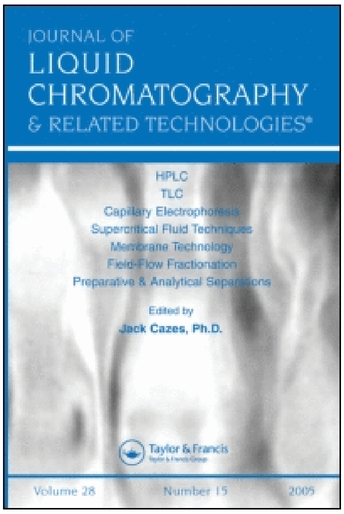
This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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 Unsaturated Polyester Resins. Possibilities and Limitations

Š. Podzimek[a]; J. Hanuš[a]; J. Klaban[a]; J. Kitzler[a]
[a] Research Institute for Synthetic Resins and Lacquers, Pardubice, Czechoslovakia

To cite this Article Podzimek, Š. , Hanuš, J. , Klaban, J. and Kitzler, J.(1990) 'Gel Permeation Chromatography of Unsaturated Polyester Resins. Possibilities and Limitations', Journal of Liquid Chromatography & Related Technologies, 13: 9, 1809 — 1824

To link to this Article: DOI: 10.1080/01483919008048993

URL: http://dx.doi.org/10.1080/01483919008048993

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.

JOURNAL OF LIQUID CHROMATOGRAPHY, 13(9), 1809-1824 (1990)

GEL PERMEATION CHROMATOGRAPHY OF UNSATURATED POLYESTER RESINS. POSSIBILITIES AND LIMITATIONS

Š. PODZIMEK, J. HANUŠ,
J. KLABAN AND J. KITZLER
Research Institute for Synthetic
Resins and Lacquers
CS-532 07 Pardubice, Czechoslovakia

ABSTRACT

The use of gel permeation chromatography (GPC) for the characterization of unsaturated polyester resins is demonstrated on several examples. Number-average molecular weights determined by this method are compared to data obtained by means of vapor pressure osmometry (VPO) and by end group analysis (EG). The determination of the polyester resin composition as a function of molecular weight by stop-and-go UV scanning procedure is described. A comparison of theoretical and experimental molecular distribution is applied to the estimation of branching extent.

INTRODUCTION

Unsaturated polyester resins are known as polydisperse polymers that usually contain a certain amount of low-molecular-weight oligoesters and, on the other hand, fractions with molecular weights running into five or even six figures.

The number-average molecular weight (M_n) and weight-average molecular weight (M_w) as well as the molecular-weight distribution (MWD) are important characteristics which determine physical properties of such products. VPO and EG have been used most frequently to evaluate the molecular weight of polyester resins. The values of M_n estimated by these methods usually lie between 1,000 and 3,000. However, M_n alone is not sufficient to characterize the MWD.

The precipitation fractionation of polyester resins can provide useful information about MWD and, in conjunction with infrared spectroscopy, about chemical composition (1), but it is very laborious, time-consuming and unsuitable for routine analyses.

A powerful and rapid method for the determination of MWD of polymers is GPC. Unfortunately, little attention has been paid to the GPC of unsaturated polyesters.

A GPC calibration method for polyester resins has been proposed by Lee (2). Lyttle (3) has published a comparison of M_n values determined by VPO and GPC. The effect of M_n and MWD on the properties of resins after crosslinking with styrene has been studied by Douglas et al. (4). Others (5,6) have used GPC to investigate the thickening reaction of polyester resins with magnesium acetylacetonate and/or magnesium oxide.

Industrial polyester resins are usually prepared by the simultaneous polycondensation of several diols and dicarboxylic acids. The reaction product contains molecules differing not only in their molecular weight, but also in chemical composition. A variation in the chemical composition of molecules emerging from a set of GPC columns leads to uncertain differences in the detector response and to an erroneous determination of concentration. Some side reactions (addition of diols on the double bonds of unsaturated acids, dehydration of diols, decarboxylation of acids and formation of cyclic molecules) can occur together with the main reaction.

