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HPLC and C-13 NMR Spectroscopy of Polymers

1. Oligomers of Poly(Styrene)

K.-F. Elgert, R. Henschel, H. Schorn and R. Kosfeld

Universität Duisburg, FB 6 Physikalische Chemie, Bismarckstraße 90,
4100 Duisburg 1, Federal Republic of Germany

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 heterogenity 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 $DP \geq 2$ contain chiral carbon atoms. Oligomers of DP=2 are mixtures of enantiomers which are undistinguishable in achiral systems, whereas oligomers with $DP \geq 3$ 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

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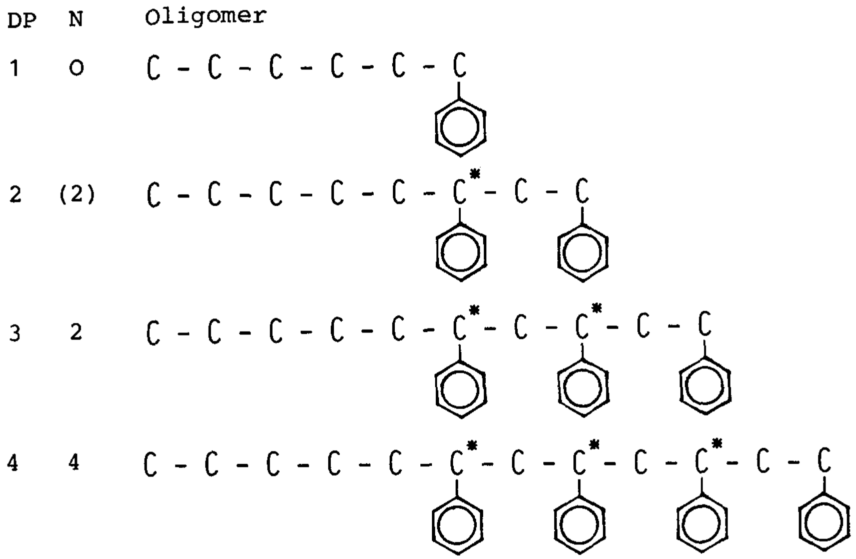


Figure 1 Constitution of Oligomers from Poly(styrene)

Initiator: butyllithium; DP = degree of polymerisation; N = number of diastereomers (enantiomers); $-C^{*}-$ = chiral carbon atom; H atoms not shown

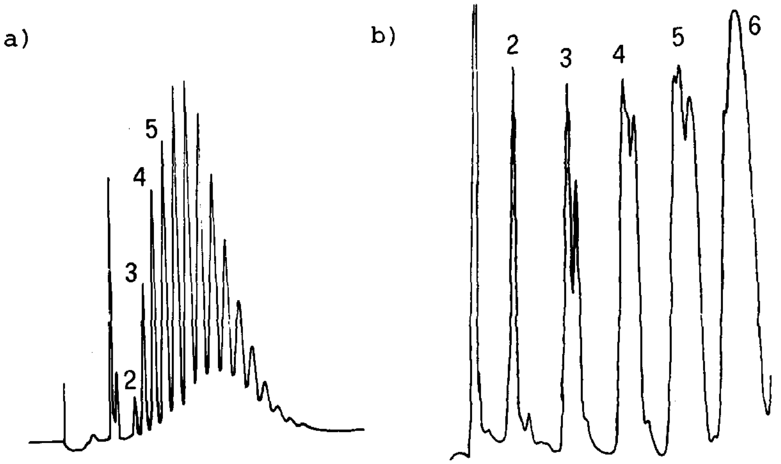


Figure 2 Chromatograms of Oligomers from Poly(styrene)

a) column: C-18 Bondapak; solvent gradient: water/THF (55%-70%); flow rate: 2 ml/min; (PRESSURE CHEMICAL)

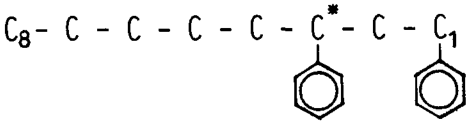
b) column: μ-Porasil; solvent gradient: n-hexane/methylene chloride (0%-40%)/acetonitrile; flow rate: 2ml/ min

peak number according to DP in a) and b); first peak does not indicate a polymer fraction fractions could be given.

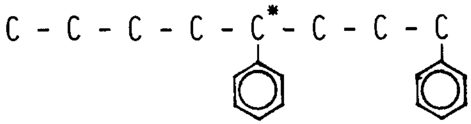
The chromatogram in fig. 2b has been run on a polar silica surface as a stationary phase. The mobile phase was a ternary system containing n-hexane, methylene chloride and acetonitrile. Resolution is comparable to EISENBEISS et al.(1978). This system could be increased to a semi-prep scale. Fraction 2 is the first oligomer of the homologous serie. 50 - 100 mg of fraction 2, 3, 3A and 3B have been accumulated for structural identification by C-13 nmr spectroscopy.

