

# Correlation of Properties with Structure in Ziegler Polypropylenes

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## SYNOPSIS

Isotactic polypropylenes, varying in molecular weight, crystallinity, and tacticity, were characterized by spectroscopic and chromatographic techniques in order to obtain suitable samples for investigating the effect of structure on properties. Mechanical and thermal properties were studied with respect to their structural dependence. Melting points and rates of crystallization were observed to be higher in the more stereoregular samples, while evidence of fractionation by molecular weight and tacticity was observed in less stereoregular samples. Tensile properties displayed marked dependence on polymer stereoregularity, while examination of fractured surfaces by microscopy showed that fracture occurred at regions of high impurity concentration. © 1992 John Wiley & Sons, Inc.

## INTRODUCTION

Isotactic polypropylene is a semicrystalline polymer of considerable commercial importance. An understanding of the relationship between property and structure is important in its processing and application.<sup>1</sup> Thermodynamic parameters, such as entropy of fusion and equilibrium melting temperature, which are important in describing crystallization and nucleation mechanisms as well as melting behavior, depend on polymer structure.<sup>2</sup>

Property-structure relationships in polymers is an area that has witnessed increased research efforts for many years.<sup>3,4</sup> With respect to polypropylene, an obvious problem has been that, in an attempt to correlate observed properties with structure, studies have been carried out mainly on samples that are not characterized or well characterized.<sup>5,6</sup> This has resulted, inevitably, in discrepancies in reported values of important thermal and physical properties of the polymer.<sup>7</sup> Well characterized iPP samples, varying not only in molecular weight and crystallinity, but also in tacticity, are needed for this kind of study.

In a recent study, an attempt was made by Burfield<sup>8</sup> to establish a calorimetric index for determining stereostructure. In this paper, an experimental study on the thermal and mechanical properties of polypropylene samples, covering the tacticity range 20 to 100%, is reported.

## EXPERIMENTAL

### Materials

The polypropylene samples used were synthesized in our laboratory using a new generation of supported Ziegler catalysts.<sup>9</sup> The polymerization method is described elsewhere.<sup>10,11</sup> The materials used, and their characteristics, are given in Table I.

### Characterization

#### *Tacticity Determination*

Carbon 13 and Proton nuclear magnetic resonance techniques were used to determine the tacticity of samples. Spectra were obtained with a JEOL GNX FT 270 spectrometer on 10% w/v dichlorobenzene solution at 413 K. The spectra were analyzed in terms of the configurational triads according to the resonance peak identification procedure of Zambelli et al.<sup>12</sup>

**Table I Polymer Materials Used and Their Characteristics**

Sample Ref.	$M_x \times 10^{-3}$ <sup>a</sup>	mm <sup>b</sup>	rr <sup>b</sup>
PP162	630	0.95	0.004
PP129	592	0.90	0.010
PP127	618	0.85	0.055
PP123	12	0.25	0.330
PP124	600	0.45	0.350
PP128	17	0.60	0.100
PP160	577	0.50	0.200

<sup>a</sup> Determined by gel permeation chromatography.

<sup>b</sup> Determined by nmr spectroscopy.

### Molecular Weight Distribution

A Waters Associate 150C ALC/GPC High Temperature Gel Permeation Chromatographic unit, interfaced to a microcomputer acting as a data station, was used to determine the molecular weight and fractionate polymer samples.

### Thermal Properties

A Perkin-Elmer DSC-2 interfaced to a microcomputer was used to collect and analyze crystallization

