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# Characterization of synthetic resins by gel permeation chromatography with a multi-angle laser light scattering detector

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## Abstract

Gel permeation chromatography coupled with a multi-angle laser-light scattering detector was applied to the characterization of various kinds of synthetic resins (epoxy, phenoxy, novolac, unsaturated polyester, alkyd resins). The relations between molecular mass and elution volume of polystyrene and particular resins were investigated and the presence of branched molecules in the resins was proved by the root mean square radius vs. molecular mass plot. The possibilities and limitations of conventional gel permeation chromatography are discussed based on the obtained results.

## 1. Introduction

Synthetic resins are a specific group of synthetic polymers of a great technical importance. They are usually used as a component of lacquers, adhesives and graphite- or glass-reinforced construction materials. The major part of the molecules even in the higher-molecular-mass types of the resins has molecular masses up to several tens of thousands, but high-molecular-mass fractions with molecular masses of the order of magnitude  $10^6$  to  $10^7$  may be present in some resins.

The combination of gel permeation chroma-

tography (GPC) with the molecular mass sensitive multi-angle laser-light scattering (MALLS) detector gives the absolute molecular mass and size distribution (providing sample chemical homogeneity). GPC-MALLS has been employed several times for the characterization of organic and water-soluble polymers [1–6], but the results concerning synthetic resins may not have been reported. The aim of this work is to show possibilities of the GPC-MALLS technique for the investigation of these materials.

The DAWN-F photometer measures the intensity of the light scattered from a flowing sample at 15 angular positions. A chromatography peak is divided into several hundreds of slices and the molecular mass and the root mean square (RMS) radius (also called the radius of gyration) are calculated for each slice. The reciprocal scattering function  $Kc/R_{90}$  is plotted as

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a function of  $\sin^2(\Theta/2)$ . The intercept of this plot  $k_0$  yields the molecular mass  $M_r$ :

$$M_r = (k_0 - 2A_2c)^{-1} \quad (1)$$

and the slope for  $\Theta \rightarrow 0$   $m_0$  gives RMS radius  $\langle r_g^2 \rangle^{1/2}$ :

$$\langle r_g^2 \rangle^{1/2} = \frac{\sqrt{3}\lambda_0}{4\pi n_0} \sqrt{m_0 M_r} \quad (2)$$

where  $A_2$  is the second virial coefficient, which often may be neglected,  $c$  is the concentration usually measured by a refractive index (RI) detector,  $\lambda_0$  is the wavelength of the incident light in vacuo,  $n_0$  is the refractive index of the solvent,  $K$  is a physical constant proportional to the square of the specific refractive index increment  $dn/dc$  and  $R_\Theta$  is the excess Rayleigh ratio proportional to the intensity of scattered light.

## 2. Experimental

The GPC–MALLS instrument consisted of a Model 510 Waters pump, an Ultrastaygel Linear column (Waters), a DAWN-F photometer (Wyatt Technology) and a Wyatt Optilab 903 refractometer. Data collection and handling were carried out using ASTRA and EASI software (Wyatt Technology). Tetrahydrofuran (THF) served as the mobile phase at the flow-rate of 1 ml/min. Samples were prepared as solutions in THF: 0.15% polystyrene (PS), 0.6% epoxy and phenoxy resins, 0.75% novolacs, 0.9% unsaturated polyesters and alkyds. Unusually high concentrations of the resin samples were used to improve the signal-to-noise ratio of the light scattering and RI detectors at the edges of the chromatograms. As a major part of the molecules in the analysed samples has molecular mass of the order of magnitude  $10^4$ , the term  $2A_2cM_r \ll 1$  and the concentrations do not significantly affect the results. The  $dn/dc$  calculation method was used for the data evaluation of PS, phenoxy and epoxy resins using the following values of  $dn/dc$ : 0.1845 ml/g (PS), 0.1773 ml/g (phenoxy resin) and 0.1869 ml/g (epoxy

resin) [7]. The mass calculation method was used for unsaturated polyesters, alkyds and novolacs.

All resins analysed were synthesized at SYNPO or obtained commercially. Broad PS was purchased from Aldrich.

## 3. Results and discussion

An example of GPC chromatograms of synthetic resin recorded by MALLS ( $90^\circ$ ) and RI detectors is presented in Fig. 1. The chromatograms do not overlap due to the different kind of response. The large volume difference between the peaks of light scattering and RI profiles gives evidence about very high polydispersity of the resin.

Molecular mass vs. elution volume plots (GPC calibration curves) of particular resins are compared with that of PS in Figs. 2–5. Fig. 2 shows that the molecular mass of epoxy resin is by about 40% lower than that of PS of the same elution volume. The plot of phenoxy resin approximately overlapped the epoxy resin curve. The molecular mass vs. elution volume plots of unsaturated polyester resin and PS (Fig. 3) cross at the molecular mass of about 20 000 and the difference between them becomes more pronounced towards high molecular masses. Calibration plots of novolac resins made using different phenol/formaldehyde ratios overlapped and the mutual course of novolac and PS curves (Fig.

