

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Liquid Chromatography & Related Technologies

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597273>

Gel Permeation Chromatography of Polyethylene Terephthalate

Saleh A. Jabarin^a; Dennis C. Balduff^a

^a Owens-Illinois, Inc. One SeaGate, Toledo, Ohio

To cite this Article Jabarin, Saleh A. and Balduff, Dennis C.(1982) 'Gel Permeation Chromatography of Polyethylene Terephthalate', *Journal of Liquid Chromatography & Related Technologies*, 5: 10, 1825 — 1845

To link to this Article: DOI: 10.1080/01483918208062857

URL: <http://dx.doi.org/10.1080/01483918208062857>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

GEL PERMEATION CHROMATOGRAPHY OF POLYETHYLENE TEREPHALATE

Saleh A. Jabarin and Dennis C. Balduff

Owens-Illinois, Inc.
One SeaGate
Toledo, Ohio 43666

ABSTRACT

This paper describes the development of the gel permeation chromatography (GPC) technique for the measurements of cyclic trimer content, molecular weights, and molecular weight distribution of polyethylene terephthalate (PET), utilizing a solvent system of o-chlorophenol-chloroform. Mark-Houwink constants for this solvent system are also described.

The GPC technique was applied to the study of the cyclic trimer content, molecular weights and molecular weight distribution of a variety of commercial PET resins. The results indicate that the cyclic trimer content in PET is dependent on molecular weight, polycondensation process and catalyst system. Solid-state polymerized PET contains less cyclic trimer than PET made by the melt-phase process of the same molecular weight. The cyclic trimer content in solid-stated PET appears to be dependent on the conditions of solid-state polymerization.

The polydispersity index determine for a variety of PET samples is higher than the theoretically predicted value of 2.0; however, there is no systematic dependence on molecular weight or polycondensation process.

INTRODUCTION

Among the important characteristics of polyethylene terephthalate (PET), which determine the physical properties and uses

of this polymer are the molecular weight and the molecular weight distribution. The most frequently used technique in industry to evaluate the molecular weight of PET is solution viscosity. The use of solution viscosity in the determination of molecular weight for PET and other linear polymers is based on an empirical relationship between viscosity and molecular weight.

The solution viscosities may be expressed by several quantities. Their nomenclature and definitions are given elsewhere (1,2); however, the viscosity parameter of most importance to the empirical relation of viscosity to molecular weight is the intrinsic viscosity (I.V.) or limiting viscosity number, which is given by:

$$[\eta] = \left(\frac{\eta_{sp}}{c} \right)_{c=0} = \left(\frac{\ln \eta_{rel}}{c} \right)_{c=0}$$

where c = concentration (g./dl).

The intrinsic viscosity or the limiting viscosity number, $[\eta]$, is related to molecular weight, M , by the Mark-Houwink equation.

$$[\eta] = KM^a$$

where K and " a " are empirical constants, which vary with the nature of the solvent.

The relationship between intrinsic viscosity and molecular weight for PET has been developed in a variety of solvents (3). Other correlations between the inherent viscosity and molecular weight are also known (4).

While the solution viscosity is a valuable tool for the molecular characterization of polymers, the procedure is laborious and time-consuming. In addition it is limited in providing direct and detailed information about the various molecular weight averages and the molecular weight distribution.

Gel permeation chromatography (4-10), GPC, is a well established technique for determining the molecular weight distribution (MWD), and in principle, can yield accurate measurements of molecular weight averages.

The application of GPC as a tool for determining molecular weight parameters of PET has been limited due to the availability of appropriate solvents. Previous work (11,12) involved the use of meta-cresol at 110-135°C as a solvent of polyethylene terephthalate for GPC; however, studies (13) have shown that meta-cresol can cause degradation of PET through acid catalyzed hydrolysis. Paschke, Bidlingmeyer and Bergmann (13) reported the development of a nitrobenzene-tetrachloroethane solvent system which can be used as a solvent for PET at room temperature.

In this paper, we describe the use of an o-chlorophenol-chloroform solvent system for the measurement of the molecular weight parameters of PET by GPC. This solvent system is also a solvent for polystyrene at room temperature; therefore, a calibration procedure, based upon polystyrene standards, can be developed to allow accurate and reproducible determination of molecular weight averages and molecular weight distribution of PET.

