65.81; H, 6.85) was obtained in a 41% yield by treatment of the salt (II, R = C_6H_5) with β-carbethoxypropionyl chloride.

Benzoylation of the magnesium chelate formed from ethyl hydrogen malonate[10] and magnesium ethoxide led to the introduction of two benzoyl residues and the formation of ethyl dibenzoylacetate.[11]

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THE "FLORY (θ) TEMPERATURE" OF ATACTIC AND ISOTACTIC POLYPROPYLENE

Sir:

Identical intrinsic viscosity–molecular weight relationships for atactic and isotactic polystyrene *in thermodynamically good solvents* have been confirmed but real differences in the second virial coefficients were detected.[1,2,3]

According to theory, the second virial coefficient depends on (1) the unperturbed dimensions of the polymer chain, (2) the enthalpy and entropy parameters κ_1 and ψ_1 and (3) the partial specific volume of the polymer. Krigbaum, *et al.*, found (3) contributes only a minor effect and proposed the main effect arose through differences in (1).

The thermodynamic interaction parameters can be evaluated through phase equilibria studies in the liquid–liquid region where the critical temperature (T_c) is related to the thermodynamic parameters by the relationship[4]

$$1/T_c = 1/\theta[1 + (1/\psi_1)(1/x^{1/2} - {}^1/_2x)] \qquad (1)$$

where

$$\theta = \kappa_1 T/\psi_1;\; x = \bar{M}_n\bar{v}_2/V_1$$

V_1 = molar volume of the solvent, $\bar{v}_2$ = specific volume of the polymer.

Phase diagrams of carefully characterized fractions[5] of atactic and isotactic polypropylene have been determined and binodials characteristic of *liquid–liquid* separations for both isomers obtain in phenyl ether at temperatures near the melting point of the isotactic polymer.

Reciprocals of the critical temperatures determined from the phase diagrams were plotted against the function $(1/x^{1/2} - 1/2x)$ according to equation (1) and the parameters ψ_1 and θ evaluated. Curves for atactic and isotactic polypropylene differ considerably in both slope and intercept and yield values for the parameters as shown in Table I.

Under these conditions the atactic polymer is less soluble than its isotactic counterpart, supporting the proposition that the atactic form is the more flexible.[3]

TABLE I
THERMODYNAMIC INTERACTION PARAMETERS IN PHENYL ETHER

	θ, °K.	Ψ_1
Isotactic	418.4	1.414
Atactic	426.5	0.986
Difference	8.1	0.426

The data predict a reversal in precipitation order above the unique condition (intersection of the two curves) where the term ψ_1 $(1 - \theta/T)$ for the two isomers is identical. The point of intersection depends on the solvent, the molecular weight and the temperature. A similar intersection appears in the data of Danusso and Moraglio[2] on the second virial coefficients of atactic and isotactic polystyrene and the unfortunate choice of a polymer near the critical molecular weight may have prevented Krigbaum, *et al.*,[3] from detecting differences in the unperturbed dimensions of polystyrene chains by viscosity ratios; however, their conjecture that the θ temperatures for the two isomers may differ is confirmed.

We finally conclude that both θ and ψ_1 as determined by phase studies may ultimately be used to reflect the degree of stereoregularity within polymer chains. As suggested by theory[6,7] intrinsic viscosity–molecular weight relationships may not be identical for conformational isomers in poor solvents where segment–segment interactions are magnified.

In a future paper we plan to reveal the unperturbed dimensions of the two isomers at their respective θ temperatures and will discuss the significance of these data in terms of structure and dilute solution behavior of polymeric stereoisomers.

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ON THE NATURE OF PROTEIN-BOUND LIPOIC ACID

Sir:

Previous work[1] indicated that lipoic acid, in its functional form in bacterial pyruvate dehydrogenation complexes, is bound to protein in covalent linkage through its carboxyl group. This communication presents evidence that lipoic acid is bound to the epsilon amino group of a lysine residue.

When *Escherichia coli* is grown aerobically in the presence of lipoic acid-S_2^{35}, radioactive lipoic acid is incorporated into the pyruvate dehydrogenation complex. A highly purified preparation[2] (176 mg.; sp. act. 678; 1.47 μg. radioactive lipoic acid per mg. protein) was treated with performic

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