

GPC and HPLC Characterization of Unsaturated Polyester Resins

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SYNOPSIS

This article is concerned with the characterization of unsaturated polyester (UP) resins by conventional gel permeation chromatography (GPC), GPC connected with multiangle laser light scattering detector (GPC-MALLS), and reversed-phase high performance liquid chromatography (HPLC). The ability of particular methods to analyze UP resins is demonstrated in several examples. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

UP resins are condensation products of unsaturated acids (mostly maleic acid), saturated acids (e.g., phthalic acid), and glycols (e.g., 1,2-propyleneglycol). Various combinations of different acids and glycols and their mol ratios give products with different properties and final applications. The polycondensation products are usually used as solutions in styrene which find utilization as a component of lacquers and bonding agents of synthetic marble, polyester concrete, or glass reinforced construction materials (e.g., for pipes and tanks in corrosive environment, power station pressure pipes, sludge separators, oil tanks, and food containers).

From the chemical point of view, the UP resins are varied mixtures of molecules differing in molecular weight, chemical composition, and degree of branching. Continuously increasing requirements on the properties of final materials together with safety regulations and environmental concerns emphasize the necessity of thorough analytical investigation of final UP resins as well as the quality control of resin manufacture. Until now, often employed hydroxyl and acid numbers are unable to describe molecular weight distribution of UP resins, to follow the course of polycondensation in detail, to distinguish differences between samples, and to find reliable relation between the structure of UP resins and properties

of final products based on them. GPC and HPLC, as separation techniques, offer to be suitable tools for the study of complicated structure of UP resins. Compared to a great technical importance of UP resins, a relatively small amount of attention has been paid to the liquid chromatographic analysis of these materials. GPC has been employed for the characterization of UP resins in the works;¹⁻⁴ examples of HPLC chromatograms can be found in the references.⁵⁻⁷

EXPERIMENTAL

GPC, GPC-MALLS and HPLC Equipment

Conventional GPC was carried out using chromatograph consisting of an HPP 4001 pump (Laboratory Instruments), one Ultrastyrigel Linear 300 × 7.8 mm column (Waters), or a set of four 250 × 7.7 mm Microgel (Chrompack) columns (50, 100, 500, 1000 Å), a UV detector Model 440 (Waters) operating at 254 and 280 nm, a differential refractometer R 401 (Waters), and an SP 4200 integrator (Spectra-Physics). Tetrahydrofuran (THF) was used as a mobile phase at a flow rate of 1 mL/min. Sample size was 50 μL of 0.15 to 0.3% solutions in THF. The columns were calibrated by means of polystyrene standards (Polymer Laboratories) covering the molecular weight range of 580 to 1,840,000.

For GPC-MALLS, a following chromatographic system was used. A Waters 510 pump, an Ultrastyrigel Linear column, a Dawn F laser photometer

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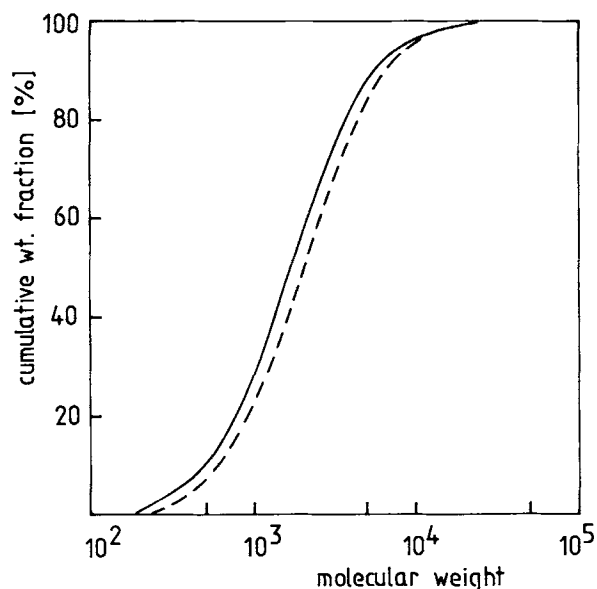


Figure 1 Cumulative weight distribution curves of UP resin determined by GPC using a single Ultrastryragel Linear column—full line, and a set of four Microgel columns (50, 100, 500, 1000 Å)—dashed line.