EXPERIMENTALMaterialsPolymer Standards

Polystyrene standards of narrow molecular weight distribution were obtained from various sources. These standards, used in both viscometry and GPC experiments, cover the molecular weight range of 2,100 M_w to 7,100,000 M_w .

PET samples with a wide range of molecular weights were used in the viscometry experiments and in preliminary GPC trials (see Table 1).

TABLE 1

PET Samples

<u>Sample #</u>	<u>I.V. (1)</u>	<u>Source</u>
1	0.206	Owens-Illinois
2	0.492	Owens-Illinois
3	0.625	Owens-Illinois
4	0.64	Goodyear
5	0.67	Celanese
6	0.70	Eastman
7	0.72	Goodyear
8	0.83	Goodyear
9	0.95	Goodyear
10	1.00	Goodyear
11	1.08	Goodyear

(1) I.V. (inherent viscosity) measurements made in 60/40 - phenol/tetrachloroethane @ 25°C @ 0.25 g./dl.

Solvents

Ortho-chlorophenol, purified grade, and spectrophotometry grade chloroform, were obtained from Fisher. With the exception of filtration, no additional treatment of either solvent was performed.

Viscometry

All of the viscosity measurements were conducted in a Cannon-Ubbelohde suspended level capillary dilution viscometer. The viscometer was suspended in a constant temperature water bath with an accuracy of $\pm 0.01^\circ\text{C}$. Efflux times for the PET and polystyrene solutions were measured manually with an electric clock timer, accurate to 0.05 seconds.

The solution preparation for both PET and polystyrene standards was identical. The concentrations used in each viscosity measurement varied with the molecular weight of the sample being measured. In general, the concentration of the polymer solutions were made to yield an efflux time of 200 seconds or more for the highest solution concentration. Orthochlorophenol was added to a known weight of polymer and heated at 110°C , with agitation, until the polymer dissolved (~ 10 to 30 minutes). After the polymer was dissolved, this solution was allowed to reach room temperature, at which time chloroform was added to make the final solution.

A given volume of the polymer-orthochlorophenol/chloroform solution was filtered into the viscometer through a Swinny-adapted syringe, with a $0.45\ \mu\text{m}$ filter. Efflux times of the

solutions were determined in triplicate, after allowing thermal equilibration of 10 minutes. The solutions were then diluted, equilibrated and remeasured for an additional three solution concentrations.

GPC

GPC experimentation was performed with a Waters Associates model ALC/GPC-201 gel permeation chromatograph equipped with a model U6K sample injector and a model R-401 differential refractometer. A circulating water bath, with an accuracy of $\pm 0.05^{\circ}\text{C}$, was attached to the differential refractometer and to temperature control blocks surrounding the column bank.

The solvents were vacuum filtered through a Millipore 0.45 μm filter. All sample solutions were also filtered through a Swinny-adapted syringe, fitted with a 0.45 μm Millipore filter.

The column bank for this system consisted of four μ -Styragel columns (Waters Associates), with porosities of 10^6 - 10^3 \AA . The quoted column efficiency was 9000 plates/meter for each column.

PET solution concentrations were maintained at 0.25% (w/v) while the polystyrene standard solutions were made to be 0.10% (w/v). The normal operating conditions for this chromatographic system were:

Temperature	= 25°C
Flow rate	= 1.0 ml./min.
Eluent	= orthochlorophenol/chloroform (25/75)
System pressure	= 700-720 psig. @ 1 ml./min. = 1300-1500 psig. @ 2 ml./min.
Attenuation	= 8X
Injection	= 0.4 ml.

RESULTS AND DISCUSSIONUniversal Calibration Curve

The hydrodynamic volume of a polymer chain, V_h , is usually measured as $([\eta]M)$, where $[\eta]$ is the intrinsic viscosity and M is the molecular weight. The parameter, $[\eta]M$, is the basis of the universal calibration curve.

