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On the Stereostructure of Polystyrene Samples Obtained by Extraction of Isotactic Polystyrene with Butanone

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Introduction

Stereospecific fractionation of polymers is of special interest in obtaining products of high stereoregularity. Extraction of highly stereoregular polystyrene has been described to be such a process and treatment of isotactic polystyrene samples with boiling butanone - which is supposed to be solvent for atactic and a nonsolvent for isotactic polystyrene - has been used in the quantitative determination of the "atactic content". (1) However so far no direct analysis of the stereostructure (2) of the extract has been performed to verify the simple assignment of the fractional amount of extracted polymer to the fractional amount of atactic structure.

Materials and methods

Styrene was polymerized at 90 deg C in n-heptane containing 30 % of monomer. Reaction conditions were as described in table 1.

TABLE 1 Reaction Conditions

sample	mmole γ-$TiCl_3$	mmole $AlEt_3$	Ti : Al	reaction time [h]
2	33	5.9	5.5:1	3
6	33	34.3	1.1:1	5
10	67	67	1 :1	3.5

Extractions were performed by butanone (Merck, analytically pure) in a soxhlet extractor for 24 h. Temperature of extraction was 76 deg C (at low level of butanone in the extraction thimble) to 70 deg C (at high level of butanone in the extraction thimble,measured at the bottom of the thimble.

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Carbon-13 NMR spectra were recorded by a BRUKER HFX-90 or a VARIAN XL-100, respectively.

Analysis of carbon-13 NMR spectra was performed according the pentad fit of K.MATSUZAKI and coworkers. (3)

DSC measurements were carried out after quenching and annealing samples for 67 h at 130 deg C using a DU PONT 990 THERMAL ANALYZER.

Results

By extraction of three samples different amounts of extracts were obtained. The material balance with respect to raffinate (R) and extract (E) and the corresponding molecular weights is shown in table 2.

TABLE 2 Extraction Experiments

sample	$M_\eta \cdot 0.001$	% R	$M_{\eta,R} \cdot 0.001$	% E	$M_{\eta,E} \cdot 0.001$
2	618	16.6	1000	83.4	51.6
10	1095	74.4	1270	25.6	399
6	2900	86.7	3360	13.3	425

Tacticities of the fractions were as described in table 3.

TABLE 3 Tacticities of Extracts and Raffinates

sample	2 E	2 R	6 E	6 R	10 E	10 R
P_R	0.59	0 (∗)	0.39	0 (∗)	0 (∗)	0 (∗)

(∗) : within accuracy of measurement

P_R : probability of racemic dyads

Degrees of crystallinity were determined from DSC measurements evaluating heats of fusion, as reference a value of 80.4 J/g was used.(4)

TABLE 4 Heats of Fusion and Degrees of Crystallinity

sample	2	2 R	2 E	6	6 R	6 E	10	10 R	10 E
H (J/g)	7.2	25.7	0	23.1	22.8	14.0	24.4	27.1	21.9
degree of cryst. (%)	9	32	0	29	28	17	30	34	27

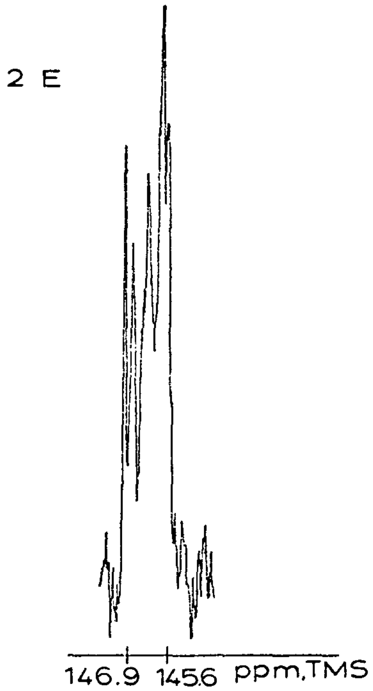

Fig. 1:

Proton noise decoupled ^{13}C NMR partial spectrum at 22.63 MHz of aromatic C_1 of polystyrene 2 E(xtract) in C_6D_6 at 60 deg C, 2600 scans, lock: C_6F_6