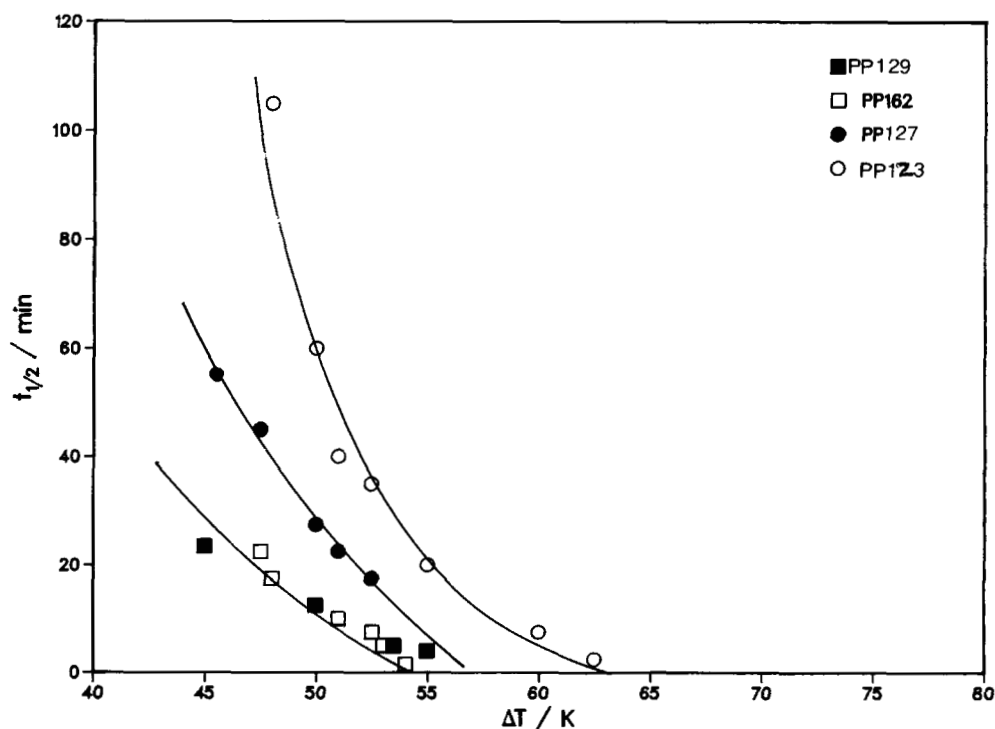
and melting data. The thermal response of the calorimeter was calibrated with the heat of fusion of ultra pure indium, 28.4 J/g, and the temperature from the melting points of indium, tin, and zinc. Experiments were carried out in an atmosphere of nitrogen.

In crystallization studies, samples weighing approximately 10 mg, were encapsulated in aluminum pans and melted at 460 K at a heating rate of 80 K/min for about 5 min before quenching at 160 K/min to the crystallization temperature.

A Lietz Dialux Polarizing microscope at a maximum magnification of 400, fitted with a metler hot stage, was used to study nucleation and growth behavior of spherulites.

### Mechanical Testing

Tensile tests on polymer specimens was carried out using an Instron floor model TT-BM tensile tester, capable of exerting a maximum load of 2.5 tonnes. Crosshead speeds in the range 0.005 cm/min to 50 cm/min could be used to an accuracy of 0.1%. Tests were carried out in a room at a constant temperature of  $295 \pm 1$  K.