EXPERIMENTAL

Materials

The unsaturated polyester resins to be tested were both commercial and laboratory samples, prepared mostly by polycondensation of phthalic anhydride, maleic anhydride and aliphatic glycols. Polystyrene standards for GPC calibration were supplied by Waters Associates and Polymer Laboratories, tetrahydrofuran (THF) was obtained from Janssen Chimica.

Gel Permeation Chromatography

A Spectra-Physics equipment was used, consisting of an SP 8100 liquid chromatograph, an SP 8440 UV-visible detector operating at 254 nm and an SP 4200 computing integrator. Four Microgel (Chrompack) columns were connected in series, each of them 250 mm x 7.7 mm I.D. and with pore sizes of 100, 500, 10^3 and 10^5 Å. THF served as a solvent at 35 °C, the flow rate was 1 ml/min. Benzene was used as an internal standard to eliminate variances in the flow rate. The concentration of samples was 0.25 % w/v (1 % in the case of samples fractionated for IR analysis), the volume injected was 100 μl.

The system provided for automatic reporting and plotting the background-corrected UV spectra and absorbance ratios in the course of a chromatographic run.

Molecular Weight Determination

The determination of M_n by VPO was carried out on a Hewlett-Packard Model 302B VPO. To determine M_n by EG, acid number and hydroxyl number were estimated as usual and M_n was then calculated from the well-known equation

$$M_n = \frac{2 \times 56 \times 1{,}000}{AN + HN} \qquad /1/$$

where AN and HN are acid number and hydroxyl number in mg KOH/g.

Infrared Spectroscopy

IR spectra of GPC fractions (0.1 mg of each) were measured on a Pye Unicam SP3-300A spectrometer by KBr disc method. The spectra were measured five times to improve the ratio signal/noise, smoothed digitally, and multiplied by fifty.

RESULTS AND DISCUSSION

Evaluation of Chromatograms

The simplest evaluation of GPC data is fingerprinting, i.e. graphical comparison of chromatograms of tested samples.

Prior to the mathematical evaluation of acquired data, the given column system should be calibrated with sufficient accuracy. Unfortunately, the direct calibration of GPC columns by means of standards with narrow MWD is in the case of unsaturated polyester resins impossible because no standards are available commercially. The use of a method of universal calibration is limited by the nature of analysed materials. In the case of polyester resins, the hydrodynamic volume, which is the base of every universal calibration method, does not depend only on the molecular weight, but also on the chemical composition, extent of branching and extent of isomerization of maleate to fumarate. Therefore, it is impossible to propose a general calibration procedure for unsaturated polyesters.

Lee has described (2) a relatively simple calibration method for unsaturated polyesters based on the comparison of M_n values determined by GPC and VPO. Regarding the nature of unsaturated polyesters, the correction factor in work (2) is valid only for a given type of polyester with the same chemical composition and the same extent of side reactions as in case of the sample used for its determination.

Kaštánek et al. have used a similar procedure (1). They plotted GPC calibration curve so as to obtain the best agreement between the values of M_n determined by VPO and those calculated from gel permeation chromatograms of fractions obtained by precipitation fractionation of polyester resin.

The application of calibration curve based on polystyrene standards for polyester resins (3) gives only apparent averages of molecular weight (average molecular weights of a hypothetical polystyrene sample with the same normalized chromatogram as that of the analysed resin) and apparent MWD. These values, however, can be very valuable for an approximate estimation of the real MWD, and if the only aim is to compare samples from different batches or manufacturers, it is, in fact, unnecessary to search for a polyester related calibration. In work (3), the values of M_n obtained by GPC are about 20 percent lower than the values obtained by VPO.

The values of M_n for several various polyesters obtained by GPC (polystyrene equivalent values), VPO, and EG are compared in Table 1. Taking into account the limitations of individual methods, we find that the values obtained by techniques used are in a relatively good agreement. The VPO method is strongly sensitive to a presence of low-molecular-weight substances such as solvents or monomers. On the other hand, the high-molecular-weight fractions can be out of the calibration range of VPO and can account for lower VPO results. The results of EG are influenced by the destruction of functional groups or by using a small amount of a monofunctional monomer. The accuracy of GPC values is dependent on the suitability of the polystyrene calibration for a given sample and on the heterogenity of chemical composition vs. molecular weight.

