Instrumental Achievements

Molecular Weight Distribution in Poly(amic-acids) by Gel Permeation Chromatography

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Although gel permeation chromatography(GPC) has been successfully applied to the measurement of molecular weight distribution in various polymers, GPC of poly(amic-acid) (PAA) is not yet been reported. This situation may be attributed to the fact that PAA molecules behave in the eluent as like polyelectrolytes which causes poor reproducibility of the GPC.

Usually, GPC of polyelectrolytes is carried out using

Fig. 1 GPC chromatograms of mono-dispersion polystyrene. (eluent, DMF).

Fig. 2 GPC chromatograms of PAA($\eta_{sp}/c=0.37$). Eluent, DMF containing H_3PO_4 .

the eluent containing low molecular weight electrolytes.¹⁻³ The present authors have assumed that this method will be applied to GPC of PAA and obtained good results recently. Thus, in this report, GPC of PAA having a good reproducibility is proposed. Three different η_{sp}/c types of PAA were investigated in this study. PAA samples were prepared from pyromellitic dianhydride and 4,4'-diaminodiphenyl-ether at 0–26°C in *N,N'*-dimethylformamide(DMF). GPC was performed at 25°C with a Hitachi Model 635A liquid chromatograph equipped with UV detector(270 nm). The columns employed were two columns of Gelpack GL-S300MD (or GL-S300MDT), these columns are commercially available from Hitachi Chemical Co., Ltd. The eluent was DMF(or DMF/THF=1/1(v/v)). The flow-rate was 1.0 ml/min and sample volume was 50 μ l. Figure 1 shows the relationship between mono-dispersion polystyrene concentration and GPC chromatograms in the DMF eluent. This figure shows that chromatogram of these polystyrenes does not depend on concentration, while chromatogram of PAA(η_{sp}/c 0.37) is not observed under the same condition of the measurement. The latter fact is assumed to be due to the adsorption of PAA on the column.

Although, we have tried the 0.06 M LiBr-DMF eluent which has been effective for GPC of polyester-based polyurethanes¹ to GPC of PAA, but again in this case, PAA chromatogram has not been observed too. As we try the 0.06 M H_3PO_4 -DMF eluent.⁴ PAA

Fig. 3 GPC chromatograms of PAA($\eta_{sp}/c=0.37$). Eluent, DMF containing LiBr and H_3PO_4 .

chromatograms have been observed as shown in Fig. 2, however, those chromatograms have varied depending

Fig. 4 GPC chromatograms of different η_{sp}/c PAA. Eluent, DMF/THF=1/1(v/v) containing 0.06 M LiBr and 0.06 M H_3PO_4 .

on the H_3PO_4 concentration in the DMF eluent. Finally, as the new eluent which contains LiBr and H_3PO_4 in DMF is tried, GPC chromatograms as shown in Fig. 3 have been obtained which show good reproducibility in the various concentration ranges of LiBr and H_3PO_4 . DMF-tetrahydrofurane(THF) eluent system can be used for GPC of some different η_{sp}/c PAA as shown in Fig. 4. This eluent system is superior to DMF eluent in column pressure. More details will be reported later.

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