(Wyatt Technology Corporation), and a Wyatt Optilab 903 refractometer. Collected data were handled by Astra and Easi software (Wyatt Technology Corporation). THF at 1 mL/min served as a mobile phase. One hundred microliters of 0.9% solutions in THF were injected.

A Spectra-Physics SP 8100 liquid chromatograph was used for HPLC measurements. The effluents were monitored with an SP 8440 UV/VIS detector (Spectra-Physics) at 254 nm. A Spectra-Physics Chromject integrator served for data handling. Se-

paron SGX C18 stainless steel column 250 × 4 mm (Tessek), particle diameter 7 μm, with gradient elution THF-methanol-water was employed for the analyses of UP resins. Samples were injected as solutions in THF. The injected amounts were 10 μL of 3 to 5% solutions. The flow rate of mobile phase was 1 mL/min.

Materials

All UP resins discussed in the text were prepared by azeotropic polycondensation in SYNPO.

RESULTS AND DISCUSSION

Our previous work has demonstrated the possibilities of GPC for thorough characterization of UP resins.⁴ The findings from this work can be summarized as follows: (1) Number average molecular weights (M_n) determined by GPC with polystyrene calibration are in fairly good agreement with values obtained by vapor phase osmometry (VPO) and end group analysis (EG). (2) GPC enables following the course of polycondensation and comparison of final samples in detail. (3) The polydispersity ratio M_w/M_n can be used as a measure of branching extent. (4) GPC with UV detection at a pair of suitable wavelengths can determine mol ratio of unsaturated acid and saturated acid as a function of molecular weight.

A single GPC column containing mixed packing instead of a classical set of several columns differing in their pore sizes can be used. The results are well comparable (Fig. 1) and the advantages of mixed gel column are several-fold: greatly simplified col-

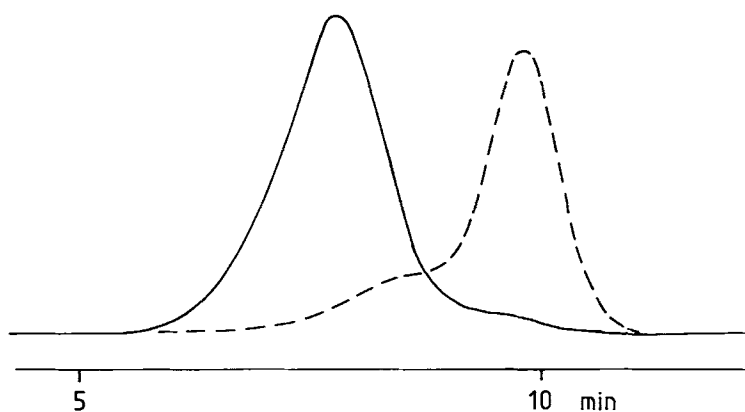


Figure 2 GPC chromatograms of UP resin obtained by MALLS 90° detector (full line) and RI detector (dashed line). Corresponding HPLC chromatogram is in Figure 7 (sample III).

umn choice, no spurious peaks caused by a wrong column arrangement, reduced analysis time, and solvent consumption. If necessary, greater resolution can be easily achieved by adding an extra column.

Connection of GPC with a molecular weight sensitive light scattering detector overcomes the basic problem of GPC, i.e., necessity of column calibration. The only limitation for correct determination of molecular weight distribution by GPC-MALLS is that the investigated sample must be chemically homogeneous. Unfortunately, this need not be necessarily obeyed in the case of UP resins. However, at least chemical homogeneity along molecular weight axis can be checked by GPC with multiwavelength UV detection.

