Fractionation of polypropylenes using Soxhlet extraction methods

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Five isotactic polypropylenes produced with different processes and different heterogeneous Ziegler–Natta catalyst systems were fractionated using n-heptane extraction in a Soxhlet apparatus. The unfractionated polymers and their heptane-soluble and heptane-insoluble fractions were analysed with size exclusion chromatography, ^{13}C nuclear magnetic resonance (n.m.r.), differential scanning calorimetry and Fourier-transform infra-red spectroscopy. The composition of the heptane-soluble fraction was somewhat dependent on the molecular structure of the original polymer. On the other hand, the heptane-insoluble material was not completely isotactic, and some syndiotactic and heterotactic polymers were found in it. Heptane extraction as a method for isotacticity determination is discussed and compared with other methods. One of the samples was also divided into four fractions using successive extractions with n-heptane, n-octane and xylene. Based on the ^{13}C n.m.r. spectroscopic pentad analysis carried out on the fractions, possible structures for stereoblock polymers are suggested. Fractionation results are also compared with an earlier fractionation performed on the same sample using fractional solution with solvent/non-solvent mixtures and vibromixer agitation.

(Keywords: isotactic polypropylene; fractionation; tacticity)

INTRODUCTION

The differential solubility of atactic and isotactic polypropylenes was already utilized by Natta and coworkers[1] in the initial characterization of these polymers. They presented the term 'isotactic index', which was equivalent to the amount of polymer material insoluble in boiling n-heptane. Further, it was shown that polypropylene could be divided into several fractions of different crystallinities and melting points by successive extractions using n-alkanes with increasing boiling points[2]. ^{13}C n.m.r. spectroscopic measurements provide the most detailed information of the tacticity, but, because heptane extraction is easy to accomplish and reproducible, it is still widely used as a standard method for isotacticity determination. However, it has been known for a long time that the heptane-soluble fraction not only consists of atactic polymer, but also contains low-molecular-weight isotactic material[3–5]. It has also been proposed that this fraction contains so-called stereoblock polymer with alternating structures of blocky isotactic and atactic placements[6].

This work was carried out to obtain a better knowledge of what kind of material is actuallly separated, when the conventional heptane extraction method is applied. The samples studied were isotactic high-molecular-weight polypropylenes previously well characterized using fractions obtained by other fractionation techniques[7–9]. One of the samples was also divided into four fractions using successive extractions, and its fractionation results are compared with earlier data obtained when the same sample was fractionated with solvent/non-solvent mixtures[7,8].

EXPERIMENTAL

Samples of around 4 g were ground using 20 mesh sieves and cooling with liquid nitrogen. The fractionations were carried out under nitrogen in a conventional Soxhlet extractor. About 0.25 g of Irganox 1010 was added to 250 ml of solvent and the extraction time was 4 h. After n-heptane extraction, the insoluble residue was dried (16 h, 70°C) and weighed. The heptane-soluble material was isolated by evaporating the solvent. For one sample (sample A) the heptane-insoluble residue was extracted further with n-octane and xylene. Materials soluble in these solvents were isolated by precipitation with acetone. The heptane-soluble fractions contained remarkable amounts of antioxidant. From the octane-soluble and xylene-soluble fractions of sample A, antioxidant was mainly removed in the precipitation and washing steps.

^{13}C n.m.r., d.s.c., s.e.c. and *FT*i.r. methods used in the characterization of the unfractionated samples and the fractions have been described previously[7,8].

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RESULTS AND DISCUSSION

The polypropylenes analysed in this work were mainly commercial film grades made by different processes and catalysts (see *Table 1*). The molecular weights of the samples were in the same range ($\bar{M}_w = (3.7\text{–}4.7) \times 10^5$), but slight differences were observed in their molecular-weight distributions (*Figure 1*). Molecular weights and molecular-weight distributions (*MWDs*) are summarized in *Table 3*.

