

effectively increased (in comparison to the vulcanizate without lignin) because portions of the crosslinking sites become non-available to the curing agents due to the masking effect of lignin.

REFERENCES

- 1 Kumaran, M. G. and De, S. K. *J. Appl. Polym. Sci.* in press
- 2 Kumaran, M. G. and De, S. K. *Kautsch. Gummi.* in press
- 3 Kumaran, M. G. and De, S. K. *Indian J. Technol.* in press
- 4 ASTM method B, 70°C, 24 h
- 5 Mukhopadhyay, R. and De, S. K. *Polymer* 1977, 18, 1243
- 6 Bristow, G. M. and Wistall, B. J. *J. Appl. Polym. Sci.*, 1965, 2, 495
- 7 Mullins, L. *J. Appl. Polym. Sci.* 1959, 2, 1
- 8 Flory, P. J. *J. Chem. Phys.* 1950, 18, 108
- 9 Saville, B. and Watson, A. A. *Rubber Chem. Technol.* 1967, 40, 100
- 10 Kraus, G. *Rubber Chem. Technol.* 1957, 30, 928
- 11 Campbell, D. S. *J. Appl. Polym. Sci.* 1969, 13, 1201
- 12 Campbell, D. S. and Saville, B. *Proc. Int. Rubber Conf., Brighton, 1967*, p.1
- 13 Dogadkin, B. A., Shumanov, L. A. and Tutorsky, I. A. *Polymer* 1968, 9, 413
- 14 BS 903: Part B 10 (1958)
- 15 Studebaker, M. L. *Rubber Chem. Technol.* 1966, 39, 1359
- 16 Blackman, E. J. and McCall, E. B. *Rubber Chem. Technol.* 1970, 43, 651
- 17 Bristow, G. M. and Tiller, R. F. *Kautsch. Gummi.* 1970, 23, 55
- 18 Loo, C. T. *Polymer* 1974, 15, 357

Evidence for a high molecular weight tail in the Dow S-102 polystyrene

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INTRODUCTION

Polystyrene (Dow S-102) is one of a series of polystyrenes prepared in benzene using n-butyllithium as the initiator¹. As a result, the members of this series should possess a near-monodisperse distribution of molecular weights. As a consequence of the near-monodisperse molecular weight distributions of these polymers, the Dow polystyrenes have long been used as 'standard' polystyrenes in a variety of physical measurements.

However, several recent papers^{2,3} have reported anomalous behaviour for several members of this polystyrene series. Penwell and Graessley² discussed the differences in the zero-shear melt viscosities between the S-109 polystyrene and other polystyrenes of comparable weight-average molecular weights. The S-109 material had the lower viscosity, by a factor of about 2, and this difference was maintained over a temperature range of 142°C to 227°C. A recent examination⁴ of the S-109 by gel permeation chromatography (g.p.c.) revealed that the low melt viscosity values for this polystyrene cannot be accounted for by the presence of a low molecular weight tail in the molecular weight distribution. In addition, the S-102 polystyrene has been reported³ to exhibit an anomalously low (by 3°C to 4°C) glass transition temperature when compared to a series of near-monodisperse polystyrenes from Pressure Chemicals Co.

Hence, it was thought to be of interest

to examine the S-102 polystyrene by g.p.c. in order to elucidate in greater detail some previously reported⁴ anomalies (an unusual *high* molecular weight tail) present in the molecular weight distribution of this polymer. Thus, fractions of the S-102 were examined in order to identify the nature of the high molecular weight components.

EXPERIMENTAL

The Waters Ana-Prep instrument was used with seven 4 ft Styragel columns. The porosity range of these columns was from 2×10^3 to 5×10^6 Å. The carrier solvent was tetrahydrofuran at 40°C. The detector was the Waters differential refractometer and solution concentrations of 1/4% (w/v) were used. The measurements were conducted at a flow rate of 1/3 ml/min. Full loop (2 ml) injections were made. The instrument was equipped with a 5 ml syphon. This syphon was covered and the syphon chamber saturated with solvent vapour in order to minimize solvent evaporation.

The calibration of this 7 column set was carried out using commercial polystyrene standards and polystyrenes synthesized and characterized in these laboratories. The column set had a plate count of 900 ppf at the 1/3 ml/min flow rate.

The S-102 polystyrene was fractionated at 30°C using methyl ethyl ketone and isopropanol. A total of 23

fractions were collected. The tacticity of the whole polymer and one of the high molecular weight fractions was examined by ¹³C n.m.r. Perdeuteriochloroform was the solvent used for the n.m.r. measurements.

