran (THF) and which have a molecular-mass range from 5×10^3 to 1×10^6.

It is not the purpose of this International Standard to explain the theory of gel permeation chromatography.

2 Principle

The molecular components of a polymer are separated on the basis of macromolecule size on a gel permeation column. A known quantity of a dilute solution of the polymer is injected into a stream of solvent, which carries it through the column at a constant rate. The concentration of the separated molecular components in the solvent stream is measured by a suitable detector. Through the use of a calibration curve, both the number-average molecular mass (M_n) and mass-average molecular mass (M_w) of the material analysed can be determined from the retention time and the corresponding concentration.

3 General

3.1 Gel permeation chromatography (GPC), which is also known as size exclusion chromatography (SEC), is a particular type of liquid chromatography which allows the separation of the various components of a polymer based on molecular size.

3.2 The molecules of a polymer do not all have the same mass, but comprise a range of different masses. For this reason, the usual concept of molecular mass is not applicable to polymeric materials. Instead, different average molecular masses are determined as shown in Table 1.

Table 1 — Definitions of various kinds of molecular mass

Mass-average molecular mass M_w	$= \Sigma(N_i M_i^2)/\Sigma(N_i M_i)$ $= \Sigma(A_i M_i)/\Sigma A_i$
Number-average molecular mass M_n	$= \Sigma(M_i N_i)/\Sigma N_i$ $= \Sigma A_i/\Sigma(A_i/M_i)$
z-Average molecular mass M_z	$= \Sigma(N_i M_i^3)/\Sigma(N_i M_i^2)$ $= \Sigma(A_i M_i^2)/\Sigma(A_i M_i)$
Peak molecular mass M_p	Molecular mass at peak maximum
where N_i is the number of molecules having a molecular mass of M_i; A_i is the area of the time-slice that corresponds to molecular mass M_i.	

The molecular-mass distribution is an important parameter in determining the properties of the polymer. It may be represented by the polydispersity D given by

$$D = M_w / M_n$$

NOTE Polymers invariably consist of macromolecules with a range of molecular sizes. Even the so-called monodisperse polystyrenes have a polydispersity of 1,1 compared to a value of 1,0 for a pure compound with a single molecular mass. As the range of molecular sizes present within the polymer increases, so does the polydispersity.

4 Reagents and materials

4.1 Tetrahydrofuran (THF), with or without 2,6-di-*tert*-butyl-4-methylphenol (BHT), solvent for the mobile phase, analytical grade.

4.2 THF containing 2,6-di-*tert*-butyl-4-methylphenol, solvent for sample dissolution, analytical grade (THF containing BHT solution).

The solution of 2,6-di-*tert*-butyl-4-methylphenol (also known as BHT, butylated hydroxytoluene) in THF is commercially available. For the purpose of this International Standard, the solution is called THF containing BHT.

When it is difficult to find this solution in the market, the alternative can be obtained by adding 100 mg to 500 mg of BHT to 1 l of THF. Preparation of this solution is also effective when a noticeable peak is not obtained for BHT.

4.3 Set of certified polystyrene reference standards (minimum 10), with molecular masses in the range 5×10^2 to 1×10^7 (depending on the sample molecular-mass range) and a very narrow molecular-mass distribution ($D < 1{,}10$) (see Table 2 for an example of such a set, available from various chemical suppliers).

Table 2 — Set of polystyrene standards

Standard No.	Actual molecular mass M_i	D (= M_w/M_n)
1	1 030 000	1,05
2	770 000	1,04
3	336 000	1,03
4	210 000	1,03
5	156 000	1,03
6	66 000	1,03
7	30 300	1,03
8	22 000	1,03
9	11 600	1,03
10	7 000	1,04
11	5 050	1,05

5 Apparatus

Ordinary laboratory apparatus, plus the following:

5.1 Gel permeation chromatograph, consisting of the components specified in 5.1.1 to 5.1.8.

5.1.1 Solvent reservoir, of sufficient capacity to complete the analysis without refilling.

NOTE A large stock of THF is needed to avoid frequent refills. Changes in the quantity of dissolved air or impurities due to addition of fresh solvent cause significant variations in the refractive index and can also affect the retention time. Air bubbles at the pump head reduce the quantity of solvent pumped (leading to errors in retention volumes and times) and can block the pump if the volume of the air bubbles reach excessive levels. After adding fresh solvent, it takes 2 h to 3 h to obtain a stable baseline.

5.1.2 Automatic online degassing system or **helium sparging of solvent reservoir**, to stabilize the solvent flow, mainly to prevent formation of bubbles in the solvent.

5.1.3 Pump, to ensure that the THF solvent flows at a constant rate, programmable over the range 0,1 ml/min to 2,0 ml/min with a high degree of precision.

5.1.4 Injector or **automatic sampler**, with a 100 mm^3 (100 µl) injection loop.

5.1.5 Columns, packed with regular, rigid, porous spheres. The pore size on the column packing material is expressed either in Angström units (1 Å = 10^{-10} m), molecular weight range or size exclusion limit molecular weight. The packing spheres are made of cross-linked polystyrene, obtained by polymerization of styrene with divinylbenzene. The spheres shall have a nominal diameter in the range 3 µm to 10 µm. The columns are generally 150 mm to 300 mm long. The pore size is selected depending on the range of molecular masses to be analysed.

NOTE 1 Four columns with pore sizes 10^3 Å, 10^4 Å, 10^4 Å and 10^5 Å were used when the repeatability and reproducibility of the method described in this International Standard were determined. The solvent first enters the column with the lowest porosity and exits from the column with the highest porosity. Other suitable columns can be used. These types of column are available from many suppliers.