**Figure 1** Crystallization kinetics: half life against supercooling.

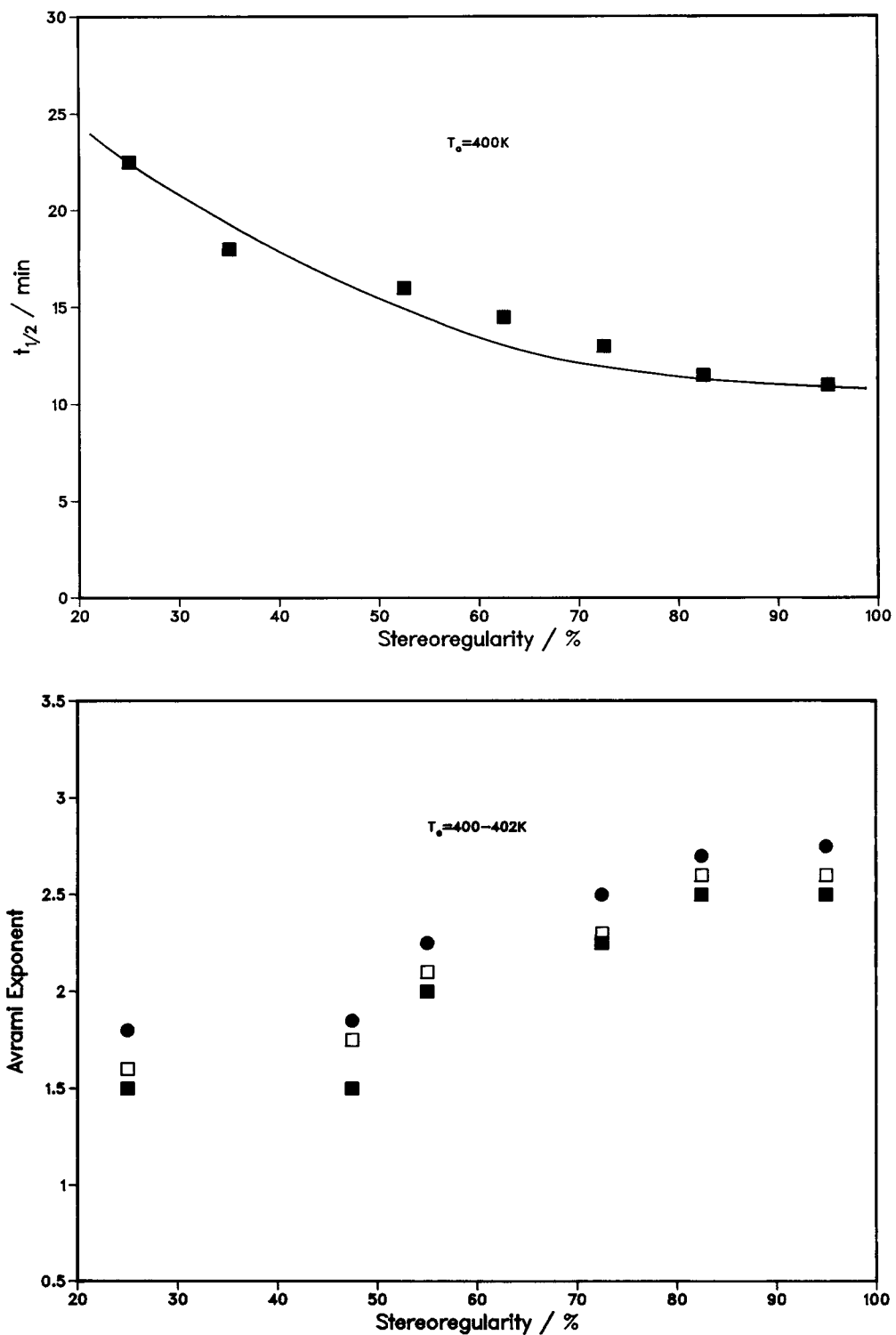


Figure 2 (a) Effect of stereoregularity on crystallization kinetics, (b) Dependence of Avrami value on stereoregularity.

## RESULTS AND DISCUSSION

## Crystallization and Melting Studies

The characteristic thermal behavior of isotactic polypropylene is, to a large extent, well known with regard to its crystallization and melting isotherms. Generally, broad and multiple fusion peaks are observed in unannealed and low tactic PP samples. These have been explained as being due to the presence of different crystalline forms, molecular weights, and differences in the distribution and types of stereodefects in the polymer.<sup>13</sup>

The analysis of crystallization behavior was carried out using the model proposed by Hoffman et al.<sup>14</sup> on crystal growth. According to this model, the growth rate of a crystal is given by

$$G = [C/n] \exp(-Q_D/RT) \exp(-Kg/T\Delta T) \quad (1)$$

where  $G$  is the growth rate,  $C$  is the frequency factor,  $n$  is the number of  $\text{CH}_2$  units in the chain,  $Q_D$  is the activation energy for steady state reptation,  $Kg$  is the rate constant,  $R$  is the gas constant, and  $T$  is temperature. Since the half life,  $t_{1/2}$ , incorporates the rates of both nucleation and growth, eq. (1) can be expressed, with some assumption,<sup>15</sup> as

$$\ln t_{1/2} = G_o + 4\sigma\sigma_e T_c^{n-1} / R\Delta H(\Delta T)^n \quad (2)$$

where  $\sigma$  and  $\sigma_e$  are the surface free energies and  $n$  is a constant diagnostic of the crystallization mechanism.

In the stereoregular samples, it was observed that crystallization onset temperatures increased in step