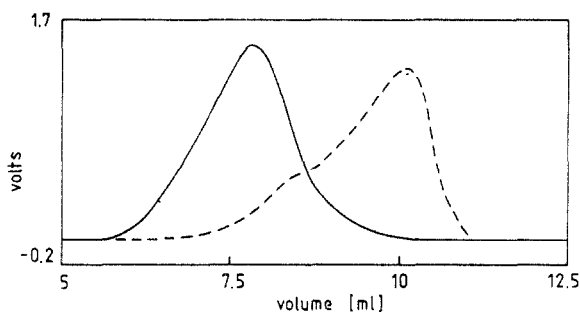


Fig. 1. RI (dashed line) and  $90^\circ$  light scattering (solid line) chromatograms of novolac resin (phenol–formaldehyde ratio 1:0.9). Column, Ultrastaygel Linear  $300 \times 7.8$  mm; particle size,  $7 \mu\text{m}$ ; mobile phase, THF; flow-rate, 1 ml/min; sample size,  $100 \mu\text{l}$ .

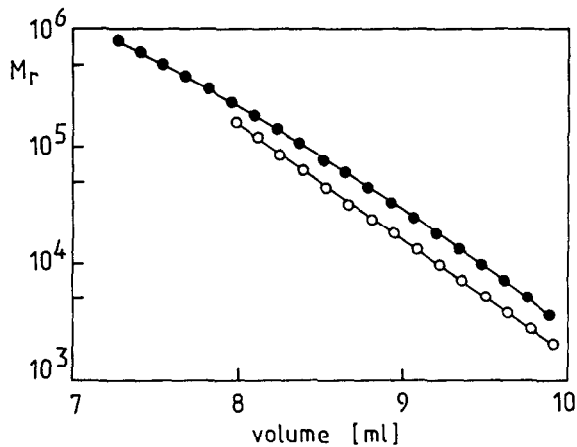


Fig. 2. Molecular mass vs. elution volume plots of PS (●) and epoxy resin (○).

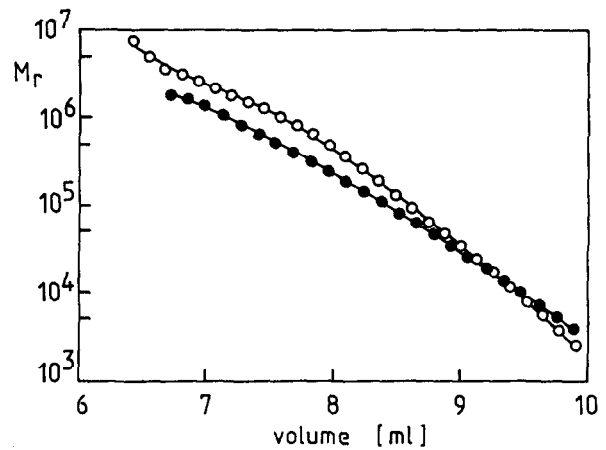


Fig. 4. Molecular mass vs. elution volume plots of PS (●) and novolac resin (○).

4) is similar as in the case of unsaturated polyester. Fig. 5 presents molecular mass vs. elution volume plots of PS and two different alkyd resins. The significant shift of calibration curves of both alkyds can be explained by different degree of branching.

RMS radius is the second important physical parameter that can be extracted from the MALLS measurement. The determination of the molecular mass and RMS radius at each volume slice provides the RMS radius vs. molecular mass plot. The plot gives information about the struc-

ture of polymer chain. In order to improve the accuracy of the measurement, high-molecular-mass fractions from unsaturated polyester, epoxy and novolac resins were isolated by the precipitation of THF solutions by hexane. An example of the RMS radius vs. molecular mass plot for a high-molecular-mass novolac fraction is shown in Fig. 6. The plot of PS is superimposed in Fig. 6. The slope of the PS plot is 0.56 which is a typical value for the linear random coils in a good solvent while all resins showed significantly lower values: 0.36 novolac, 0.36 unsaturated polyester,

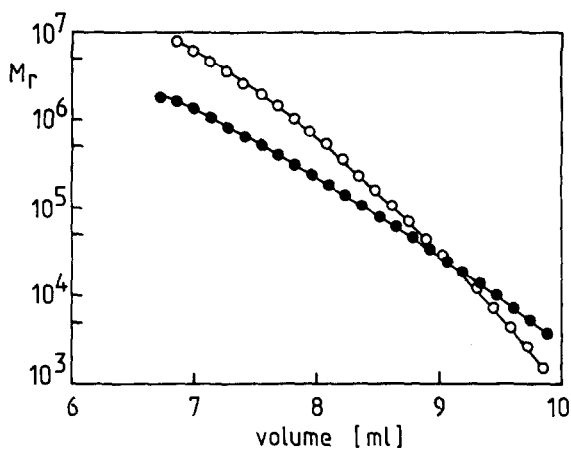


Fig. 3. Molecular mass vs. elution volume plots of PS (●) and unsaturated polyester resin (○).