RESULTS AND DISCUSSION

S-102 polystyrene has been characterized with regard to molecular weights by various groups^{1,5-10}. Ratios for \bar{M}_w/\bar{M}_n ranging from 1.05 to 1.11 were reported. These results seemingly indicate that the S-102 sample can be classified as having a narrowly dispersed molecular weight. However, an inspection of the fractionation data of Breitenbach and Streichsbier¹¹ reveals that their fraction 1 (out of a total of 7) had an intrinsic viscosity of 0.55 dl/g in toluene, a value which corresponds to a molecular weight of approximately 1.2×10^5 g/mol. The existence of some high molecular weight species

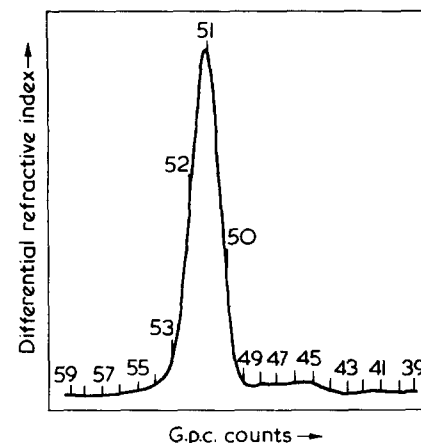


Figure 1 Chromatogram of the unfractionated Dow S-102 polystyrene. $\bar{M}_w = 8.1 \times 10^4$ g/mol; $\bar{M}_n = 7.4 \times 10^4$ g/mol

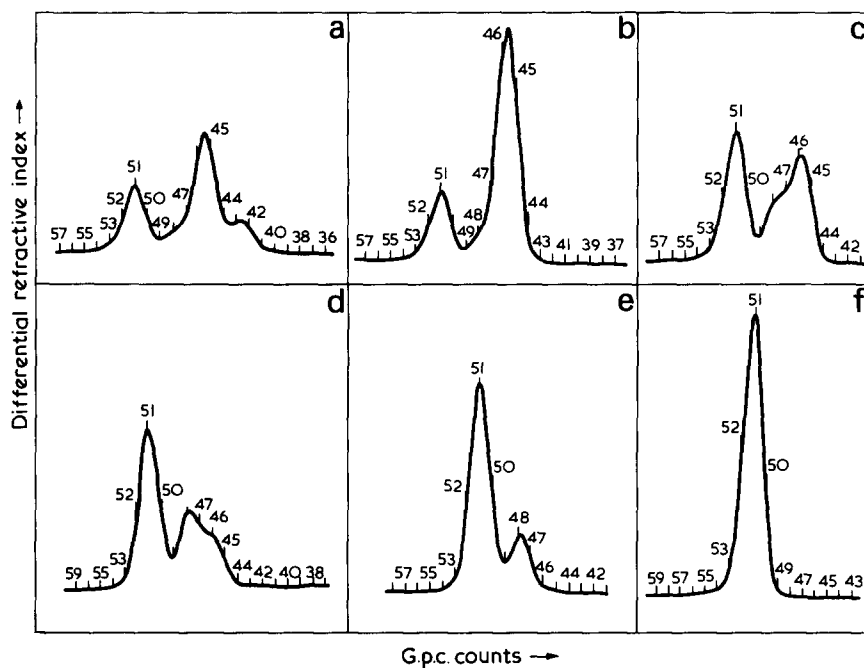


Figure 2 Chromatograms of high molecular weight Dow S-102 fractions. (a) Fraction A; (b) fraction C; (c) fraction H; (d) fraction I; (e) fraction J; (f) fraction M

in the S-102 is also indicated by Lutje's⁷ value of 1.13 for the \bar{M}_z/\bar{M}_w ratio. More recently⁴, a chromatogram of the S-102 polystyrene revealed the presence of an anomalous high molecular weight fraction. As a consequence of these observations, fractions of the Dow S-102 were examined by g.p.c. at the slow flow rate.