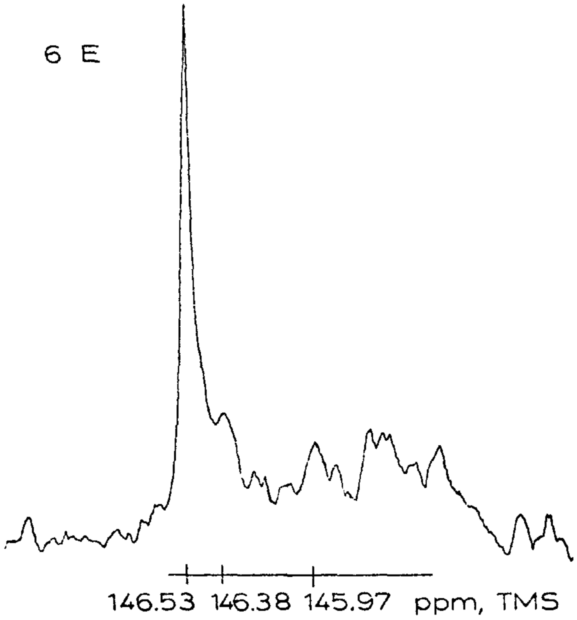

Fig. 2:

Proton noise desoupled ^{13}C NMR partial spectrum at 25.2 MHz of aromatic C_1 of polystyrene 6 E in 1.2.4-trichlorbenzene at 120 deg C, 8914 scans, lock:1.1.2.2-dideuterodichloroethane

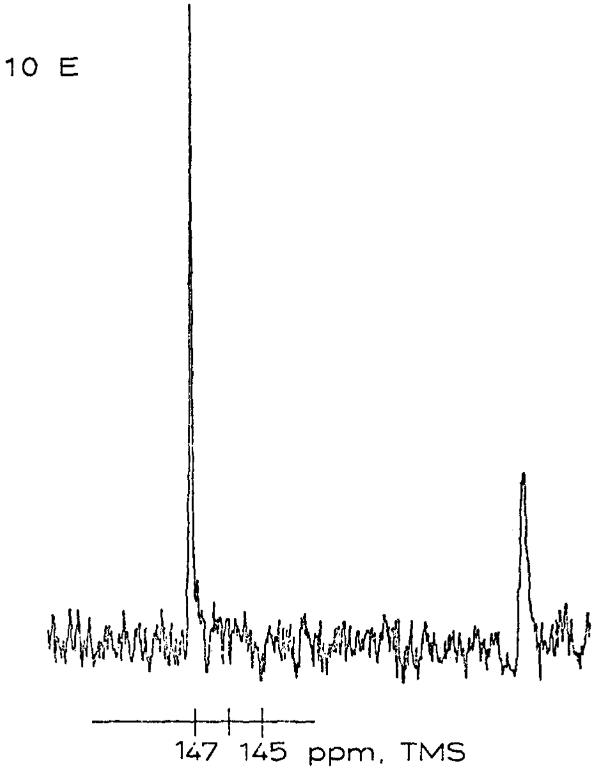

Fig. 3:

Proton noise decoupled ^{13}C NMR partial spectrum at 22.63 MHz of aromatic C_1 of polystyrene 10 E in toluene-d_8 at 80 deg C, 13669 scans, lock:C_6F_6

Discussion

Concerning the three raw polymers, sample 2 contains predominantly atactic polystyrene, sample 6 contains a small portion of atactic polystyrene and sample 10 is isotactic within accuracy of measurement. This can be explained by the increasing content of $AlEt_3$ in the catalyst-cocatalyst system.

Investigating soluble catalysts, REICHERT has shown that in the presence of protic contaminents a cationic polymerization of styrene is initiated by $AlEtCl_2$ at lower contents of $AlEt_3$. (5) This side reaction is suppressed at higher contents of $AlEt_3$, and this agrees with our observations.

As can be seen from table 2, extraction of the raw polymer samples with butanone gives fractions of predominantly lower molecular weight, as has been shown recently by GPC analysis as well. (6)

Our results from table 3 furthermore indicate that the extract may contain atactic as well as isotactic material. If the raw polymer (as sample 2) mainly consists of atactic material, carbon-13 NMR analysis of extract only shows this, in the absence of a greater amount of atactic material, however, still a low molecular weight fraction is extracted which now is mainly isotactic. Extraction of isotactic polystyrene is therefore a seperation process based on molecular weight dependent solubility only. (7), (8) This molecular weight effect has then always to be considered to overlap with the effect of separation based on stereoregularity.

We have to conclude therefore that quantitative evaluation of an extraction process is justified only if the steric composition of the extract has been determined independently. While NMR analysis doubtless is the most powerful tool to an approach like this, DSC analysis could be used for a more semiquantitative estimation as well.

Conclusions based on material balance only may be very misleading, as has been demonstrated by the results for sample 10.

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