The polymers were fractionated with n-heptane extraction. Isotacticities of the samples were determined by ^{13}C n.m.r. spectroscopy (triad percentages) and *FT*i.r., and their crystallinities were measured with d.s.c. In *Table 2* the percentages of heptane-insoluble residues are compared with isotacticities obtained by other methods. The amounts of heptane-insoluble residues lay within 1% for all five samples, but somewhat larger deviations in isotacticity were detected by other methods. However, all five samples were highly isotactic as measured by any of these methods. Isotactic indices from heptane extraction were slightly higher for slurry-polymerized samples B and D. When isotacticity was determined by n.m.r. spectroscopy, which is the only method for determining the actual stereochemical order in the polymer chain, these two samples did not show higher isotacticities compared to the other samples. Thus, the high isotactic index of sample D probably originated from some atactic material being removed from it during purification steps included in the polymerization process. The laboratory polymerized sample B contained 1.6% of polymer soluble in the reaction medium (heptane), and that material was removed as well. Sample B was originally obtained as a reactor powder, while the other samples were in pelleted form. However, all the samples were ground before extraction and the effect of processing on the accuracy of the method (see e.g. ref. 10) should be minimal. From the fractions analysed earlier[7,8], it was also observed that, though sample B was the least isotactic of the samples

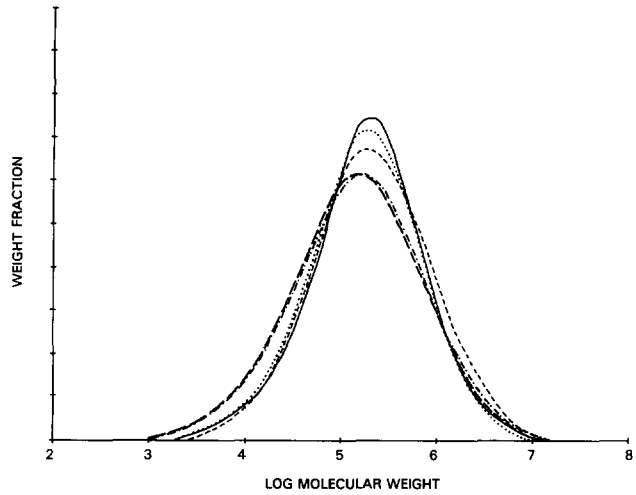

Figure 1 Molecular-weight distributions of the unfractionated polymers: (—) sample A; (– – –) sample B; (· · · ·) sample C; (– · – · –) sample D; and (— —) sample E

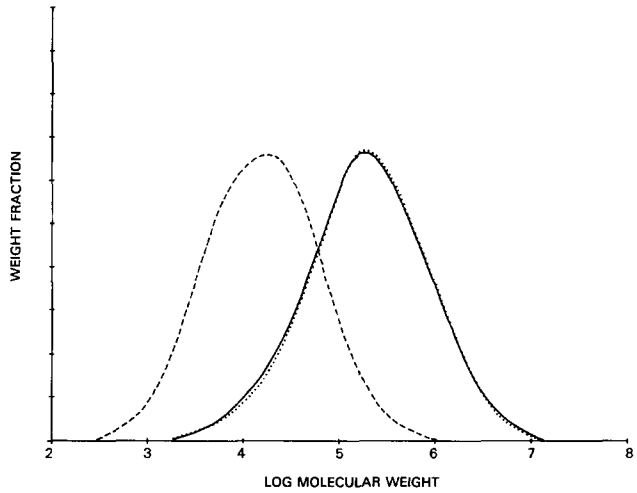

Figure 2 Molecular-weight distributions of sample B and its heptane-soluble (B/HS) and heptane-insoluble (B/HI) fractions: (—) B (ground); (– – –) B/HS; (· · · ·) BH/I

Table 1 Polymerization processes and catalyst systems used in the production of the polypropylenes studied

Sample	Catalyst system	Process
A	HY[a]	Gas phase
B	HY	Slurry (lab. process)
C	HY	Bulk
D	LY[b]	Slurry
E	HY	Gas phase

[a] HY = $MgCl_2$ or $TiCl_3$ supported
[b] LY = first-generation catalyst system

Table 2 Comparison of isotacticities determined by different methods (d.s.c. crystallinity included)

Sample	Heptane extraction (% isotactic)[a]	^{13}C n.m.r. (% mm)	*FT*i.r. (% isotactic)[a]	D.s.c. (% crystalline)[a]
A	95.9	94.9	92.5	46.5
B	96.8	92.2	94.2	46.1
C	95.8	92.7	89.0	45.3
D	96.8	93.0	91.3	46.0
E	96.4	94.4	93.9	47.6

