nine variables (one of them, $lg_{23}° - g_{13}°$, very small[5,6]) may be too many with respect to the nine equations Y.

When we put $\chi_T° \equiv (\chi_T°)_0$ and $g_T° \equiv (g_T°)_0$ with $lg_{23}° - g_{13}° = 0.0$, we found reasonable $\chi_{23}°$ values, and reasonable "averaged" values for $g_T°$ and $\chi_T°$, even from a "truncated" Y–u_2 curve (Table II). The Y–u_2 curve in this case is described as well as it is in Table I. We ascribe this to the fact that the Y–u_2 curve is determined to a large extent by the g_{12} function[4,6,8] (which is the same in Tables I and II).

Inclusion of the λ values of Chu and Munk[5,6] in our calculations did not give results better than those represented in Table I or II. They became even worse as regards $\chi_T°$ and $g_T°$. Fully nonsensical results for $g_T°$ and $\chi_T°$, as well as a bad reproduction of the Y–u_2 curve, were obtained with $\lambda = 0$. Thus the single-liquid approximation appears to be inappropriate for our procedure.

Discussion

Handling a restricted range of Y data as a system of M nonlinear equations in N unknowns may give a reasonable estimation of $\chi_{23}°$ and of $g_T°$ and $\chi_T°$ (and thus of the initial slope of $g_T°$ to ϕ_3). This might be sufficient for instance, for a tentative calculation of a ternary isothermal demixing diagram for a polymer–solvent–nonsolvent system.[11]

The approximate calculation of g parameters as proposed in this paper only works when several requirements are fulfilled. First, g_{12} has to be known over the whole solvent composition range. Second, the solvents should not differ too much in quality: the assumption that $lg_{23}° - g_{13}°$ is negligibly small turned out to be rather crucial to our results for $\chi_{23}°$, $\chi_T°$, and $g_T°$. Third, the theory for the calculation of Y from $[\eta]$ should be adequate for the system in question and allow the calculation of thermodynamically right (and molecular weight dependent) Y values. Fourth, K_θ has to be known, and finally, Φ_0 has to be established separately for the studied system when the "universal" value of 2.5×10^{23} appears to be incompatible[16] with K_θ determined in several independent ways.

Thus we were not able to extract a consistent set of K_θ and Φ_0 values from the literature[16] for the system cellulose acetate–acetone–water. We therefore did not succeed in calculating g parameters for this system from $[\eta]$ data in accordance with g parameters determined from λ and A_2, as published elsewhere.[11]

An objection to our application of the NAG procedure E04FDF might be that the results depend slightly on initial guesses of parameters, even when the output of E04FDF is such as to indicate that the parameters calculated are real minima at the data set introduced. A more elaborate numerical procedure might give better results. We did not pursue this matter further.

A final objection that might be raised against our procedure has to do with the physical meaning of $g_T°$ and thus with our eq 1, i.e., with the extension by Pouchlý et al. of the Flory–Huggins expression for the free energy of mixing.[3,4] Horta and Fernández-Piérola argue that derivatives like $\partial g_T°/\partial u_1$ and $(\partial g_T/\partial \phi_3)°$, figuring in Y (eq 4) and in the preferential sorption parameter[3–6] λ, are empirical parameters lacking a clear physical meaning. Furthermore, according to these authors, including such derivatives in calculations (i.e., putting $g_T° \neq \chi_T°$) does not improve the simultaneous representation of Y and λ as functions of u_2 (this, however, is not in accordance with Chu and Munk's findings[5,6]). Horta and Fernández-Piérola therefore prefer the use of one adjustable parameter, with a physical meaning based on the Flory–Prigogine–Patterson theory:[9] the contact surface of the polymer molecule. Such a parameter, however, could be calculated easily with our procedure in the same way as we calculated $g_T°$ and $\chi_T°$.

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Athermal Exchange between Lithium Salts of High Molecular Weight Living Polymers and the Analogous Salts of Oligomers in Hydrocarbon Solvents

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In a paper published in *Macromolecules*,[1] Morton, Pett, and Fetters presented a proof of the dimeric nature of lithium salts of living polymers in hydrocarbon solvents based on the athermal exchange between the aggregates of high molecular weight salts, $(P_nM^-,Li^+)_n$, and analogous oligomeric salts, $(RM^-,Li^+)_n$. The aggregates are in a rapidly established dynamic equilibrium with minute fractions of lower aggregates; e.g., dimeric aggregates are in equilibrium with their monomeric polymers

$$(PM^-,Li^+)_2 \overset{K_1}{\rightleftharpoons} 2PM^-,Li^+$$

$$(RM^-,Li^+)_2 \overset{K_2}{\rightleftharpoons} 2RM^-,Li^+$$

The above reactions represent *homo*dimerizations; i.e., the dimers are formed by the association of *any* two monomeric species. Since the end groups responsible for the association are similar for the high molecular salt and the oligomeric salt, one expects $K_1 = K_2$, provided that the degree of polymerization of the oligomers is not too low, say 10. This indeed was assumed by the authors.