The precision of GPC was determined by a ten-fold analysis of the same sample. The relative standard deviations of M_n and M_w were 0.38 % and 0.53 %, respectively.

Fig. 1 shows chromatograms of three different batches of unsaturated polyester. The chromatograms are treated so that the elution time axis is converted to the molecular weight axis and the maximum heights of chromatograms are the same. Chromatograms treated in this way are to a certain extent independent on flow rate variances and sample amounts injected and they are very suitable for the comparison of samples. It is seen from Fig. 1

TABLE 1

Number-average molecular weights of polyester resins determined by GPC, VPO and EG

Sample	M_n		
	VPO	GPC	EG
1	1,100	1,260	1,380
2	1,100	1,300	1,350
3	1,170	1,310	1,330
4	1,060	1,250	1,310
5	1,160	1,250	1,300
6	1,690	2,380	1,880
7	1,140	1,420	1,180
8	1,160	1,350	1,420
9	1,070	1,490	1,490
10	1,310	1,610	1,560

that the chromatograms of individual batches are obviously different, giving evidence about not very good production reproducibility.

Fig. 2 shows chromatograms of samples taken from the batch during the synthesis of sample B3. Such series of chromatograms illustrates the increase of the molecular weight during polycondensation and can be used to check the course of synthesis instead of acid number and hydroxyl number which are only average characteristics giving no information about MWD.

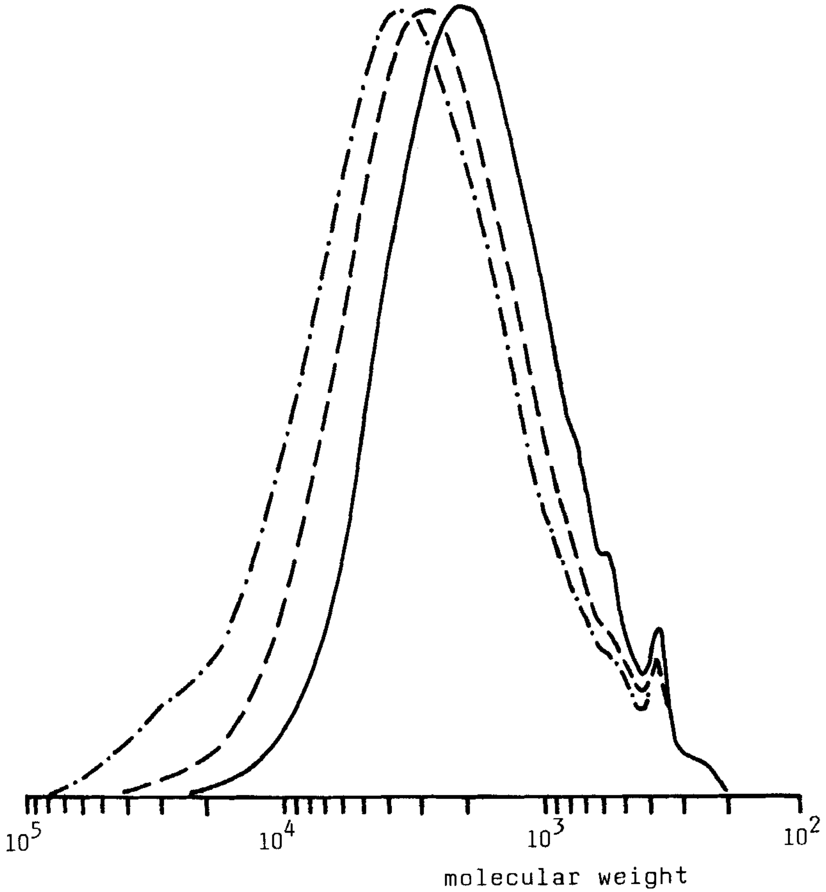


FIGURE 1. GPC chromatograms of three different batches of polyester resin,
batch B1 ———, B2 — — —, B3 — · — · —