[a] Determined from ground samples

Table 3 Molecular weights and molecular-weight distributions of the whole polymers[a] and their heptane-soluble (HS) and heptane-insoluble (HI) fractions

Sample	$\bar{M}_w/10^3$	$\bar{M}_w/\bar{M}_n$
A	396	5.2
A/HS[b]	25	9.1
A/HI	418	4.9
B	469	6.1
B/HS	45	5.4
B/HI	462	5.9
C	369	5.1
C/HS[b]	29	10.0
C/HI	343	3.9
D	367	6.6
D/HS	25	4.0
D/HI	381	5.9
E	378	6.8
E/HS	13	6.0
E/HI	401	5.2

[a] Determined from ground samples
[b] Antioxidant is broadening the *MWD* and lowering the $\bar{M}_w$ of A/HS and C/HS fractions

according to the n.m.r. measurements made on the whole polymers, it contained no highly atactic material.

The other two indirect methods for isotacticity determination, *FT*i.r. spectroscopy and d.s.c. crystallinity, both related to the supermolecular structure of the material, showed a good correlation with each other, but not with heptane extraction or n.m.r. triad isotacticity. Melt-pressed films were used in the *FT*i.r. measurements, and the high value for i.r. isotacticity of sample B should be considered as being a result of its different morphology, which influenced the film pressing step. As was mentioned earlier, this sample was obtained as a reactor powder, while the other samples were originally in pelleted form. The *FT*i.r. method as well as the isothermal crystallization method for d.s.c. (reported in ref. 8) were distinctly sensitive to the morphology of the samples.

Considering some tacticity determinations reported in the literature for high-molecular-weight, highly isotactic polypropylenes, Martuscelli *et al.*[11], for example, found a good correlation between heptane extraction and ^{13}C n.m.r. spectroscopy. They reported about 2% deviations between isotacticities measured by these two methods. Bothe and Dietz[12] compared isotacticities determined by both spectroscopic (n.m.r. and i.r.) and solvent extraction methods. They obtained coincident isotacticities by n.m.r. and i.r. Heptane extraction isotacticities diverged more from n.m.r. tacticities, but they were still usable when high accuracy was not needed.

Removal of heptane-soluble (HS) fraction (3.2–4.1% m/m) did not have any remarkable influence on the molecular-weight distributions of the polymers (*Table 3, Figure 2*). In most cases a small increase in $\bar{M}_w$ was observed, but the *MWD*s of heptane-insoluble fractions were broad as well. Only for sample E, which had a low-molecular-weight tail in its distribution curve, was a clear narrowing of *MWD* observed. The molecular weight of the HS fraction of this sample was low, indicating that it really was the short-chain material that had dissolved in heptane. The heptane-soluble fraction of sample B had a relatively high molecular weight ($\bar{M}_w = 45\,000$). Fractions A/HS and C/HS contained larger amounts of antioxidant, which broadened the *MWD* and lowered the $\bar{M}_w$ of these fractions. For the other samples, enough heptane-soluble material was left, so that antioxidant could be removed by washing with acetone, and the s.e.c. measurement repeated.

The heptane-soluble fractions were not totally amorphous, but contained 4–18% of crystalline material (*Table 4*). The amount of crystalline material was lowest in A/HS and C/HS fractions, whereas the crystallinity in the heptane-soluble material of sample B was almost 18%. Since the n.m.r. spectroscopic triad tacticity of B/HS fraction was similar to those of other heptane-soluble fractions (*Figure 4c*), the higher crystallinity of this fraction can be attributed to its higher molecular weight. Only the spectrum of A/HS fraction showed almost 1:1:1 ratios for mm:mr:rr, while this ratio was ~2:1:1 for the other HS fractions. Of course, there can be differences in the distribution of heterotactic and syndiotactic sequences inside polymer chains, even though their average amounts are similar. However, the different crystallinities of the fractions indicate that the composition of heptane-soluble material depends also on the structure of the original polymer, and is not similar in each extraction.