The rapid dissociation–association leads to the formation of *hetero*dimers when $(PM^-,Li^+)_2$ and $(RM^-,Li^+)_2$ are mixed together

$$(PM^-,Li^+)_2 + (RM^-,Li^+)_2 \overset{K_{ex}}{\rightleftharpoons} 2(PM^-,Li^+;RM^-,Li^+)$$

and their proportion in equilibrated mixtures could be determined by a viscometric technique. For concentrated solutions of high molecular weight polymers in the entanglement region, their viscosity, η, is proportional to power α of the weight-average molecular weight of the dissolved polymers; viz, $\eta \sim \bar{M}_w^\alpha$, with α being in the range 3.3–3.5. Hence, the viscosity of a solution of *uniform*, high molecular weight dimers decreases by a factor of $2^\alpha \approx 10$

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Table I[a]
Polymer-Lithium Association at 30 °C

2×10^3-$[(PM^-,Li^+)_2]$/M	2×10^3-$[(RM^-,Li^+)_2]$/M	N_w[b]	K_{ex}
Polyisoprenyllithium in *n*-Hexane			
1.1	6.8	1.34	0.85
1.0	4.6	1.40	0.90
2.5	5.3	1.53	1.1
Polystyryllithium in Benzene			
2.0	2.0	1.67	0.97
2.0	4.0	1.52	1.1

[a] From: Morton, M.; Pett, R. A.; Fetters, L. J. *Macromolecules* **1970**, *3*, 334. [b] The symbol N_w is the weight-average degree of association.

on destruction of their aggregation, arising, for example, through protonation. Similarly, the viscosity of such a solution decreases on addition of living dimeric oligomers since the athermal exchange yields the heterodimers, which behave like monomeric polymers in the viscosity measurements.

At a constant concentration of high molecular weight polymers, the addition of the oligomers insignificantly affects the weight of the solution but drastically reduces its viscosity. Denote by γ the ultimate weight fraction of the homodimers $(PM^-,Li^+)_2$ in an equilibrated mixture and by $1 - \gamma$ that of the formed heterodimers. The reduction of viscosity caused by the addition of oligomers is given then by $\{2/(1 + \gamma)\}^\alpha$. Since γ depends on the initial mole concentrations of $(PM^-,Li^+)_2$ and $(RM^-,Li^+)_2$, freely chosen by the experimenter, as well as on K_{ex}, the latter could be calculated from the experimentally determined decrease of viscosity resulting from the addition of the oligomeric salts to a solution of high molecular weight salts. The constancy of the thus-calculated K_{ex} would confirm then the dimeric nature of the investigated polymers.

In the Appendix of their paper,[1] Morton, Pett, and Fetters provide the following argument for the "theoretical" value of K_{ex}:

$$(PM^-,Li^+)_2 \overset{K_1}{\rightleftharpoons} 2PM^-,Li^+ \quad \text{(homodissociation)} \quad (1)$$

$$(RM^-,Li^+)_2 \overset{K_2}{\rightleftharpoons} 2RM^-,Li^+ \quad \text{(homodissociation)} \quad (2)$$

$$(PM^-,Li^+;RM^-,Li^+) \overset{K_3}{\rightleftharpoons} PM^-,Li^+ + RM^-,Li^+ \quad \text{(heterodissociation)} \quad (3)$$

and

$$K_{ex} = [(PM^-,Li^+;RM^-,Li^+)]^2/[(PM^-,Li^+)_2][(RM^-,Li^+)_2] = K_1K_2/K_3^2$$

Lack of appreciation of the difference between the homo- and heterodissociation led them to believe that $K_1 = K_2 = K_3$ and thence $K_{ex} = 1$. However, their experiments *distinguish* between $(PM^-,Li^+)_2$ and $(RM^-,Li^+)_2$ or $(PM^-,Li^+;RM^-,Li^+)$ and therefore $K_3 = {}^1/_2K_1 = {}^1/_2K_2$, leading to the correct value of $K_{ex} = 4$. In other words, the symmetry of homodissociation differs from that of heterodissociation.