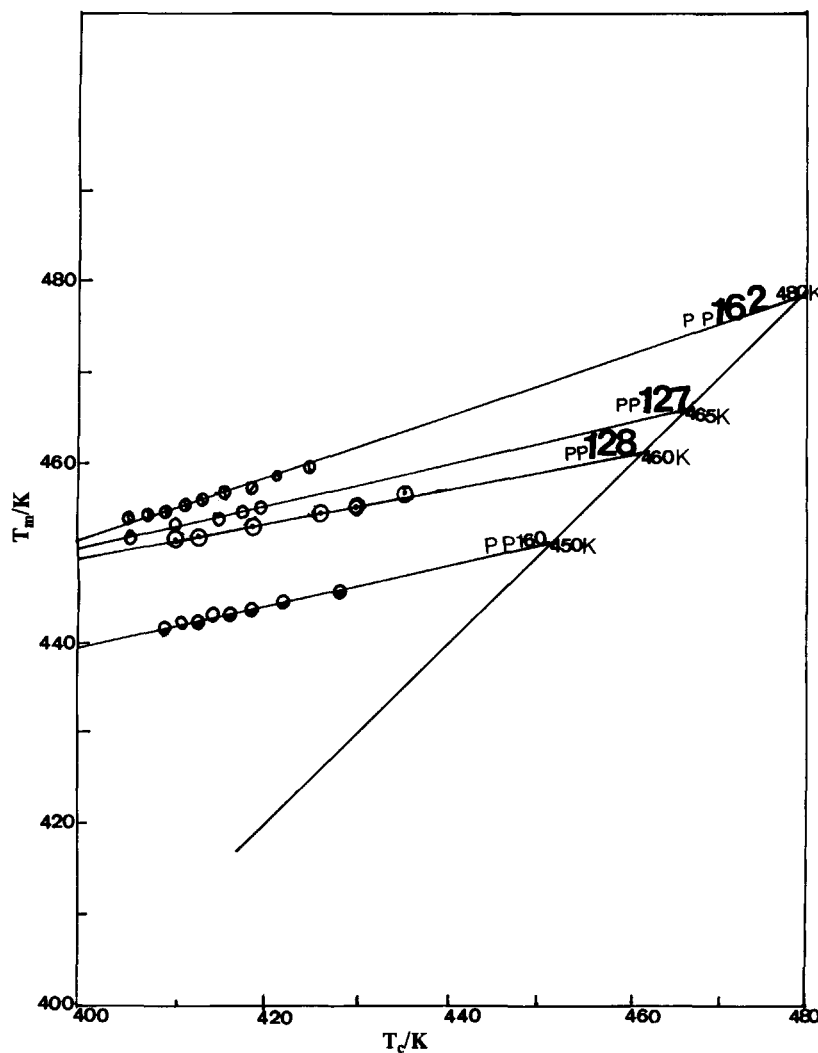


Figure 3  $T_m$  against  $T_c$ .

with increased tacticity. The plot of the half life of crystallization,  $t_{1/2}$ , against supercooling,  $\Delta T$  (Fig. 1), shows that at the same crystallization temperature, the overall rate constant,  $Kg$ , of sample PP123, is lower than the rate constants for samples PP162, 129, and 127. This is further evident in the plots of the half life and the Avrami value against isotacticity (stereoregularity), Figs. 2(a, b). It is obvious from the plot that at the same  $T_c$ , sample PP123, with the lowest tacticity, crystallized at a much slower rate. On the other hand, the observed  $n$  values for samples PP162, 127, and 129 increased with increasing isotacticity. It has been suggested that the  $n$  value is an indication of the number of degrees of freedom in crystal growth.<sup>16</sup> In the stereoirregular samples, therefore, crystallite formation is inhibited by the presence of defects or faults in the polymer structure. This decreases the  $n$  value. The differences in the observed  $n$  values are thus attributable to differences in structure, the more stereoregular structure having higher values.

In the primary crystallization process, the  $n$  values obtained were about 3.0 for the highly tactic samples, which indicates a similar mechanism of primary nucleation and growth. However, in samples of low tacticity, such as PP 123, 124, and PP 128, the secondary process proceeds at a slower rate with an  $n$  value of less than 2.0. This describes a crys-

tallization process with one dimensional growth, linear growth, and heterogeneous nucleation, as has also been observed by Madelkern<sup>17</sup> and Zachmann and Stuart.<sup>18</sup> Only the low stereoregular samples had a clearly defined secondary process. A model for this type of crystallization has been proposed.<sup>19</sup>

### Melting Studies

The equilibrium melting point,  $Tm^0$ , is important in describing the relationship of polymer properties to structure and in the analysis of crystallization and nucleation processes. The melting process of samples was studied in an attempt to characterize their behavior and, hence, to determine the effect of melting on the crystallization temperature. This allows for the determination of  $Tm^0$ .