Slightly increased i.r. isotacticities, crystallization temperatures and crystallinities were obtained for heptane-

Table 4 I.r. isotacticities and crystallization and melting behaviour of the whole polymers[a] and their haptane-soluble (HS) and heptane-insoluble (HI) fractions

Sample	I.r. isotact. (%)	T_c (°C)	δH_c ($J g^{-1}$)	T_m (°C)	Cryst. (%)
A	92.5	110.8	93.6	163.7	46.5
A/HS	n.d.[b]	79.3	10.0	116.6	4.8
A/HI	93.8	110.8	91.0	162.1	47.2
B	94.2	110.6	92.5	160.9	46.1
B/HS	n.d.	95.4	34.7	133.1[c]	17.6
B/HI	93.4	110.7	90.3	160.5	46.1
C	89.0	109.9	94.8	164.6	45.3
C/HS	n.d.	71.0	10.5	112.4	6.4
C/HI	92.4	112.5	94.0	164.5	45.3
D	91.3	109.9	95.3	163.8	46.0
D/HS	n.d.	86.2	21.3	124.8[d]	11.0
D/HI	92.8	110.8	94.5	161.2	46.8
E	93.9	110.9	97.1	164.5	47.6
E/HS	n.d.	81.1	18.0	118.1	9.2
E/HI	95.0	111.0	97.6	163.6	48.5

[a] Ground samples
[b] n.d. = not determined
[c] $T_{m2} = 142.2°C$
[d] $T_{m2} = 134.8°C$

Table 5 ^{13}C n.m.r. triad isotacticities of the whole polymers and their heptane-soluble (HS) and heptane-insoluble (HI) fractions

Sample	Percentage of mm	mr	rr
A	94.9	3.0	2.1
A/HS	36.9	33.0	30.1
A/HI	97.5	1.7	0.8
B	92.2	3.9	3.9
B/HS	50.5	23.4	26.1
B/HI	93.4	3.2	3.4
C	92.7	3.5	3.8
C/HS	45.4	22.8	31.9
C/HI	94.4	3.1	2.5
D	93.0	3.5	3.5
D/HS	51.5	20.2	28.3
D/HI	94.5	3.9	1.6
E	94.4	2.9	2.7
E/HS	52.2	23.6	24.2
E/HI	95.5	2.6	1.9

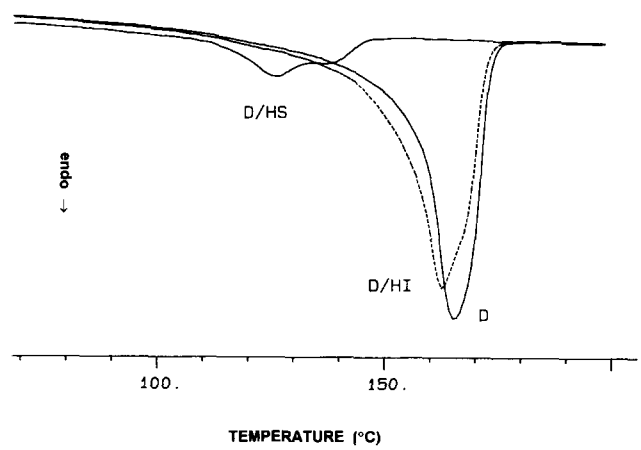

Figure 3 D.s.c. melting endotherms of sample D (ground) and its heptane-soluble (D/HS) and heptane-insoluble (D/HI) fractions