The conversion from one polymer system to another involves the use of the Mark-Houwink equation

$$[\eta] = KM^a \quad (1)$$

The hydrodynamic volumes of polymers 1 and 2 can be written as

$$[\eta]M = K_1M_1^{a_1+1} \quad (2)$$

$$[\eta]M = K_2M_2^{a_2+1} \quad (3)$$

If the column combination, solvent, elution rate and temperature are constant when conducting the GPC experiment of the two polymers, then at a given elution volume, the relation

$$K_1M_1^{a_1+1} = K_2M_2^{a_2+1} \quad (4)$$

will hold. The molecular weight of polymer 2 may be obtained from polymer 1 by solving equation 4

$$\log M_2 = \frac{a_1+1}{a_2+1} \log M_1 + \frac{1}{a_2+1} \log \left(\frac{K_1}{K_2} \right) \quad (5)$$

The use of the universal calibration curve requires a knowledge of the Mark-Houwink constants which can be experimentally determined as described in the next section.

Solution Properties

Intrinsic viscosities were determined according to the Huggins and Kraemer equations

$$\frac{\eta_{sp}}{C} = [\eta] + K' [\eta]^2 C \quad (6)$$

$$\ln \left(\frac{\eta_{rel}}{C} \right) = [\eta] - K'' [\eta]^2 C \quad (7)$$

A typical plot according to these equations is given in Figure 1, for low and high molecular weight PET. Similar treat-

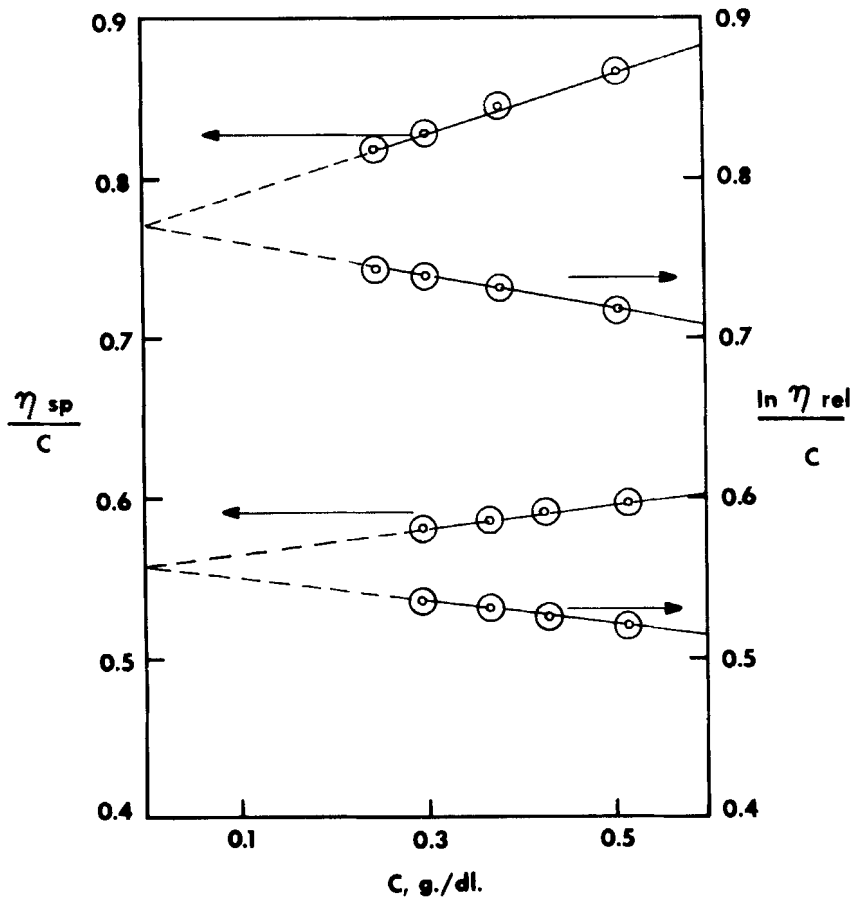


Figure 1 η_{sp}/C and $\ln \eta_{rel}/C$ versus concentration for a low and high molecular weight PET sample.

ment of viscosity data for the polystyrene standards is also required.