Figure 2 shows chromatograms of UP resin recorded by refractive index (RI) detector and MALLS detector at scattering angle of 90° . MALLS detector detects very sensitively the molecules with high molecular weights, while RI detector monitors mainly lower molecular weights, while RI detector monitors mainly lower molecular weights present at higher concentrations. High molecular weight fractions in UP resins prepared from bifunctional monomers can arise only by side reactions, i.e., addition of water and/or glycols on double bonds of unsaturated acid⁷⁻⁹ and formation of branched molecules and/or polymerization of double bonds. Consequently, the high sensitive determination of the high molecular weight by-products in UP resins by MALLS detector can be very useful and can give valuable information about polycondensation process.

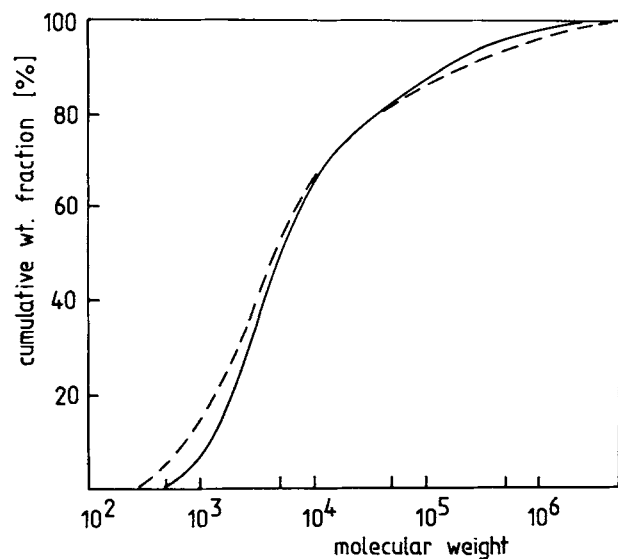


Figure 3 Cumulative weight distribution curves of the sample whose GPC chromatogram is in Figure 2 determined by GPC (full line) and GPC-MALLS (dashed line).

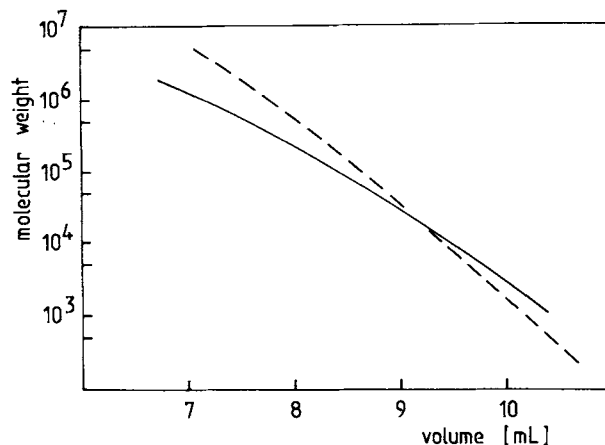


Figure 4 Molecular weight vs. volume plots for UP resin (GPC chromatogram see Fig. 2)—dashed line, and polystyrene (full line). UP resin composition: 1,2-propyleneglycol, maleic anhydride, phthalic anhydride.

Cumulative weight distribution curves of a UP resin sample determined by conventional GPC and GPC-MALLS are compared in Figure 3. The agreement of both curves is very good.