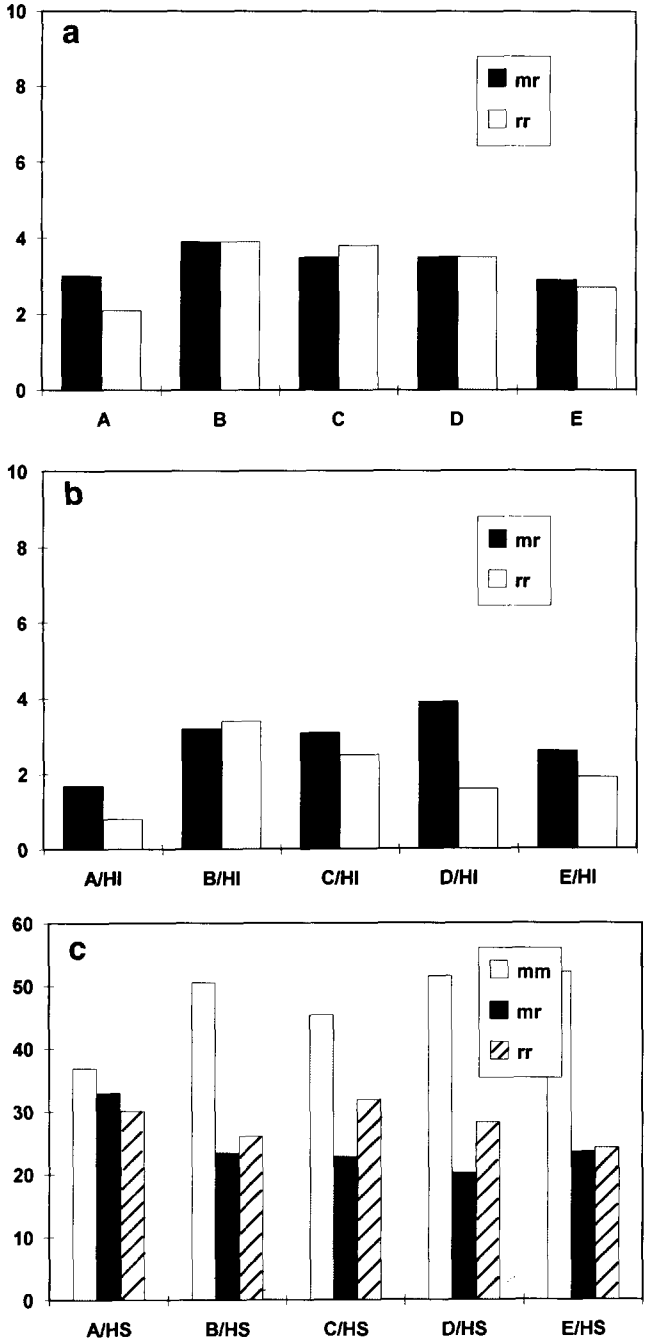

Figure 4 Percentages of heterotactic (mr) and syndiotactic (rr) triads (a) in unfractionated polymers and (b) in their heptane-insoluble fractions; and (c) percentages of mm, mr and rr triads in heptane-soluble fractions

insoluble fractions, when compared with the unfractionated polymers. For sample C the increase in i.r. isotacticity and crystallization temperature was more pronounced. The melting temperature decreased slightly for most samples (see also *Figure 3*). A similar decrease in T_m was also observed for a slurry-polymerized high-molecular-weight sample extracted earlier[13]. Thus, removal of atactic and low-molecular-weight material decreased the lamellar thickness of the residue. Correspondingly, Yan *et al.*[14] have reported that the crystalline lamellae became thinner when a portion of atactic material was removed by etching.

When unfractionated samples and their heptane-insoluble fractions are compared, a 1–3% increase in mm triad percentage is observed (*Table 5*, see also *Figures 4b* and *4c*). However, the heptane-insoluble fraction still contains atactic and syndiotactic materials. If the polymer dissolved in heptane were totally atactic, it would show signals of mm, mr and rr triads in its n.m.r. spectrum in a ratio 1:2:1. *Figure 4c* shows that these fractions were mainly isotactic, but contained also syndiotactic blocks, because the percentage of rr triads was higher than that of mr triads. *Figures 4a* and *4b*, which represent the amounts of heterotactic and syndiotactic triads in the whole polymers and their heptane-insoluble fractions, indicate that mainly heterotactic defects were left in heptane-insoluble residues of samples D and A. In contrast, the heptane-insoluble residues of polymers B and C contained almost equal amounts of mr and rr triads. This can again be explained with the help of the data obtained from earlier fractionations. These samples, especially sample B, had blocky errors in the same chain with isotactic sequences in long-chain molecules[7]. So, long isotactic sequences made this material insoluble in heptane.

As was mentioned earlier, what is dissolved in heptane extraction, and how stereoregular the insoluble residue is, depend partly on the structure of the original polymer. Solubility in heptane depends on both tacticity and molecular weight, and, in addition to atactic material, syndiotactic and low-molecular-weight isotactic polymer is dissolved. Syndiotactic material dissolved in heptane is either in totally syndiotactic chains or in the same chains with relatively short isotactic sequences. On the other hand, atactic and syndiotactic blocks located in the same chains with long isotactic sequences remain in the heptane-insoluble residue. The non-isotactic material contained in that kind of block cannot be separated from isotactic polymer by any type of single-solvent fractionation (when the temperature is constant and only two fractions are isolated). In the n.m.r. method this kind of defect is also detected, and this is causing deviations in the isotacticities measured by n.m.r. and extraction methods.

