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$[\eta]$ – *M* relationship for isotactic polypropylene obtained with 'high-mileage' catalysts

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A new catalyst system, denominated 'high-mileage' (*HM*) catalyst, has been recently set up for the synthesis of isotactic polypropylene[1]. Its characteristic is that the weight ratio of polymer produced to Ti used in the catalyst system is higher by two orders of magnitude than that from traditional Ziegler–Natta catalysts (ZN).

The advantages that such new catalysts may offer in industrial practice may easily be seen, especially in view of the final polymer purification from inorganic residues.

Since the behaviour of *HM* polypropylene in some technical applications seems to differ slightly from that of the ZN polymer[2] we were led to undertake research aiming at establishing any possible structural difference by a close comparison of the two polypropylenes.

The preliminary results obtained from an investigation on dilute fraction solutions are reported in this Note.

EXPERIMENTAL

Polymer samples

Two *HM* polypropylene samples were prepared and denominated *HMa* and *HMb*. A sample, ZN 30, was chosen from polypropylene obtained in the presence of a traditional catalyst. All three samples show an intrinsic viscosity of 1.65 ± 0.01 (100 cm^3/g) in tetrahydronaphthalene at 135°C.

Fractionations

Fractionations were carried out according to the technique of the fractional solution by using a sand-packed column, which is fundamentally of the Baker–Williams type[3]. Tetrahydronaphthalene and diethyleneglycol-monoethyl ether were used as a solvent–non solvent pair. The temperature used was 145°C and atmospheric oxygen was rigorously excluded. Since the fractionation column only provided 0.05 g of the fractions, insufficient for physicochemical determinations, 6 to 8 samples from each polymer were fractionated: the fractions exhibiting quite similar $[\eta]$ values were collected together to form the larger amounts necessary for measurements. These cumulative fractions were first homogenized and then subjected to a polydispersity control through gel permeation chromatography by determining the $\bar{M}_w/\bar{M}_n$ ratio.

Viscosimetry

Viscosimetric determinations were carried out by a Desreaux–Bischoff type viscosimeter, manufactured in such a way as to obtain negligible kinetic energy effects. The solvent used was tetrahydronaphthalene at 135°C.

Molecular weight determination

Measurements were carried out by a photogoniodiffusometer Sofica 50, with unpolarized light (λ = 5461 Å) using α-chloronaphthalene at 150°C as a solvent.

For calculations, use was made of $dn/dc = -0.190\ cm^3/g$ and of a Rayleigh ratio of benzene at 23°C equal to $15.8 \times 10^{-6}\ cm^{-1}$. Each fraction was measured at five different concentrations, at angles between 30° and 150°.

The linearity of the Zimm plots obtained allowed a fairly accurate molecular weight determination.

RESULTS AND DISCUSSION

The final data are reported in *Table 1*. As shown in column 3 of the Table, the fractions we used maintain a considerable polydispersity residue. This is not unexpected since our fractions actually consist of mixtures, though presumably of very similar fractions, and since only the fractionation does not generally guarantee narrow fractions, especially in the case wide-distributed raw polymers. Under such conditions, the $[\eta]-\bar{M}_w$ relationships that may be calculated for the two polymer types do not serve validly to compare the rheological and conformational behaviour of the two polypropylenes.

With regard to the fractions, by analogy with other workers[4] we think it more convenient to propose a residual molecular weight distribution of the Wesslau type[5] and then to apply the following expression:

$$\bar{M}_v = \bar{M}_w d^{-1-a/2} \qquad (1)$$

Table 1 Data on *HM* and *ZN* polypropylene fractions ($[\eta]$ in tetrahydronaphthalene at 135°C (100 cm^3/g); $d = \bar{M}_w/\bar{M}_n$ by gel permeation chromatography; $\bar{M}_v$ calculated from equation (1) with a = 0.74 and $\bar{M}_w$ by light scattering measurements)

Fractions		$[\eta]$	$d = \dfrac{\bar{M}_w}{\bar{M}_n}$	$\bar{M}_v \times 10^{-3}$
HMa	18	4.22	1.92	710
HMa	17	3.34	1.82	569
HMb	14	2.97	1.89	469
HMa	16	2.58	1.67	394
HMb	13	2.35	1.72	356
HMb	10	1.21	1.21	128
HMa	12	1.12	1.30	117
HMa	9	0.64	1.24	58
HMb	7	0.57	1.20	46
HMa	7	0.41	1.20	35
ZN	18	4.40	2.35	745
ZN	17	3.94	2.10	625
ZN	15	2.33	1.80	333
ZN	11	1.15	1.35	130
ZN	8	0.57	1.30	48
ZN	6	0.42	1.15	33

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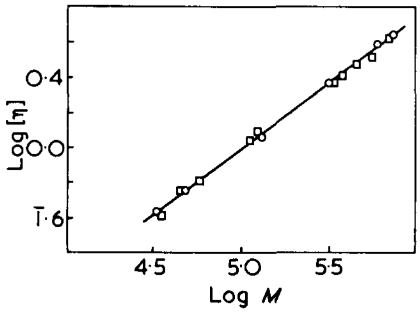

Figure 1 Double logarithmic plot of the data in *Table 1*: ○, fraction of polypropylene ZN; □, fraction of polypropylene HM; ——, linear regression of log [η]— log *M* for all the data of *Table 1*

where $d = \bar{M}_w/\bar{M}_n$ and a is the exponent of the Mark–Houwink equation.

Hence, within the reliability limits of the hypothesis, the [η] –M relationships are no longer influenced by the residual dispersity, and coincide with the relationships that might be obtained with more strictly monodispersed samples.

For this reason the molecular weight values reported in the Table were determined by using the $\bar{M}_w$ data of light scattering and the d values of the third column with $a = 0.74$ as obtained from the literature[6].

Using a linear data regression we have calculated the Mark–Houwink relationships for the two polypropylenes from the second and the fourth column of the Table. Such relationships are practically equivalent. As a matter of fact by applying them to molecular weights of 3 x 10^4 and 7 x 10^4, which represent the extremes of the molecular weight range examined by us, differences in [η] respectively of ~1% and ~4% are obtained. Such differences are well within the experimental errors.

This fact is realized in the double logarithmic plot (*Figure 1*) where [η] and M values for the two polypropylenes are reported. In it the straight line has been calculated using the linear regression of all [η] –M data of the Table and it follows that:

$$[\eta] = 1.81 \times 10^{-4} M^{0.745} \qquad (2)$$

Equation (2) is quite similar to that we previously found by osmotic measurements on very narrow ZN polypropylene fractions prepared by adopting a different fractionation technique[6]:

$$[\eta] = 1.93 \times 10^{-4} M^{0.74} \qquad (3)$$

As a matter of fact, for M ranging between 10^4 and 10^6, the [η] calculated by equations (2) and (3) give values which differ at most by 1.7%.

Hence isotactic *ZN* polypropylene and isotactic *HM* polypropylene do not show any noticeable difference in the rheologic and structural behaviours of dilute solutions; in particular, on the basis of the [η] –M relationship, isotactic *HM* polypropylene can be considered to consist of highly linear chains.

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Editorial Announcement

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