The intrinsic viscosities of PET are plotted as a function of M_w in Figure 2. Examination of the data in Figure 2 shows that the temperature effect on the $[\eta]$ - M relationship is negligible over the temperature range 20–30°C. The Mark-Houwink equations for PET and polystyrene were obtained by a least-squares fit. The results are

$$[\eta] = 1.49 \times 10^{-4} M_w^{0.56} \quad (\text{PET}) \quad (8)$$

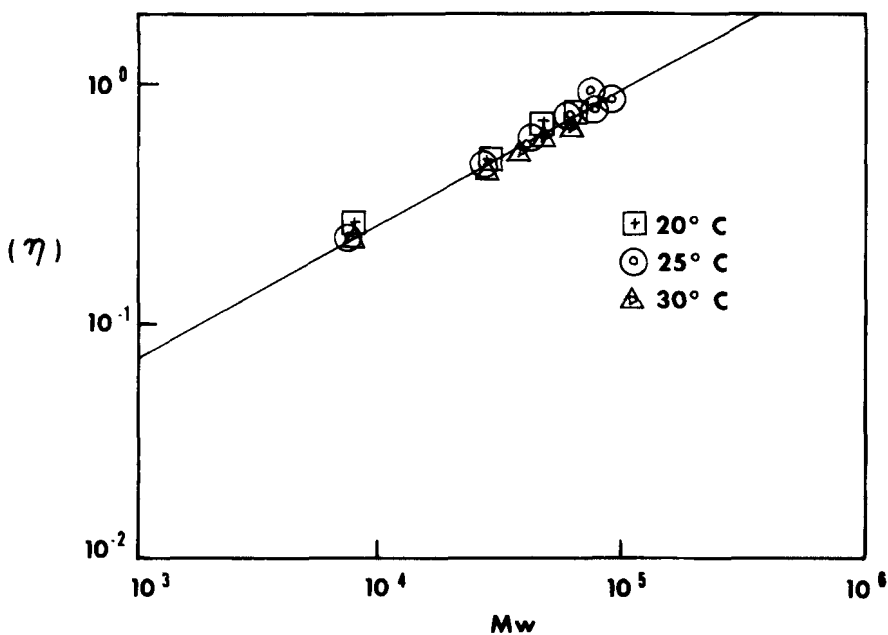


Figure 2 Intrinsic viscosity as a function of weight average molecular weight for PET in (25/75%) ortho-chlorophenol-chloroform.

$$[\eta] = 2.20 \times 10^{-4} M_w^{0.67} \quad (\text{Polystyrene}) \quad (9)$$

The K (1.49×10^{-4}) and "a" (0.56) values for PET in orthochlorophenol-chloroform solvent system at 25°C determined in this study differ somewhat from those obtained for other solvent systems (3,4,14). The K value obtained here is in the same general range of K values obtained for other solvent systems. The value of the exponent "a" is low compared to other solvent systems; however, since the value of "a" is higher than 0.50, the solvent system can be considered as a good solvent for PET.

As indicated above, the effect of temperature on the viscosity - molecular weight relationship is negligible over the temperature range 20-30°C. This indicates that there is no association of the polymer in this solvent system.

The stability of PET in orthochlorophenol-chloroform solvent system was evaluated by solution viscosity. The results are shown in Table 2 for two PET samples having different molecular weights. It is seen that the efflux time is constant over

TABLE 2

Efflux Time (seconds) After Dissolving Samples in Orthochlorophenol-Chloroform Solvent System at 25°C

<u>Period</u> <u>Min.</u>	<u>High M_w Sample</u> <u>C = 0.502 gm/dl</u>	<u>Period</u> <u>Min.</u>	<u>Low M_w Sample</u> <u>C = 0.613 gm/dl</u>
31	223.40	25	211.67
160	223.37	139	211.73
1,731	223.38	1,420	221.68
2,881	223.30	3,039	221.34

extended periods, indicating that there is no breakdown in molecular weight.

Molecular Weight and Molecular Weight Distribution

Construction of Calibration Curves

Molecular weights for PET which have the same hydrodynamic volume ($[\eta]M$) and elute at the same elution volume as the polystyrene standards can be calculated from equation 5, using the Mark-Houwink constants given in equations 8 and 9. The results of these calculations are given in Table 3. The data are plotted

TABLE 3

Weight Average Molecular Weight,
 \bar{M}_w for PET Calculated from Hydrodynamic Volume

Elution Volume V_e , ml	\bar{M}_w
15.9	6,330,120
16.0	3,516,620
16.4	2,168,470
17.5	505,770
17.8	368,150
19.6	138,640
20.8	73,820
23.3	32,100
25.7	12,290
27.2	5,790
29.1	2,100
29.9	1,060

in Figure 3, where M_w is plotted against elution volume. The results in Figure 3 constitute a calibration for PET in this solvent at 25°C.