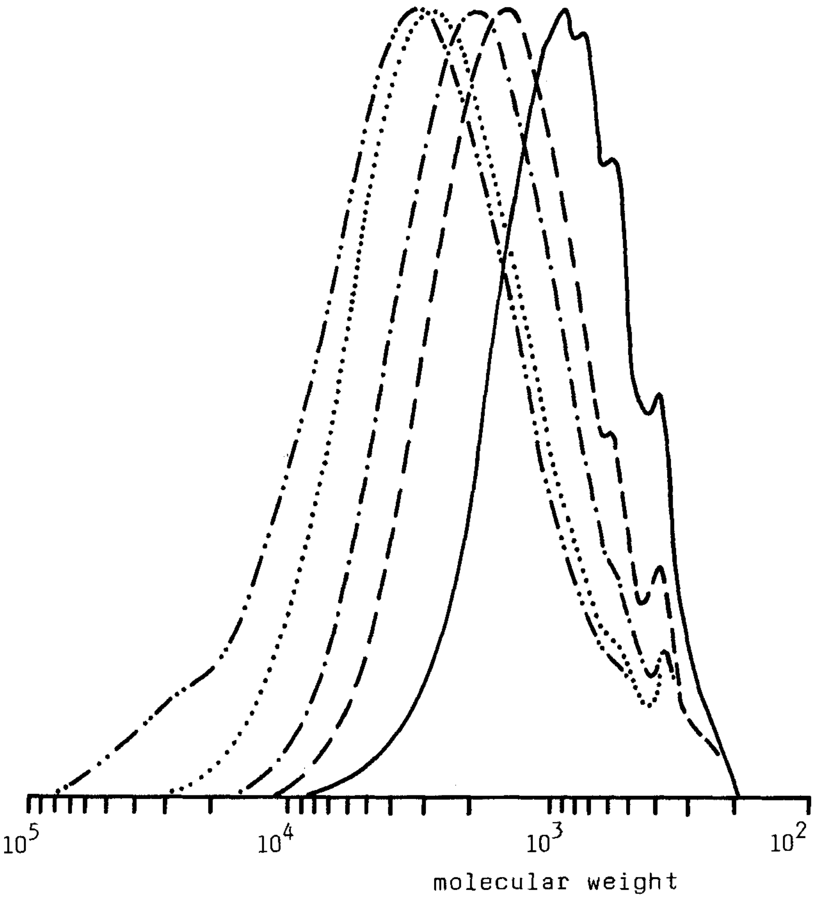


FIGURE 2. GPC chromatograms of samples taken from the batch during the synthesis of resin B3, ——— 2 hr, — — — — 5 hr, — · — · — 7 hr, ······ 11.5 hr, — ·· — final sample after evacuation

The comparison of the chromatograms of the final samples with the chromatogram of a reference sample can serve for the consideration of batch-to-batch variability. The GPC analysis can verify that a fresh resin batch has specifications required. This permits to start the subsequent batch immediately, thereby eliminating the wait for various laboratory test results to become available. The GPC analysis can provide information for corrections required to bring subsequent batches completely into conformity. Thus, increased production rate can be achieved, and product uniformity improved.

Determination of Chemical Composition as a Function of Molecular Weight

The relationship between the chemical composition of polyester resins and the molecular weight is a parameter affecting their physico-chemical and mechanical properties.

Stop-and-go scanning of UV spectrum in the flow-through cell of the detector can be a rapid technique for the determination of resin composition.