Figure 1 is the chromatogram of the unfractionated S-102. The chromatogram shows the presence of a high molecular weight portion. Figure 2 shows 6 chromatograms of 6 different fractions. An examination of these chromatograms reveals that the high molecular weight tail present in the S-102 polystyrene apparently consists of three 'near-monodisperse' components. These three species have, based on their peak elution counts, weight-average molecular weights of 5×10^5 , 2.5×10^5 and 1.5×10^5 g/mol, respectively. These values may be compared with an \bar{M}_w of 7.5×10^4 g/mol for fraction 'M', representing the centre portion of the main polymer peak. In rough terms there are high molecular weight components representing an apparent two-, three- and seven-fold increase in the molecular weight of the main peak. The presence of the material with the apparent molecular weight of 1.5×10^5 g/mol can be explained by the fact that the presence of oxygen or carbon dioxide during termination can cause the

coupling of organolithium species¹²⁻¹⁴. However, no ready explanation exists, from a polymerization viewpoint, which can explain the presence of the two fractions with the apparent weight-average molecular weights of 2.5 and 5×10^5 g/mol. Nonetheless, it is important to recognize that the S-102 polystyrene contains a high molecular weight tail and that this tail contains material with an apparent \bar{M}_w of up to 5×10^5 g/mol. However, this latter material seemingly constitutes only about 0.1 wt % of the overall material.

In view of the reported low glass transition temperature exhibited by the unfractionated S-102, the tacticity of the unfractionated material and fraction 'G' were examined by ¹³C n.m.r. Both samples exhibited identical spectra, and the tacticity corresponded to that observed for a Pressure Chemicals polystyrene and the NBS 706 polystyrene prepared by thermal polymerization in bulk¹⁶. Hence, the low value for the T_g of the S-102 polystyrene cannot apparently be explained by the presence of some variable tacticity irregularity in the unfractionated material.

Furthermore, the apparent low T_g of the S-102 polystyrene cannot be explained as being caused by the presence of low molecular weight material. Chromatograms of the final three low molecular weight fractions Q, T, and W, failed to show any trace of a low

molecular weight tail, the lowest molecular weight fraction, W₁ had an \bar{M}_w of 5.0×10^4 g/mol and an \bar{M}_n of 4.6×10^4 g/mol from gel permeation chromatography.

Hence, the reported³ low T_g of this polystyrene apparently cannot be explained in a conventional fashion since the n.m.r. and g.p.c. results fail to show the existence of any non-polystyrene components or low molecular weight species. Parenthetically, it should be noted that the reported² low melt viscosities reported for the Dow S-109 can be explained² by invoking a low T_g , by approximately 3°C, for this polystyrene. However, a previously reported⁴ g.p.c. analysis of this polystyrene apparently showed that the S-109 polystyrene, like the S-102 sample, does not possess any low molecular weight material.

In conclusion, it should be noted that our fractionation data and Figure 2 reveal that the high molecular weight components in the S-102 polystyrene can be eliminated at the cost of about 30 wt % of the unfractionated polymer since fraction 'M' was the first fraction to show no trace of the high molecular weight tail.

REFERENCES

- Rudd, J. F. *J. Polym. Sci.* 1960, **44**, 459
- Penwell, R. C. and Graessley, W. W. *J. Polym. Sci. (Polym. Phys. Edn.)* 1974, **12**, 213
- Rudin, A. and Burgin, D. B. *Polymer* 1975, **16**, 291
- Fetters, L. J. *J. Appl. Polym. Sci.* 1976, **20**, 3437
- Cowie, J. M. G., Worsfold, D. J. and Bywater, S. *Trans. Faraday Soc.* 1961, **57**, 705
- Homma, T., Kawahara, K., Fujita, H. and Ueda, M. *Makromol. Chem.* 1963, **67**, 132
- Lutje, H. *Makromol. Chem.* 1964, **72**, 210
- Stratton, R. A. *J. Colloid Sci.* 1966, **22**, 517
- Nordhaus, D. E. and Kinsinger, J. B. *J. Polym. Sci. (C)* 1973, **43**, 251
- Utracki, L. A. and Roovers, J. E. L. *Macromolecules* 1973, **6**, 366
- Breitenbach, J. W. and Streichsbier, O. *Kolloid Z. Z. Polym.* 1962, **182**, 35
- Wyman, D. P., Allen, V. R. and Altares Jr, T. *J. Polym. Sci. (A)* 1964, **2**, 4545
- Yasuda, H., Walczak, M., Rhine, W. and Stucky, G. *J. Organomet. Chem.* 1975, **90**, 123
- Fetters, L. J. and Firer, E. *Polymer* 1977, **18**, 306
- National Bureau of Standards Certificate, Standard Sample 706, Polystyrene