However, a better separation using xylene as a fractionation solvent has been reported, for example by Van der Ven[15]. In our own previous study, both heptane- and xylene-solubles were separated[13]. According to d.s.c. measurements, the xylene-soluble material, though its weight fraction was as large as that of the heptane-soluble fraction, was totally amorphous. The molecular weight of the xylene-soluble fraction was also higher than that of

Table 6 Characteristics of the fractions obtained by successive extractions using solvents with increasing boiling points

Sample[a]	Wt (%)	$\bar{M}_w/10^3$	$\bar{M}_w/\bar{M}_n$	T_m (°C)	Cryst. (%)
A (ground)		396	5.2	163.7	46.5
A/HS	4.1	25[b]	9.1[b]	116.6	4.8
A/OS	3.9	84	5.4	154.9[c]	38.0
A/XS	2.9	200	3.6	162.4	45.7
A/XI	89.1	481	4.5	164.1	46.8

[a] HS = heptane-soluble, OS = octane-soluble, XS = xylene-soluble, XI = xylene-insoluble fractions

[b] Antioxidant is broadening the *MWD* and lowering the $\bar{M}_w$ of HS fraction

[c] $T_{m2} = 163.4$°C

Table 7 ^{13}C n.m.r. characterization of the fractions obtained from sample A by successive extractions with solvents of increasing boiling points

Fraction	Percentage of									Av. m seq./ propene units[a]
	mmmm	mmmr	rmmr	mmrr	mmrm & rmrr	rmrm	rrrr	mrrr	mrrm	
A	92.5[b]	2.1	0.3	2.0	1.0	0.0	0.6	0.6	0.9	62
A/HS	20.2	10.2	6.6	12.7	14.3	6.0	14.0	10.1	5.9	3
A/OS	78.7	5.8	1.1	6.1	2.0	0.0	2.4	1.9	2.0	20
A/XS	90.6	2.1	0.3	2.5	1.1	0.0	1.2	0.8	1.4	57
A/XI	96.5	1.3	0.1	1.4	0.2	0.0	0.0	0.0	0.5	120

[a] Determined as in ref. 7
[b] Relative error <0.5% for mmmm pentads, <5% for other pentads

the heptane-soluble fraction, indicating that the fractionation method using xylene as a solvent is less molecular-weight-dependent and the fractionation takes place merely according to tacticity (no n.m.r. analysis was performed on the xylene-soluble fraction). The basic difference in the fractionation techniques may be one possible source for differences observed in composition of the fractions: heptane extraction is a fractional solution method, whereas the determination of xylene-solubles is a recrystallization method.

The heptane-insoluble residue of sample A was fractionated further by successive extractions with n-octane and xylene. Weight fractions from these extractions and the characteristics of the fractions are presented in *Tables 6* and *7*.

The octane-soluble fraction had distinctly higher isotacticity (85.6% mm) than the heptane-soluble fraction. Its molecular weight (84×10^3) was of the same order as the molecular weight reported for stereoblock polymers isolated by Van der Ven[15], and its molecular-weight distribution was broad. This fraction showed a double peak in its melting endotherm (*Figure 5*).

The fraction soluble in xylene had isotacticity of 93.0% (mm triad percentage), but it still contained small amounts of defects of various kinds (*Table 7*). These defects are located in the same chains with isotactic sequences, because this material did not dissolve until in this fraction.

As was mentioned before, pentads mmmr, mmrr and mrrm are caused by the defect mmmrrmmm. The appearance of this defect means that, despite an accidental steric inversion, the isospecific catalytic site remains unchanged. Because all pentads do not appear in the ^{13}C n.m.r. spectra of the fractions (if the HS fraction is excluded), it is possible to make some hypotheses concerning the other defects in the chain structures. On the basis of the sequence percentages measured for the octane-soluble (OS) and the xylene-soluble (XS) fractions, we suggest that rrrr, mrrr, rrmr and rmmr pentads are caused by the same steric inversion repeating immediately (*Figures 6a* and *6b*), causing pentads rrrr and mrrr, or after one (*Figure 6c*, rrmr) or two (*Figure 6d*, rmmr) m placements. Similar features, absence of mrmr pentads and a large amount of mrrr pentads compared to rrrr units, were also observed for several fractions from fractionations using solvent/non-solvent systems[7,9]. The large quantity of mrrr pentads supports the assumption that syndiotactic material is located in short sequences. Syndiotactic blocks appear only together with mmmr, mmrr and mrrm pentads (the same as observed in ref. 7). If the syndiotactic sequences were longer and, for example, located in the chain ends, structures like that in *Figure 6e* would be obtained.