An example of such analysis for two samples made of neopentylglycol, isophthalic and fumaric acids is given in Fig. 3. The ratio of absorbance at 262 nm to absorbance at 275 nm was used as a measure of chemical composition. The ratio A_{262}/A_{275} expresses a mutual ratio of fumaric and isophthalic segments in polyester molecules of a given molecular weight. Of course, another suitable pair of wavelengths can be used. To calculate the resin composition as a function of molecular weight, calibration curve for absorbance ratio A_{262}/A_{275} vs. mole fraction of fumaric acid was con-

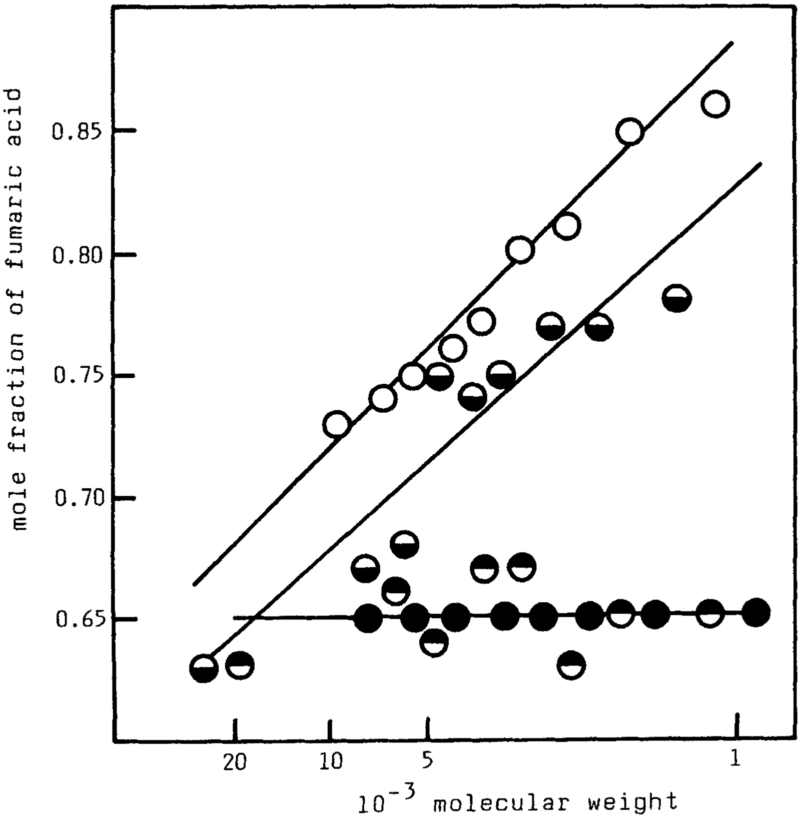


FIGURE 3. Chemical composition of polyester resins synthetized of fumaric acid, isophthalic acid and neopentylglycol as a function of molecular weight,
Sample A: GPC-UV ● Sample B: GPC-UV ○
GPC-IR ◓ GPC-IR ◒

structed by means of model copolyesters or mixtures of homopolyesters with different composition - Fig. 4. The absorbance ratio A_{262}/A_{275} was measured by injecting the solutions of copolyester or a mixture of homopolyesters of a known composition into UV-visible detector with GPC columns disconnected.