To compare GPC calibration curve of UP resin

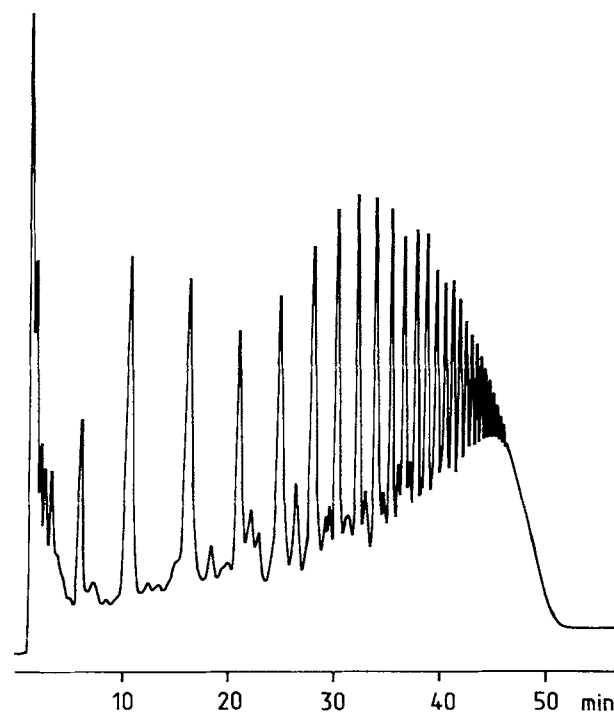


Figure 5 HPLC chromatogram of model poly(1,2-propyleneglycol phthalate). Gradient THF-methanol-water (0 min—25% THF, 20% methanol; 60 min—50% THF, 45% methanol). GPC: $M_n = 1,640$; $M_w = 2,810$.

with that of polystyrene, a polystyrene sample with broad molecular weight distribution was analyzed after the analysis of the UP resin. Obtained molecular weight vs. elution volume plots are in Figure 4. The mutual course of the two curves in the region of higher volumes corresponds to the previously reported higher M_n values estimated by GPC with those obtained by means of VPO.⁴ The curves cross at the molecular weight of about 20,000 and their difference becomes more significant towards the lower elution volumes (i.e., higher molecular weights). In a randomly branched polymer, the fractions with higher molecular weights are more branched than those with lower molecular weights. Consequently, the highly branched polyester molecules are more compact with lower hydrodynamic volumes than those of linear polystyrene of the same molecular weights. The similar relation between polystyrene and UP resin calibration curves was found for a UP resin containing trifunctional monomer trimethylolpropan.

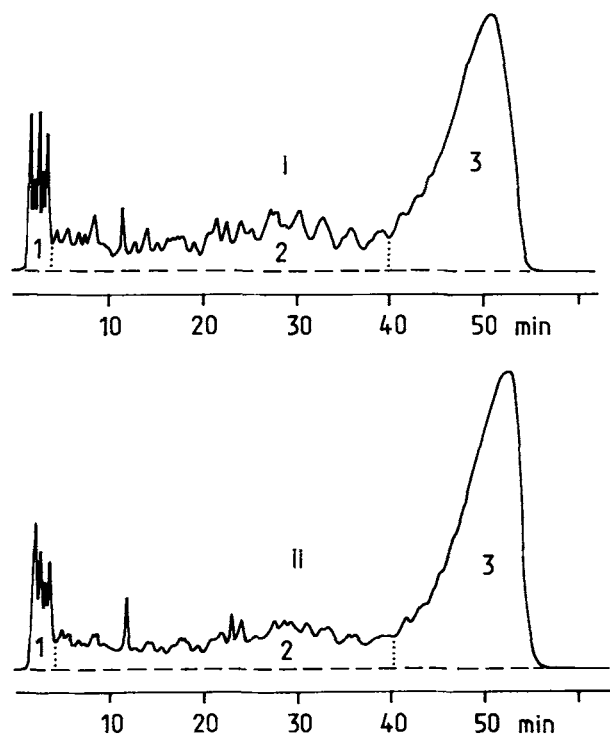


Figure 6 HPLC chromatograms of two batches of UP resin. Gradient THF-methanol-water (0 min—15% THF, 20% methanol; 25 min—30% THF, 25% methanol; 35 min—30% THF, 25% methanol; 60 min—60% THF, 40% methanol). HPLC relative areas: sample I: 1—5.8%; 2—35.5%; 3—58.7%; sample II: 1—5.6%; 2—29.7%; 3—64.7%. GPC: sample I: $M_n = 2,220$; $M_w = 6,990$; sample II: $M_n = 2,890$; $M_w = 9,520$.