A linear increase of  $Tm$  with  $T_c$  was observed in accordance with Hoffman's relation.<sup>20</sup>

$$Tm = Tm^0(1 - 1/2\beta) + Tc/2\beta \quad (3)$$

where  $Tm$  is the melting point,  $Tm^0$  is the equilibrium melting point,  $T_c$  is the crystallization temperature, and  $\beta$  is a constant. The slope of the linear relation,  $Tm$  against  $T_c$  (Fig. 3), was between 0.43 and 0.84. These values are close to the expected 0.5 so that it must be concluded that  $\beta$  does not vary

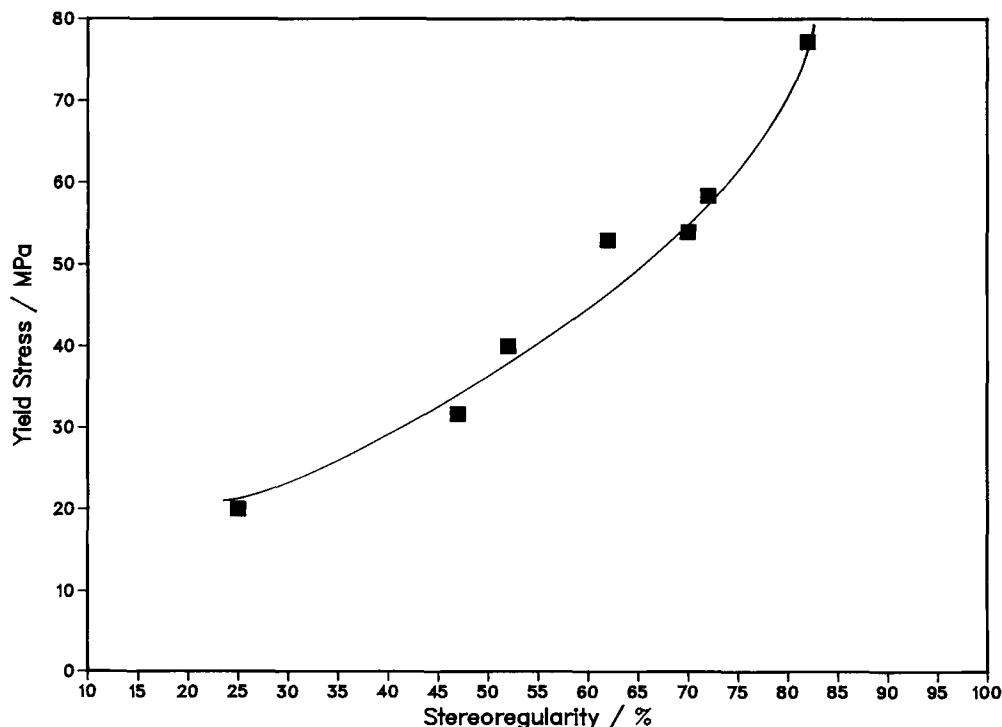


Figure 4 Effect of stereoregularity on yield stress.

much from unity. Values greater than unity are attributable to annealing effects, which suggests that the crystal fold length increased in value on crys-

tallization. As can be seen in the plot, the higher the stereoregularity of sample, the higher the melting and equilibrium melting temperature observed. This