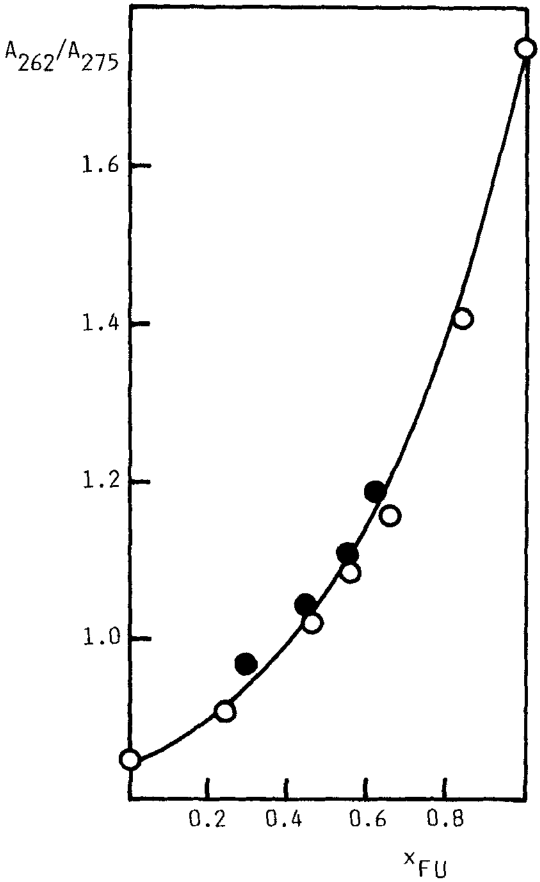


FIGURE 4. Plot of absorbance ratio A_{262}/A_{275} against mole fraction of fumaric acid (x_{FU}) in copolyesters or mixtures of homopolyesters prepared by polycondensation of neopentylglycol with isophthalic acid and/or fumaric acid
copolyester ●
mixture of homopolyesters ○

The data in Fig. 3 show that within the molecular weight range, the chemical composition of the sample A remains constant, while the composition of the sample B is strongly changed along the molecular weight axis.

In order to check this technique by another method, the relationship between chemical composition and molecular weight of samples A and B was determined by collecting fractions from the chromatograph. The composition of polyester in each fraction was determined by infrared spectroscopy. The mole fraction of fumaric segments was determined using absorbance ratio A_{775}/A_{738} (in cm^{-1}). The data are included in Fig. 3. It can be seen that IR results confirm the previous ones.

Estimation of Branching

The addition of hydroxyl groups of diols on double bonds of unsaturated acids during the synthesis of unsaturated polyesters (7,8,9) is one of the most important side reaction which influences the course of polycondensation and the mechanical properties of styrene-crosslinked final materials. It results in the formation of branched molecules with higher molecular weight than that of corresponding linear molecules at the same extent of reaction.

The theoretical differential weight distribution of linear polycondensates is expressed by equation derived by Flory (10)

$$f_w(P) = P(1 - q)^2 \, q^{P-1} \qquad /2/$$

Here, P is the polymerization degree and q is the extent of reaction. Equation /2/ can be simplified by
$\ln q \approx q - 1 = -1/P_n$, $P - 1 \doteq P$, $(1 - q)^2 = 1/P_n^2$,
$q = \exp(\ln q)$, and integrated to

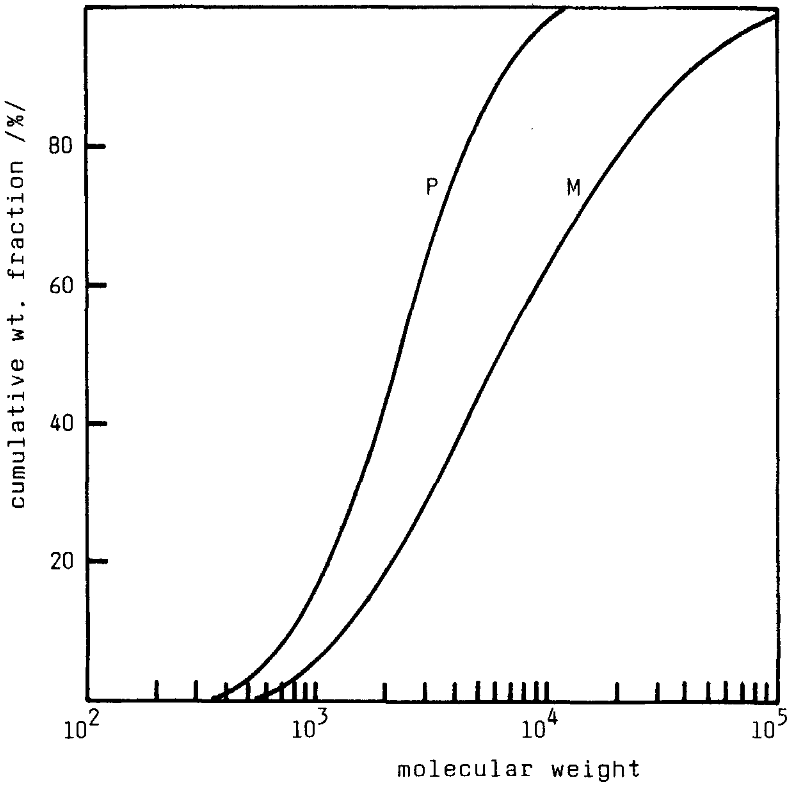


FIGURE 5. Cumulative weight distribution curves of poly(propylene maleate) (M) and poly(propylene phthalate) (P), $M_n(M) = 2{,}920$; $M_n(P)$ □ 1,610

$$I_w(M) = 1 - \exp(-M/M_n)(1 + M/M_n) \qquad /3/$$

P_n is the number-average polymerization degree, $I_w(M)$ is the cumulative weight distribution function, M is the molecular weight.