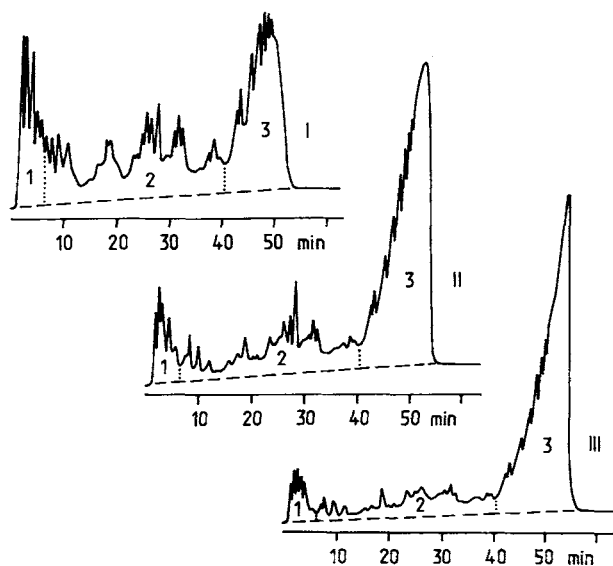


Figure 7 HPLC chromatograms of samples taken from the batch during the synthesis of UP resin. Gradient as in Figure 6. HPLC relative areas: sample I (3.5 h): 1—11.3%; 2—49.7%; 3—39.0%; sample II (6 h): 1—7.5%; 2—26.3%; 3—66.2%; sample III (7.2 h): 1—5.0%; 2—21.4%; 3—73.6%. GPC: sample I: $M_n = 1,420$; $M_w = 2,790$; sample II: $M_n = 2,130$; $M_w = 5,370$; sample III: $M_n = 3,050$; $M_w = 73,000$.

In contrast to GPC, HPLC has not been routinely used for the characterization of UP resins. Chromatogram of a model resin poly(1,2-propyleneglycol phthalate) in Figure 5 shows potential possibilities of HPLC for UP resin analysis. Unfortunately, the chromatograms of real samples are much less clear because oligomers contain different acid and glycol segments.

HPLC chromatograms of two different batches of UP resin are compared in Figure 6. The example shows the ability of the method to distinguish between the samples. To make the comparison of chromatograms easier, they were separated into three parts whose relative areas are included in the figure caption. The first group of peaks with the lowest retention times may be assigned to low molecular weight polar compounds, the middle group to lower oligoesters, and the third group with the highest retention times to molecules with the highest molecular weights. An interesting finding is that the two samples contain the same amount of low molecular weight polar compounds, regardless of their different molecular weights.

Figure 7 shows HPLC chromatograms of samples taken from the batch during UP resin preparation. The changes of relative areas of individual chromatogram zones correspond to the build up of poly-

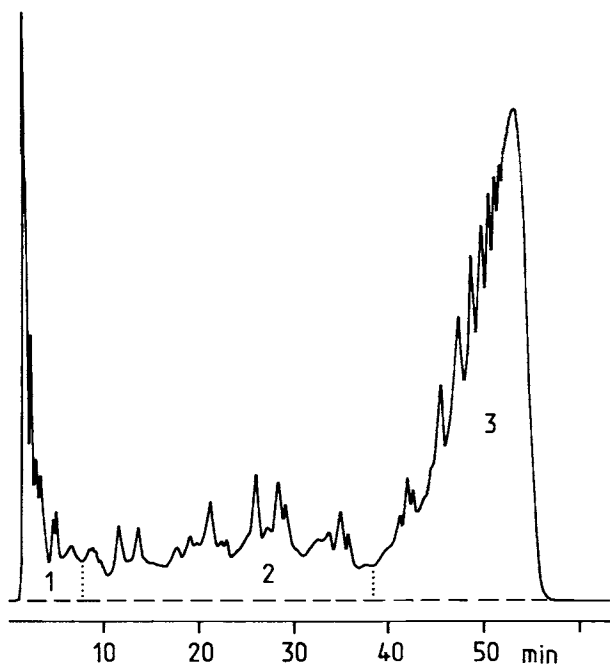


Figure 8 HPLC chromatogram of UP resin prepared with mol ratio of maleic anhydride : phthalic anhydride 1.5 : 1. Gradient as in Figure 6. HPLC and GPC data—see Table I.

ester chains during polycondensation and accord with increasing molecular weight.

