NOTES

Gel Permeation Chromatography of Polysulfones

Attempts to determine molecular weight distribution of poly(butene sulfone) by gel permeation chromatography (GPC) were reported by James et al.[1] to be unsatisfactory. They claimed that the polysulfones "hung up" on the GPC columns, resulting in severe plugging and deterioration of the column system with concomitant rapid pressure increase. The instrument used in their analyses was a modified Waters Model 200 gel permeation chromatograph equipped with five Styragel columns with pore sizes ranging from 1×10^6 Å to 1×10^3 Å. They attributed the problem to reaction between the polysulfone and the Styragel beads which necessitated complete column refurbishing.

We have also been interested in determining molecular weight distributions of these polymers as a function of radiation dose by GPC and have found none of the above problems. Our instrument is a Waters Model 540 gel permeation chromatograph equipped with five columns with pore sizes (in descending order) 1×10^7 Å, 1×10^6 Å, 1×10^5 Å, 9×10^3 Å, and 1×10^3 Å. A typical chromatogram of poly(butene-1 sulfone) prepared by free-radical initiation (azobisisobutyronitrile) at 40°C is shown in Figure 1. The solvent was tetrahydrofuran (technical grade, Fischer certified) stabilized with ~0.025% butylated hydroxytoluene.

The molecular weight of the polysulfone is extremely high. The elution volume was much less than that of the highest polystyrene standard ($\bar{M}_w = 2.6 \times 10^{-6}$) and hence was beyond the limits of our calibration curve. It would appear that the polymer spans a molecular weight range of $\sim 10^6$–10^7. The viscosity-average molecular weight calculated from the equation[2] $[\eta]^{30}_{\text{cyclohexanone}} = 5.7 \times 10^{-3} \bar{M}_v^{0.72}$ was 4.62×10^6.

Also shown in Figure 1 is the same polymer after 3 Mrad of γ-irradiation. The polystyrene equivalent molecular weight averages calculated by the method of Cazes[3] were $\bar{M}_n = 30{,}130$ and $\bar{M}_w = 82{,}940$ ($\bar{M}_w/\bar{M}_n = 2.75$). The viscosity-average molecular weight was 1.58×10^5. For many polymers, $\bar{M}_v$ is ~10–20% below $\bar{M}_w$. The error in the computed value of $\bar{M}_w$ is to be expected given the differences in polymer–solvent interaction between polystyrene and the polysulfone and also the different Q factors (molecular weight per angstrom of chain length) of the two polymers.

We have been carrying out such measurements for over six months with no apparent difficulties. Hence, whereas our experimental conditions appear to be the same as those of James et al., we must conclude that their results are misleading without further knowledge of their experimental conditions, etc. Certainly, there appears to be no interaction per se btween Styragel and the polysulfone, as suggested by James et al.

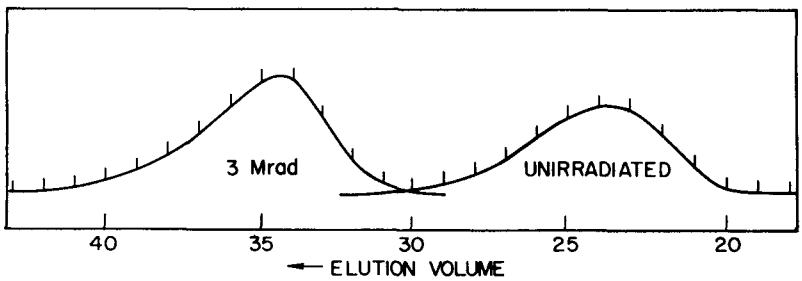

Fig. 1.

It is possible that the polymer used in their investigation may have crosslinked during passage through the GPC, crosslinking being initiated by peroxides present either in the THF (James et al. do not specify the quality of their THF) or else formed during the elution process. Evidently, the plumbing of the Waters Model 200 GPC (pre-1969 models) is considered notorious for its large hold-up volume and for the use of a fair amount of brass fittings which can accelerate THF decomposition. However, Brown and O'Donnell[4] also measured molecular weight distributions of poly(butene-1 sulfone) in THF at 40°C using a Waters Model 200 GPC without any reported adverse effects.

References

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