C-13 nmr spectra of the aliphatic carbon atoms concerning fraction 2, 3, 3A and 3B are shown in fig. 3, 4 and 5. All resonance signals have been assigned by hetero decoupling and by empirical shift parameters calculated from suitable model compounds, e.g. n-hexyl benzene and n-octyl benzene. Corresponding assignments have been completed in the resonance region of the aromatic carbon atoms (STOTHERS (1972)).

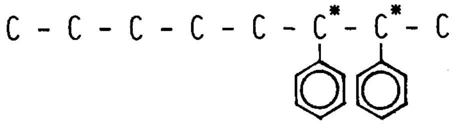
Fig. 3 shows the C-13 nmr spectrum of fraction 2 corresponding to DP=2. Eight different carbon atoms are assigned to a mixture of the enantiomers of 1,3-diphenyl octane. Three possible isomers of different constitution have not been detected in this oligomer mixture:



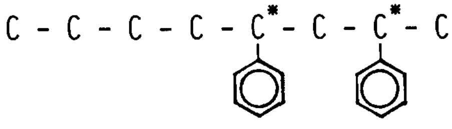
DP = 2; 1,3-diphenyl octane



1,4-diphenyl octane



2,3-diphenyl octane



2,4-diphenyl octane

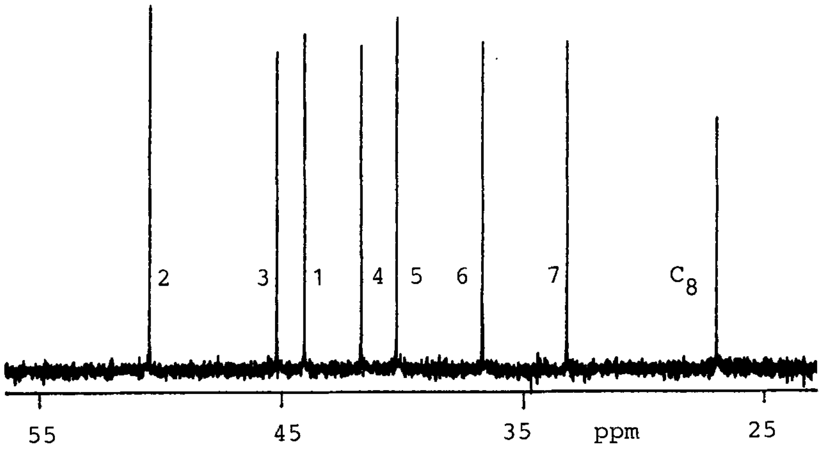


Figure 3 C-13 NMR Spectrum of Fraction 2

Spectrum of aliphatic carbon atoms of 1,3-diphenyl octane
C-13 frequency: 67.89 MHz; sweep width: 5 kHz; pulse: 25 μsec; 1H broadband decoupling; solvent: $CDCl_3$;
TMS = 0 ppm

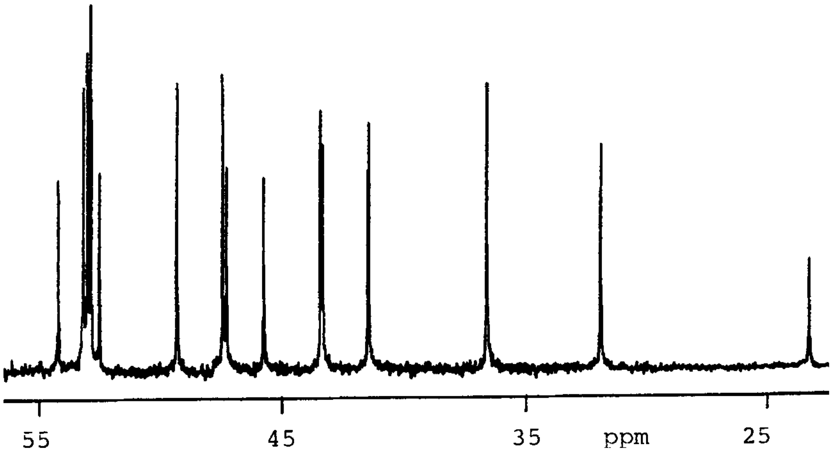


Figure 4 C-13 NMR Spectrum of Fraction 3

Mixture of diastereomers of 1,3,5-triphenyl decane; for spectral data see fig. 3

The nmr spectrum of fraction 3 in fig. 4 cannot be interpreted unambigously. By succeeding fractionation of this fraction 3A and 3B have been isolated in a ratio of 60:40. Both fractions are of DP=3. Ten different carbon atoms have been assigned in the corresponding spectra in fig. 5a and 5b to threo-1,3,5-triphenyl decane and erythro-1,3,5-triphenyl decane, respectively.