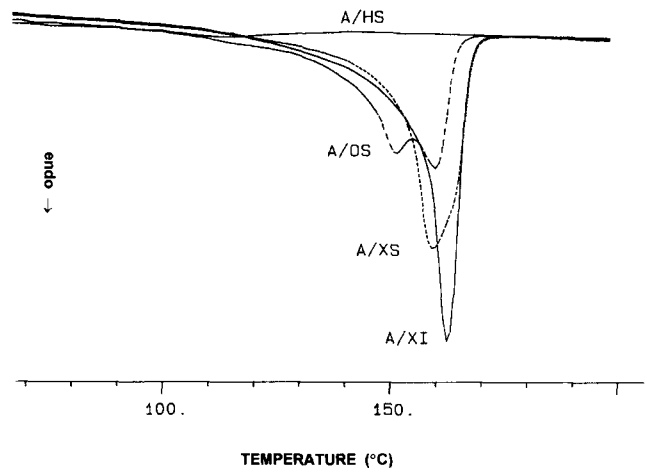

Figure 5 D.s.c. melting curves of fractions obtained from sample A by successive Soxhlet extractions: A/HS = heptane-soluble, A/OS = octane-soluble, A/XS = xylene-soluble and A/XI = xylene-insoluble fractions

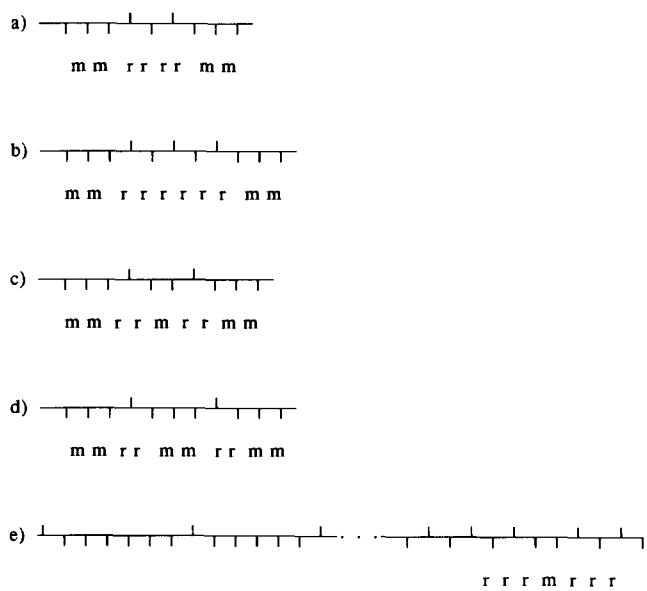

Figure 6 Possible chain structures for defects in isotactic propagation

The material in the xylene-insoluble residue was produced in isospecific centres and only the defect mmmrrmmm was detected in it. Also, statistical analysis of the n.m.r. sequence distributions supported that observation. A two-site model, a combination of Bernoullian

and enantiomorphic reaction probability models[16,17], was applied to the data obtained from these fractions. The optimum values of the three parameters of this model are presented in *Table 8*. The weight fraction of polymer produced in isospecific centres (ω) was 0.99 for xylene-insoluble fraction. Otherwise the value of ω increased in the course of fractionation. A similar trend was observed for the value of α (probability of selecting a $d(l)$ unit at a $d(l)$-preferring site in the enantiomorphic site propagation model). The increase of α can, on the one hand, be considered as a sign of fractionation truly occurring according to tacticity. On the other hand, the α value should be similar for each fraction obtained from the same sample. Inoue *et al.*[17] have explained this discrepancy in α values as due to an insufficient number of catalytic sites. Another cause according to these authors is the non-adherence to dynamic equilibrium of the growing chain end between the two possible sites. If our assumption for the source of the defects other than mmmrrmmm is valid, it would mean that molecules that are tendentially, but not completely, isotactic were also produced in originally isospecific sites, which, as a result of a reversible structural variation, for a short while acted as syndiospecific or aspecific centres.