Typical GPC Data

GPC Chromatograms

A typical GPC Chromatogram of PET in (25/75%) orthochlorophenol-chloroform at 25°C is given in Figure 4. The major portion of the chromatogram for this PET sample peaks at about 22 ml elution volume, with a minor peak at 31 ml. The identification and further characterization of this minor peak will be discussed in a later section.

Calculations

From the chromatogram a number of molecular weight parameters can be obtained. These include:

- Weight Average Molecular Weight (M_w)
- Number Average Molecular Weight (M_n)
- Polydispersity Index (D_n)

These molecular weight averages are calculated according to the general equation

$$M_a = \frac{\sum_{i=1}^Q N_i M_i^a}{\sum_{i=1}^Q N_i M_i^{a-1}} \quad (10)$$

where $a = 1, 2, 3$ or 4 . When $a = 1$, M_n is obtained. Higher weight-averages are obtained when $a = 2, 3$ or 4 . These are: $a = 2$ (M_w), $a = 3$ (M_z) and $a = 4$ ($M_z + 1$). The polydispersity index is expressed as the ratio of M_w/M_n and given the designation of D_n .

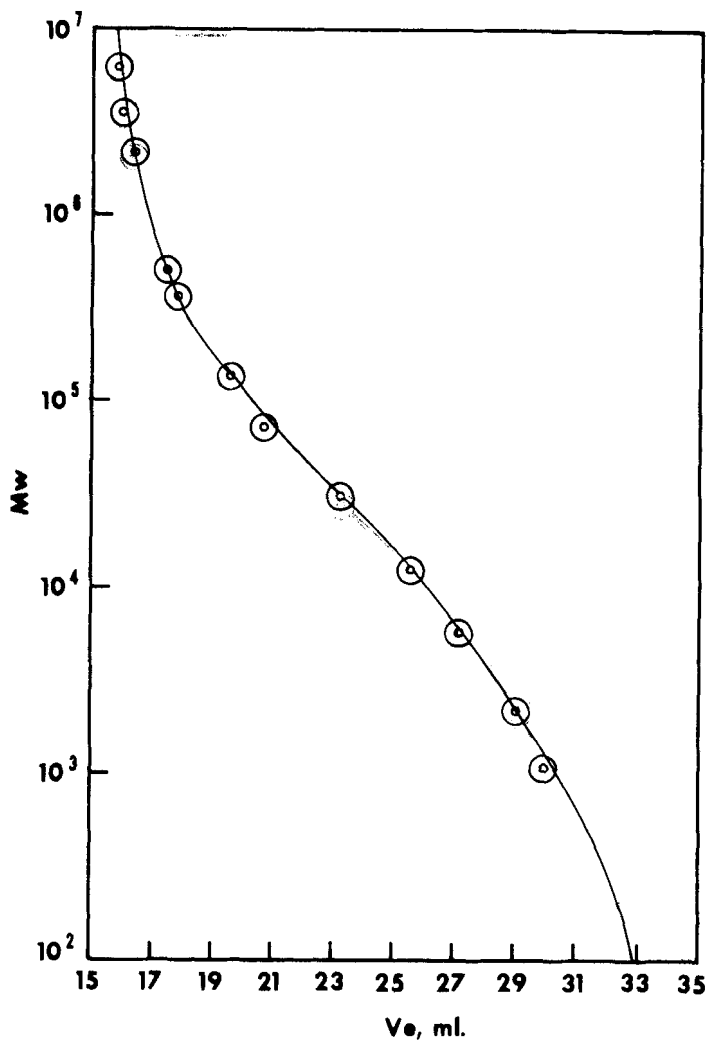


Figure 3 Weight average molecular weight of PET as a function of elution volume in (25/75%) ortho-chlorophenol-chloroform.