A chromatogram of UP resin prepared from 1,2-propyleneglycol, phthalic anhydride, and maleic anhydride is shown in Figure 8. The chromatogram is separated into three parts, similarly, as in the case of previous samples. Three other resins prepared from the same monomers, but with various mol ratio

of phthalic anhydride and maleic anhydride were analyzed in the same way. Table I summarizes relative areas of HPLC zones together with acid and hydroxyl numbers, M_n values, and weight average molecular weights (M_w). In spite of approximately the same conversion (see acid and hydroxyl numbers), the values of M_w and M_w/M_n increase markedly with increasing content of unsaturated acid. As a system with a higher degree of branching has generally a broader molecular weight distribution, the presence of branched by-products arising by side reactions of double bonds explains the finding. A different HPLC behavior was observed compared with the previous samples (Figs. 6 and 7). The relative area of the third group in HPLC chromatograms decreases with increasing values of M_n and M_w . This means that retention increases with increasing content of phenyl nuclei and, in this case, separation according to chemical composition, prevails over separation according to molecular weight.

CONCLUSIONS

Conventional GPC with polystyrene calibration provides good molecular characterization of UP resins with a slight tendency to overestimate M_n and, in the case of samples containing high molecular weight fractions, to underestimate M_w values. The method measures the ratios of molecular weights of corresponding samples with a much better accuracy than the absolute molecular weights. Satisfactory results can be obtained using a single column packed by a mixed gel packing. GPC-MALLS facilitates very sensitive determination of even trace amount of high molecular weight by-products. These by-

Table I Relative Areas of Groups 1, 2, 3 in HPLC Chromatograms, M_n , M_w , M_w/M_n , Acid Numbers, and Hydroxyl Numbers of UP Resins Prepared by Polycondensation of 1,2-Propylene Glycol and Different Amount of Maleic Anhydride and Phthalic Anhydride

Mol Ratio MA:FA	HPLC Relative Area (%) of Zones			M_n	M_w	M_w/M_n	AN	HN
	1	2	3					
0:1	10.7	23.1	66.1	1,640	2,810	1.7	24.0	42.0
0.7:1	12.2	25.1	62.8	1,730	4,070	2.4	26.4	35.4
1.5:1	14.2	26.3	59.5	1,820	4,930	2.7	26.1	34.9
3.5:1	17.2	26.9	55.9	1,860	7,690	4.1	29.1	38.4

MA—maleic anhydride.

FA—phthalic anhydride.

AN—acid number in mg KOH/g.

HN—hydroxyl number in mg KOH/g.

products are branched and arise by side reactions of double bonds. HPLC can serve as an additional auxiliary method capable to complete information about investigated samples.

REFERENCES

1. W. Y. Lee, *J. Appl. Polym. Sci.*, **22**, 3343 (1978).
2. B. W. Lyttle, *37th Annual Conference, Reinforced Plastics Composites Institute, The Society of the Plastics Industry, Inc.* January 11–15, **Session 23-A**, 1 (1982).
3. W. E. Douglas, J. S. Ghotra, Dawn Ho, and G. Pritchard, *Br. Polym. J.*, **16**, 139 (1984).
4. Š. Podzimek, J. Hanuš, J. Klaban, and J. Kitzler, *J. Liquid Chromatogr.*, **13**, 1809 (1990).
5. Š. Podzimek, *Chromatografia*, **33**, 377 (1992).
6. C. Kuo, T. Provder, R. M. Holsworth, and A. F. Kah, in *Liquid Chromatography of Polymers and Related Materials III*, J. Cazes, Ed., Marcel Dekker, Inc., New York, 1981, p. 169.
7. M. Paci, V. Crescenzi, N. Supino, and F. Campana, *Makromol. Chem.*, **183**, 377 (1982).
8. Z. Ordelt, *Makromol. Chem.*, **63**, 153 (1963).
9. A. Fradet and E. Marechal, *Makromol. Chem.*, **183**, 319 (1982).

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