In contrast, the deviation in σ values was not so large, except for the xylene-insoluble fraction (now it should be noted that σ becomes poorly defined when ω approaches the value 1; see equations in refs 16 and 17). Similar results, an increase in α value while σ remained constant, were also obtained for the multiple-solvent extraction by Kawamura *et al.*[18]. On the basis of these results, they suggested that both molecular-weight and tacticity fractionations occurred for isotactic polymer, while only molecular-weight fractionation occurred for atactic material.

Table 8 The optimum values of the parameters for the two-site model

Sample	α	ω	σ	S.d./10^{-3}
A	0.990	0.97	0.31	1.2
A/HS	0.800	0.62	0.24	13.3
A/OS	0.967	0.93	0.24	4.8
A/XS	0.988	0.96	0.26	1.4
A/XI	0.994	0.99	0.71	0.7

α = probability of selecting a $d(l)$ unit at a $d(l)$-preferring site in the enantiomorphic-site propagation model
ω = weight fraction of the polymer produced at enantiomorphic sites
σ = probability of selecting a meso dyad configuration in the Bernoullian model site
S.d. = standard deviation between the observed and calculated pentad sequence distributions

Table 9 Cumulative weight fractions for the two types of fractionations

Soxhlet extraction		Fractional solution with solvent/non-solvent system	
Fraction	$\sum\omega_i$ (%)	Fraction	$\sum\omega_i$ (%)
A/HS	4.1	A/1	5.3
A/OS	8.0	A/2	7.3
A/XS	10.9	A/6	13.8
A/XI	100.0	A/9	29.8
		A/11	38.3
		A/14	63.8
		A/15	100.0

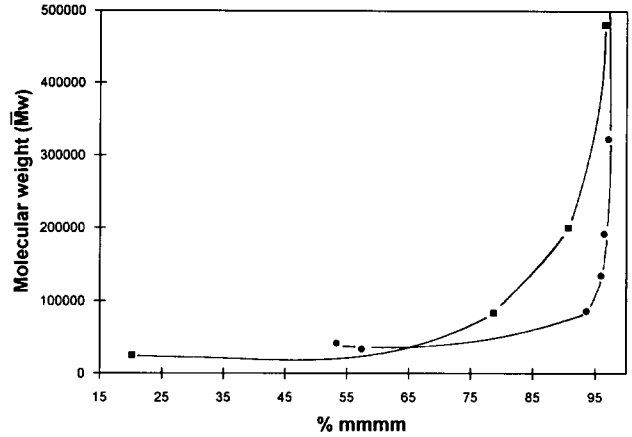

Figure 7 Molecular weight as a function of isotactic pentad fraction for the fractions obtained by successive Soxhlet extractions (■), and for the fractions obtained by fractional solution with solvent/non-solvent mixtures (●)

From our results it was obvious that the successive extraction method was less molecular-weight-dependent than the solution fractionation performed earlier on the same sample[7,8]. Though a fractionation carried out using xylene/ethylene glycol monoethyl ether solvent/non-solvent system also separated mainly on the basis of stereoregularity, no material as non-isotactic as the heptane-soluble fraction of Soxhlet extraction was isolated. All samples gave similar results, not only sample A. The fractions obtained in the fractionation with solvent/non-solvent mixtures also had narrower *MWD*s, indicating that these fractions were more homogeneous in molecular weight as well, while fractions obtained in successive extractions were homogeneous only in tacticity. These two types of fractionations are compared in *Figure 7*. Cumulative weights of the fractions are presented in *Table 9*.

CONCLUSIONS

Because solubility in heptane is dependent on both tacticity and molecular weight, heptane extraction, when used as a method for isotacticity determination, gives only a rough estimate of polypropylene stereoregularity. Low-molecular-weight isotactic material is dissolved in heptane, whereas non-isotactic material located as blocks in the same chains with long isotactic sequences remains in the heptane-insoluble residue. Successive Soxhlet extraction with solvents of increasing boiling points separates mainly according to tacticity, with a slight molecular-weight dependence.

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