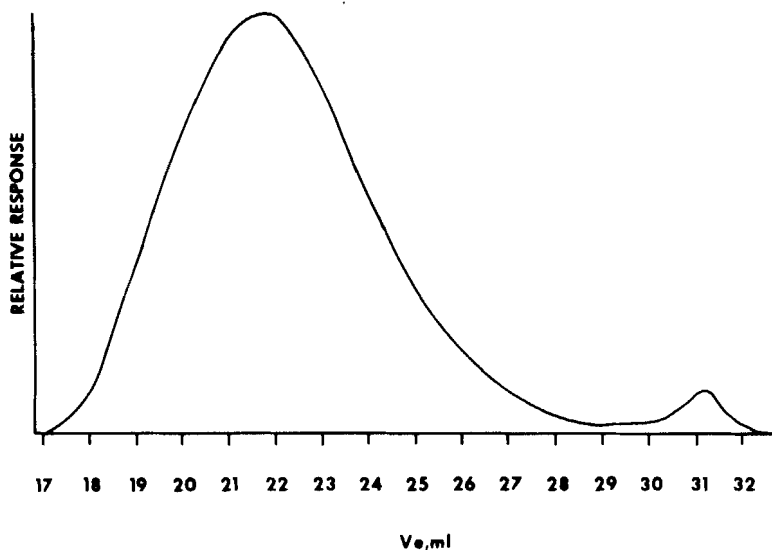


Figure 4 Typical GPC chromatogram of PET in (25/75%) ortho-chlorophenol-chloroform at 25°C.

Molecular Weights and Polydispersity Index

The molecular weight parameters for a variety of PET samples prepared by solid-state and melt-phase polymerization processes are given in Table 4. The polydispersity index M_w/M_n for all the samples studied is somewhat higher than the theoretically predicted value of approximately 2.0 (15) for polycondensation polymers; however, the polydispersity index values obtained here are in close agreement with other experimentally determined values (13). The results in Table 4 indicate that polydispersity indices for the melt-phase samples are, in general, lower than those of the solid-state samples.

TABLE 4

Molecular Weight Parameters Obtained by GPC of Various PET Samples

PET	I.V.*	Polymerization Process	M_w	M_n	\bar{M}_w/\bar{M}_n
Goodyear 5041	1.00	Solid-State	66,630	25,960	2.57
Goodyear 5737	0.72	Solid-State	52,870	18,640	2.84
Goodyear (O-I 11)	0.64	Solid-State	42,080	15,180	2.77
Celanese PT 101C	0.67	Solid-State	47,860	18,160	2.64
Eastman 44C	0.70	Melt-Phase	49,740	20,890	2.38
Owens-Illinois	0.86	Melt-Phase	59,180	25,450	2.33
Owens-Illinois	0.63	Melt-Phase	35,720	14,330	2.49
Owens-Illinois	0.49	Melt-Phase	29,540	12,990	2.27

*I.V. = inherent viscosity in (60/40) phenol-tetrachloroethane at 25°C and 0.25 gm./100 ml.

Correlations with Viscosity Data

From the GPC weight average molecular weights one can calculate the corresponding inherent viscosity, I.V., using the following relationship (4):

$$I.V. = 4.68 \times 10^{-4} (\bar{M}_w)^{0.68}$$

(60/40) phenol-tetrachloroethane at 25°C and 0.25 gm./100 ml.

Table 5 gives the calculated I.V. along with the experimentally determined I.V. A fair agreement is obtained over a wide range of I.V.

Low Molecular Weight Components

As was indicated above, all of the GPC chromatograms of PET exhibit a small peak at 31 ml elution volume. The corresponding

TABLE 5

Comparison Between Measured and Calculated I.V. of PET Samples

\bar{M}_w GPC	Measured I.V. \pm .01	Calculated I.V.
66,630	0.90	0.90
59,180	0.79	0.82
52,870	0.73	0.76
49,740	0.69	0.73
47,860	0.67	0.71
35,720	0.65	0.58
29,540	0.51	0.51

Measured I.V. was obtained in (60/40) phenol-teretrachloroethane @ 25°C and 0.25 gm/100 ml. Calculated I.V. was obtained using the GPC \bar{M}_w in the relationship I.V. (calc.) = $4.68 \times 10^{-4} (\bar{M}_w)^{0.68}$.

molecular weight is 550 to 610 according to the calibration curve in Figure 3. The fact that this peak encompasses the molecular weight of cyclic trimer and that cyclic trimers are often found in PET (16) leads one to conclude that the peak at 31 ml elution volume results from the presence of cyclic trimer. This conclusion was further confirmed by dissolving a sample of cyclic trimer and injecting into the GPC. The sample eluted with peak elution volume of 31 ml.