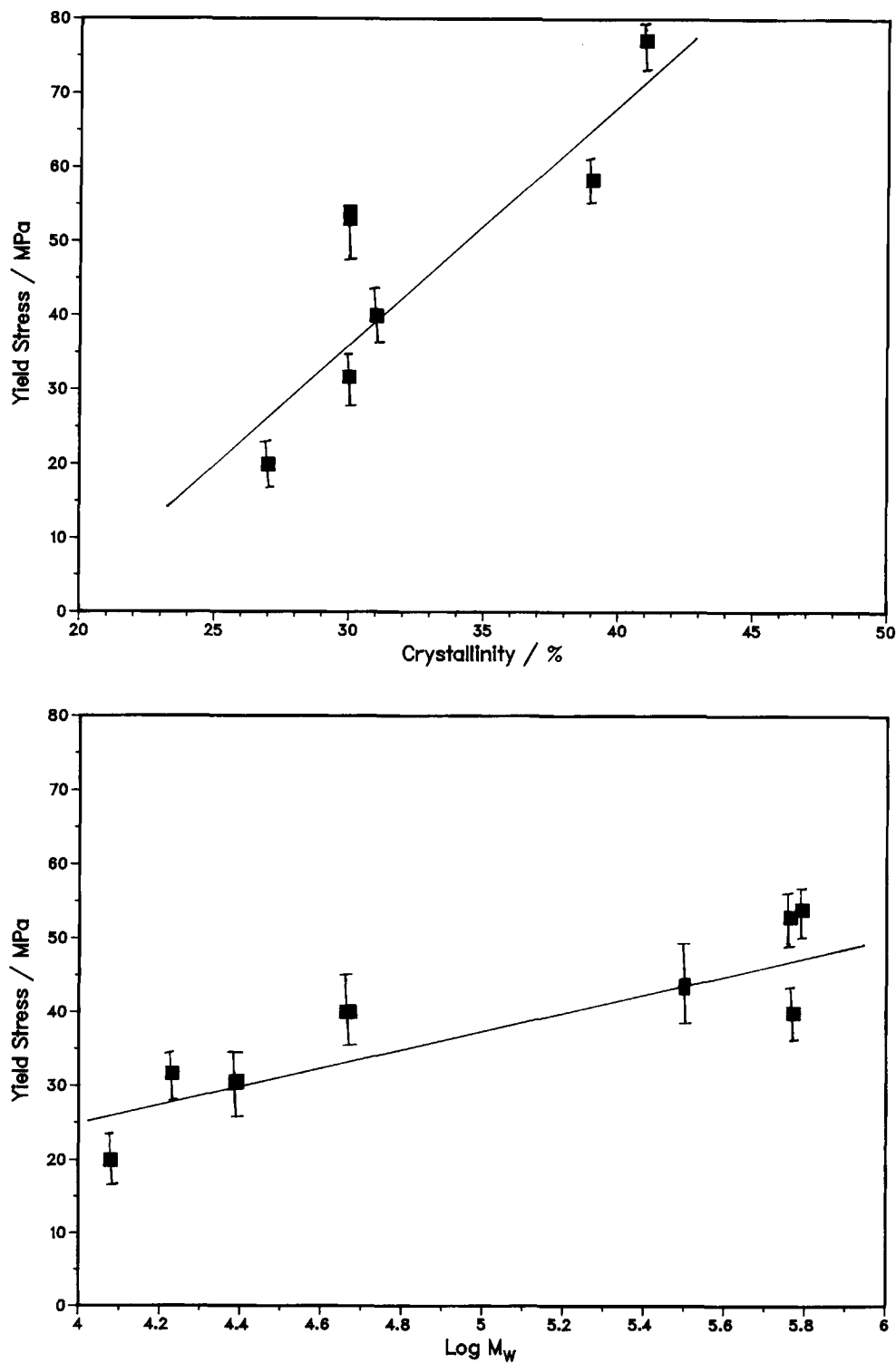


Figure 5 (a) Yield stress against crystallinity, (b) Effect of mol wt on yield stress at approximately 35% crystallinity.

is in agreement with crystallization data and is hence not unexpected.

### Mechanical Properties

Although the mechanical behavior of uncharacterized/semicrystalline polymers is difficult to interpret,<sup>21</sup> the effect of structure on mechanical response can be observed from simple stress-strain profiles of polymer specimens. Such tests were carried out on various polymer samples. The plot of the yield stress against stereoregularity (Fig. 4) shows that the yield stress increased with tacticity. The much reduced yield stress, observed in the lower tactic samples, is attributable to structural irregularity in the polymer chain. These are weak points from which, invariably, yielding occurs. An examination of the fractured surface by microscopy confirmed this. It is expected that impurities rejected by advancing spherulites during growth are swept into the boundaries and, hence, it is in these regions that failure occurs.

The plot of the yield stress against crystallinity [Fig. 5(a)] shows an increase in the yield stress with crystallinity. Thus, there is a one-to-one correlation between crystallinity and isotacticity, the more crystalline and more isotactic samples having a higher yield stress, as shown in Figures 4 and 5(a). On the other hand, the increase in yield stress with molecular weight [Fig. 5(b)] cannot be attributed to differences in isotacticity or crystallinity since the crystallinity of these samples, PP127, 128, 129, and 160 is the same, about 35%. The increase in yield stress can only be attributed to molecular weight differences in the samples investigated.

### CONCLUSION

An attempt has been made to relate observed polymer properties to structure using a combination of thermal analytical and mechanical techniques. The results show a clear relationship between isotacticity and thermal properties, such as crystallization and melting. As for mechanical properties, they are more difficult to correlate with structure because of the numerous variables that affect the interpretation of

mechanical data for semi-crystalline materials. However, from the stress-strain profiles, the likely effect of structure on property can be deduced.

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