The cumulative weight distribution curves of two model polyesters determined by GPC are shown in Fig. 5. According to eq. /3/, only 0.005 % of molecules in sample P and 0.8 % of molecules in sample M should exceed the molecular weight 20,000. This condition is well obeyed by the sample P which does not contain any double bonds capable of addition, whereas the sample M contains about 20 % of molecules with a molecular weight over 20,000. Similarly, the dispersion ratio M_w/M_n of the sample P does not exceed the theoretical value 2 ($M_w/M_n = 1.8$), while the dispersion ratio of the sample M is 5.0 .

Hence the deviations of molecular distribution from the theoretical values can be used as a semiquantitative measure of branching extent.

CONCLUSION

The accurate molecular-weight characterization of unsaturated polyester resins cannot be achieved by GPC owing to the character of these materials. The apparent values of molecular weight and apparent MWD can be obtained by means of polystyrene calibration. The agreement among the values of M_n determined by GPC, VPO and EG is mostly fairly good.

GPC may play a great role in plant control of technological processes and in checking the batch-to-batch uniformity of polyester resins. The test sample can be checked merely by comparing the profile of the GPC curve with the chromatogram of a reference sample and/or by comparing the apparent values of molecular weight and distribution curves. GPC also may be used for optimizing the processing time or other reaction conditions. Other applications of this technique are the determination of chemical composition as a function of molecular weight and the estimation of branching extent.

REFERENCES

1. Kaštánek, A., Zelenka, J., and Hájek, K., Molecular Weight Distribution of an Unsaturated Polyester, J. Appl. Polym. Sci., 26, 4117, 1981.

2. Lee, W. Y., Calibration of the Gel Permeation Chromatography Polyester Resins, J. Appl. Polym. Sci., 22, 3343, 1978.

3. Lyttle, B. W., Evaluation of Size Exclusion Chromatography as a Replacement for the Vapor Pressure Method in Analysis of Low Molecular Weight Polyester Resins, 37th Annual Conference, Reinforced Plastics Composites Institute, The Society of the Plastics Industry, Inc. January 11-15, Session 23-A, 1, 1982.

4. Douglas, W. E., Ghotra, J. S., Dawn Ho, and Pritchard, G., Molecular Weight Averages and Distributions of Unsaturated Polyesters: Their Effect on the Properties of Styrene-crosslinked Networks, Br. Polym. J., 16, 139, 1984.

5. Laleg, M., Blanchard, F., Chabert, B., and Pascault, J. P., Contribution à l'étude du mécanisme de murissement de résines polyesters insaturées en présence de MgO, Eur. Polym. J., 21, 591, 1985.

6. Judas, D., Fradet, A., and Marechal, E., Mechanism of the Thickening Reaction of Polyester Resins: Study on Models, J. Polym. Sci., Polym. Chem. Ed., 22, 3309, 1984.

7. Ordelt, Z., Über die Reaktion von Glykolen mit der olefinischen Doppelbindung bei der Darstellung von ungesättigten Polyestern durch Schmelzkondensation, Makromol. Chem., 63, 153, 1963.

8. Fradet, A. and Marechal, E., Study on Models of Double Bond Saturation During the Synthesis of Unsaturated Polyesters, Makromol. Chem., 183, 319, 1982.

9. Paci, M., Crescenzi, V., Supino, N., and Campana, F., Structural Characterization of Unsaturated Polyesters, Makromol. Chem., 183, 377, 1982.

10. Flory, P. J., Principles of Polymer Chemistry, Cornell University Press, New York, 1953, p. 320.