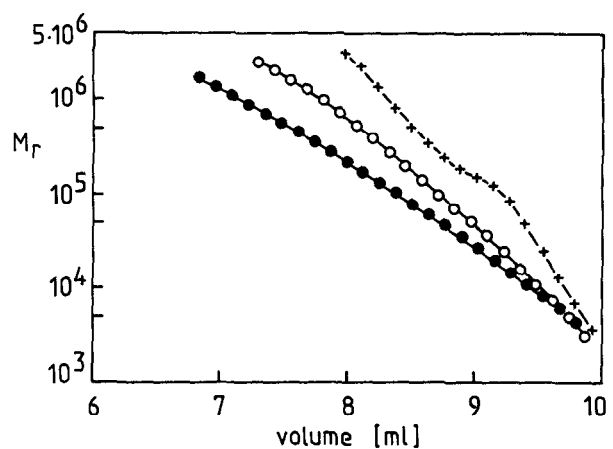


Fig. 5. Molecular mass vs. elution volume plots of PS (●) and two alkyd resins (○, +).

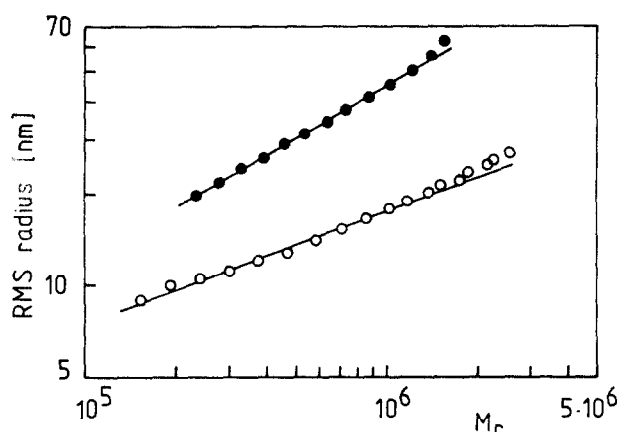


Fig. 6. RMS radius vs. molecular mass plots of high-molecular-mass novolac fraction (○) and PS (●); slopes: 0.56 (PS) and 0.36 (novolac).

0.37 epoxy resin, 0.38 alkyd. The lower slopes prove the presence of more compact branched molecules.

#### 4. Conclusions

The following notes concerning conventional GPC can be drawn from the obtained results:

(1) Epoxy and phenoxy resins: the application of PS calibration gives higher values of number-average molecular mass ( $M_n$ ) and mass-average molecular mass ( $M_w$ ).

(2) Novolac and unsaturated polyester resins: calibration based on PS standards has tendency to overestimate  $M_n$  and, for samples containing high-molecular-mass fractions, underestimate  $M_w$ . The relation between molecular masses of novolac and styrene oligomers proposed in ref. [8] can be used only for low-molecular-mass novolacs and mainly for the determination of  $M_n$ . Its application to the determination of  $M_w$  values of high-molecular-mass novolac resins yields misleading results lower up to ten times.

(3) Alkyd resins: PS calibration underestimates  $M_n$  and mainly  $M_w$ . Alkyds are usually the most branched resins and consequently conven-

tional GPC may give even confusing results as shown in Fig. 5. The most useful application of conventional GPC in the production of alkyd resins may be following the course of polycondensation.

GPC-MALLS provides the absolute molecular mass distribution and very sensitive determination of high-molecular-mass fractions. The method can prove the presence of branched molecules and to characterize them. This capability seems very useful because the highly branched compact molecules may have reduced reactivity with respect to the curing agents due to the lack of reactive positions and their steric hindrance. The branched particles may affect as microscopic defects and influence unfavourably the properties of the cured resins.

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#### References

- [1] P.J. Wyatt, *Anal. Chim. Acta*, 272 (1993) 1.
- [2] P.J. Wyatt, *J. Liq. Chromatogr.*, 14 (1991) 2351.
- [3] C. Jackson, L.M. Nilsson and P.J. Wyatt, *J. Appl. Polym. Sci.: Appl. Polym. Symp.*, 43 (1989) 99.
- [4] C. Jackson, L.M. Nilsson and P.J. Wyatt, *J. Appl. Polym. Sci.: Appl. Polym. Symp.*, 45 (1990) 191.
- [5] B. Bednar and J.P. Hennessey, Jr., *Carbohydr. Res.*, 243 (1993) 115.
- [6] Š. Podzimek, *J. Appl. Polym. Sci.*, submitted for publication.
- [7] *Application Notes 1 and 2*, Chromatix, Sunnyvale, CA, 1976 and 1977.
- [8] Š. Podzimek and L. Hroch, *J. Appl. Polym. Sci.*, 47 (1993) 2005.