HPLC and C-13 NMR Spectroscopy of Polymers
1. Oligomers of Poly(Styrene)

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Summary

Constitutional and configurational structure of oligomers from poly(styrene) have been determined by joint liquid chromatography and C-13 nmr spectroscopy.

Introduction

Molecular weight distribution, constitutional and configurational properties of polymer chains are true records of specific steps of the polymerisation reaction under study. Many analytical problems and limitations arise from using high molecular weight samples. Consequently, oligomers if available are recommended materials. Fractionation and subsequent analytical characterisation are required due to constitutional and configurational heterogeneity caused by the stochastic nature of polyreactions.

Results and Discussion

In the case of butyllithium as an initiator fig. 1 gives the constitutional structures of oligomers from poly(styrene) with increasing order of polymerisation degree, DP. Molecules with DP≥2 contain chiral carbon atoms. Oligomers of DP=2 are mixtures of enantiomers which are undistinguishable in achiral systems, whereas oligomers with DP≥3 are mixtures of corresponding diastereomers.

Liquid chromatography (HPLC) offers a wide variety of selective fractionations depending on the relative polarity of solute, mobile and stationary phases.

The chromatogram of a commercial standard sample (Lot 61217, PRESSURE CHEMICAL) in fig. 2a has been obtained on an unpolar, reversed phase column by a water/THF elution gradient. Fractionation occurs with respect to the molar mass of the oligomers. EISENBEISS et al. (1978) observed further fractionation in an isocratic system (solvent: acetonitrile) with excellent resolution. However, as these investigations have been performed on an analytical scale no structural information on the
Figure 1 Constitution of Oligomers from Poly(styrene)
Initiator: butyllithium; DP = degree of polymerisation; N = number of diastereomers (enantiomers); -C' = chiral carbon atom; H atoms not shown

Figure 2 Chromatograms of Oligomers from Poly(styrene)

a) column: C-18 Bondapak; solvent gradient: water/THF (55%-70%); flow rate: 2 ml/min; (PRESSURE CHEMICAL)
b) column: µ-Porasil; solvent gradient: n-hexane/methylene chloride (0%-40%)/acetonitrile; flow rate: 2ml/min
peak number according to DP in a) and b); first peak does not indicate a polymer fraction