The cyclic trimer used in this study was obtained from Goodyear Company. It is a white, crystalline powder with a reported melting point of 319°C.

In order to establish a calibration for a semi-quantitative analysis of this oligomer, a "spiking" experiment was performed.

Six sample solutions with varying amounts of cyclic trimer were added to a PET sample and chromatographed.

The weight percentage of the oligomer in the solution was calculated from:

$$\text{weight \%} = \frac{\text{weight of cyclic trimer}}{\text{weight of PET}} \times 100$$

The weight percentage of the oligomer ranged from 0.206% to 3.55%. A solution containing only PET and no cyclic trimer was run as a control.

The peak height at 31 ml elution volume was measured for each solution containing the "spiked" samples. The peak height for the solution containing only PET was also measured and subtracted from the values obtained for the "spiked" samples.

The results of the "spiking" experiment are given in Figure 5. This is a calibration line which can be used to determine the amount of cyclic trimer in PET samples.

Table 6 gives the cyclic trimer content as determined by the above procedure for a variety of experimental and commercial PET resins. The quantitative content of the cyclic trimer in PET determined here is in good agreement with previous studies (16,17).

The quantitation of cyclic trimer in PET by this method demonstrates that the concentration is greater in melt-phase polymerized PET than in solid-state resins and that for melt-phase polymerized PET, the concentration of cyclic trimer decreases with increasing molecular weight. An additional correlation of molecular weight and cyclic trimer content may be found within solid-

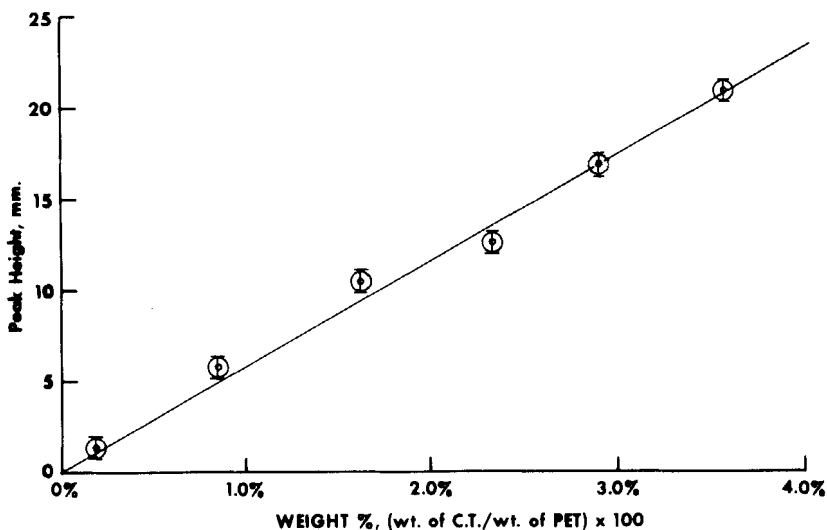


Figure 5 Peak height versus weight percent of cyclic trimer.

state polymerized PET utilizing the same catalyst system (i.e., Goodyear), with cyclic trimer content decreasing with increasing molecular weight. Furthermore, cyclic trimer content in PET prepared by solid-state polymerization, with PET samples of about the same molecular weight, appears to be dependent on the catalyst system used. Although these differences appear to be dependent on the catalyst system, a more likely cause is the solid-state polymerization conditions.

CONCLUSIONS

The gel permeation chromatography (GPC) technique has been developed for the measurements of cyclic trimer content, molecular weights and molecular weight distribution of PET, utilizing a solvent system of *o*-chlorophenol-chloroform.