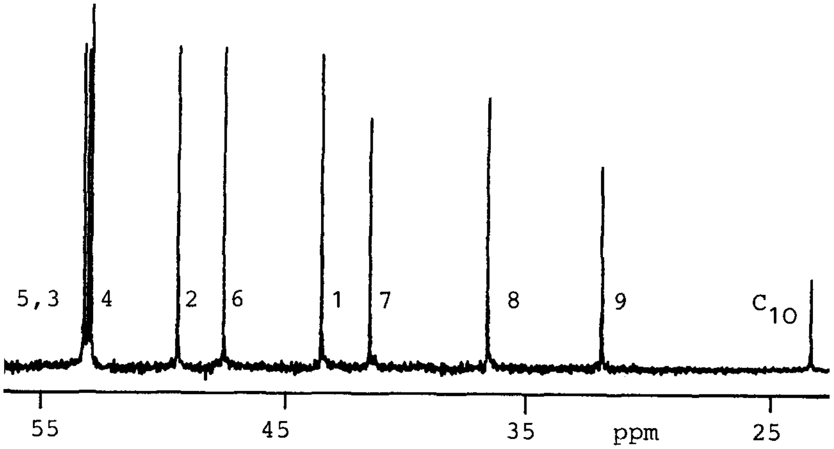
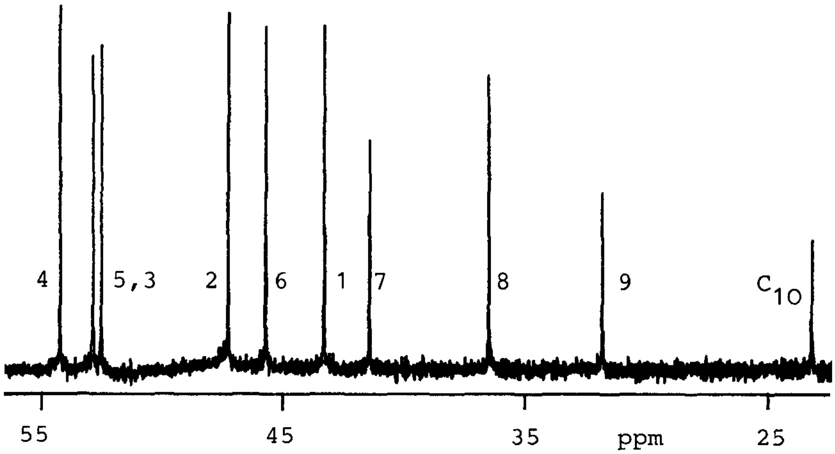
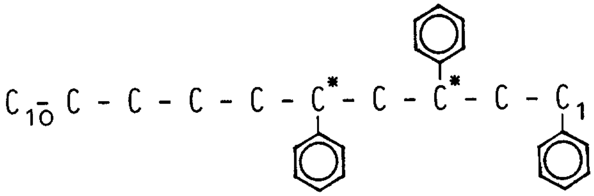


Figure 5 C-13 NMR Spectrum of Fraction 3

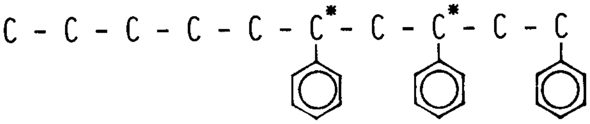
a) fraction 3A, threo-1,3,5-triphenyl decane; for spectral data see fig. 3



b) fraction 3B, erythro-1,3,5-triphenyl decane; for spectral data see fig. 3



3A: threo-1,3,5-triphenyl decane



3B: erythro-1,3,5-triphenyl decane

The tendency of the stereosequence dependent chemical shift differences between threo and erythro isomer is in a good agreement with values predicted by TONELLI (1979) for model compounds of poly(styrene) oligomers. The structures of fraction 2, 3A and 3B confirm head-to-tail enchainment of monomer units which has to be exspected in this type of polyreaction. The relative amounts of 3A and 3B are equivalent to iso and syndiotactic monomer placements in high molecular weight poly(styrene) prepared under identical conditions.

Further improvement of the chromatographic system will provide efficient separation and identification of diastereomers in fraction 4 and 5 (see fig. 2b). Complete details will be qiven elsewhere (ELGERT, KOSFELD (1981)).

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