TABLE 6

Cyclic Trimer Content in PET as Measured by the
Peak Height Calibration in Figure 5

<u>Resin</u>	<u>I.V.</u>	<u>Catalyst System</u>	<u>Polymerization Process</u>	<u>Weight % Cyclic Trimer</u>
Eastman (experimental)	0.51	Sb-Ti-Co-Mn	Melt-phase	1.25
Zimmer (experimental)	0.62	Sb	Melt-phase	1.13
Eastman (experimental)	0.63	Sb-Ti-Co-Mn	Melt-phase	0.98
Eastman (experimental)	0.70	Sb-Ti-Co-Mn	Melt-phase	0.80
Goodyear (experimental)	0.64	Sb	Solid-state	0.60
Goodyear 5877	0.72	Sb	Solid-state	0.35
Celanese 2113 (Lot #202)	0.76	Sb	Solid-state	0.63
Eastman 7352	0.70	Sb-Ti-Co-Mn	Solid-state	0.62
Goodyear 5041	0.90	Sb	Solid-state	0.24
Goodyear 5041	1.0	Sb	Solid-state	less than 0.2

•The molecular weights determined by inherent viscosity (I.V.) measurement and those determined by GPC are in good agreement.

•The polydispersity index determined for a variety of PET samples is higher than the theoretically predicted value of 2.0; however, there is no systematic dependence on molecular weight or polycondensation process.

•The amount of cyclic trimer is greater in a melt-phase polymerized PET than that in a solid-state resin.

- For a melt-phase polymerized PET, the amount of cyclic trimer decreases with increasing molecular weight (or I.V.).
- For a solid-state polymerized PET having the same catalyst system, the cyclic trimer content decreases with increasing molecular weight.
- The cyclic trimer content in PET prepared by the solid-state polymerization process and having about the same molecular weight appear to be dependent on the catalyst system used and the solid-state polycondensation conditions.

REFERENCES

1. Van Krevelen, D. W., Properties of Polymers, Correlanous with Chemical Structure, Elsevier Publishing Company, Amsterdam-London-New York, 1972
2. Billmeyer, F. W., Jr., Textbook of Polymer Science, 2nd Ed., Wiley-Interscience, New York, 1971, 62-95.
3. Moore, W. R. and Sanderson, D., Viscosities of Dilute Solutions of Polyethylene Terephthalate, Polymer, 9, 153, 1968.
4. Moore, L. D., Jr., Cleveland ACS, Meeting 4, Vol. 1, 1960.
5. Cantow, M. J. R., Polymer Fractionation, Academic Press, New York, 1967.
6. Pebbles, L. H., Jr., Molecular Weight Distribution in Polymers, Interscience, New York, 1971, 190-232.
7. Moore, J. C., Chem. Eng. News, 40, No. 51, 43, 1962.
8. Moore, J. C., Gel Permeation Chromatography. I. A New Method for Molecular Weight Distribution of High Polymers, J. Poly. Sci., 2, 835, 1964.
9. Moore, J. C. Hendrickson, J. G., Gel Permeation Chromatography. II. The Nature of the Separation, J. Poly. Sci., 8, 233, 1965.

10. Johnson, J. F., Porter, R. S., Analytical Gel Permeation Chromatography, Cantow, M. J. R., ed., New York, 1967.
11. Shaw, G., Proceedings of the Seventh International GPC Seminar, Monte Carlo, Waters Associates, 1969, 309.
12. Overton, J. R., Rash, J., Moore, L. D., Jr., The Molecular Composition of Polyethylene Terephthalate as Determined by Gel Permeation Chromatography, Proceedings of Sixth International GPC Seminar, Miami Beach, Florida, Waters Associates, 1968, 422.
13. Paschke, E. E., Bidlingmeyer, B. A., Bergmann, J. G., A New Solvent System for Gel Permeation Chromatography of Polyethylene Terephthalate, *J. Poly. Sci.*, 15, 983, 1977.
14. Brandup, I., Immergut, E. H., Polymer Handbook, Wiley Interscience, New York, 1965, VI-20.
15. Flory, P. J., Principles of Polymer Chemistry, Cornell University Press, Ithaca, New York, 1953.
16. Cooper, D. R., Semlyen, J. A., Equilibrium Ring Concentrations and the Statistical Conformations of Polymer Chains: Part II. Cyclics in Polyethylene Terephthalate, *Polymer*, 14, 185, 1973.
17. Pebbles, L. H., Jr., Huffman, M. W., Ableh, C. T., Isolation and Identification of the Linear and Cyclic Oligomers of Polyethylene Terephthalate and the Mechanism of Cyclic Oligomer Formation, *J. Poly. Sci.*, 7, 479, 1969.