The necessity for $K_{ex} = 4$ could be seen without even involving K_1, K_2, and K_3. It arises from the simple fact that two long polymers, say L, can be combined into a dimer in one way only; the same applies to two oligomers, say Ol, yielding $(Ol)_2$, whereas a heterodimer, (L,Ol), could be formed in two ways, by combining L with Ol or Ol with L. The result is general and applies in many branches of chemistry and physics. Nevertheless, when this note was sent to three referees for review referee I insisted that $K_{ex} = 1$, arguing that it is immaterial whether long, short, or mixed chains form a dimer and hence $K_1 = K_2 = K_3$. Moreover, this referee claimed that the equality $K_1 = K_2 = 2K_3$ carries with it a fundamental error in logic. That argument was refuted by referees II and III, one of whom stated "The value of 4 is introduced by symmetry, indeed, and does not indicate any mysterious molecular weight effect" while the other stated "$K_{ex} = 4$ is undoubtedly correct".

To verify their "theoretical" deduction, Morton, Pett, and Fetters[1] investigated two kinds of polymeric salts, namely, polyisoprenyllithium in *n*-hexane and polystyryllithium in benzene. Their experimental results were presented in Table I of their paper and are reproduced in Table I.

The following experimental data are used in the calculation of K_{ex}: (i) the composition α of the equilibrated solution, defined as α = (moles of high molecular weight polymers)/(moles of oligomers), these being given in the first two columns of Table I; (ii) the weight-average degree of association, N_w, of the equilibrated polymers, given in the third column of Table I and determined from the ratios of viscosities of the equilibrated solutions measured before and after destruction of the lithium salts.

Let a, b, and c denote the number of moles at equilibrium of homodimers, $(PM^-,Li^+)_2$ and $(RM^-,Li^+)_2$, and of heterodimers, $(PM^-,Li^+;RM^-,Li^+)$, respectively. Then

$$\alpha = (2a + c)/(2b + c)$$

while

$$N_w = (4a + c)/(2a + c)$$

leading to

$$K_{ex} = c^2/ab = 4\alpha(2 - N_w)^2/(N_w - 1)\{1 + (N_w - 2)\alpha\}$$

As readily verified for both systems, all five experiments led to the values of N_w's yielding on calculation the erroneous values of $K_{ex} \sim 1$ listed in the last column of Table I instead of the correct value of 4. It follows that the viscosity measurements were at fault, giving the wrong values of N_w. To put these findings in still a sharper perspective, let us calculate the flow times measured in a viscometer before and after the addition of the oligomers, basing the calculations first on $K_{ex} = 1$ and then on $K_{ex} = 4$.

Say the flow time of a solution of high molecular weight lithium salt before the addition of the oligomers is 1000 s (a typical value). Let the ratio of the initial concentrations of $(PM^-,Li^+)_2$ and $(RM^-,Li^+)_2$ be 1:1 (experiment 4 of Table I) and take $\alpha = 3.4$. Denoting the mole fraction of the heterodimers in an equilibrated mixture by x, one finds that

$$4x^2/(1 - x)^2 = K_{ex}$$

i.e., for $K_{ex} = 1$, $x = {}^1/_3$ and the weight fraction of the homodimers, γ, is ${}^2/_3$, while for $K_{ex} = 4$, the respective values are $x = {}^1/_2$ and $\gamma = {}^1/_2$. Hence, the flow time measured after addition of the oligomers would be 538 s for $K_{ex} = 1$, but only 376 s for $K_{ex} = 4$. Again, large differences of the flow times are found for other ratios of concentrations, e.g., for the ratio 1:4.6 (experiment 2 of Table I), respective calculated flow times are 283 s for $K_{ex} = 1$ but only 173 s for $K_{ex} = 4$. These calculations were checked by the referee and found to be correct.

The above errors in viscosity measurements are much too large to be unnoted. It is imperative to explain the source of such errors because similar causes could vitiate other findings of the authors and invalidate their claims, e.g., those reported in ref 1–6. Clarification of this issue is of utmost important since it could help to resolve the controversies created by various claims of the authors that

contradict the findings and conclusion of other workers reported in ref 7–10.

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Communications to the Editor

Hemitactic Polypropylene: An Example of a Novel Kind of Polymer Tacticity

Polypropylene, almost 30 years after its discovery, is still a central point in macromolecular stereochemistry. Many studies have been carried out recently by means of ^{13}C NMR spectroscopy to determine the configuration sequences in samples obtained by direct polymerization or after equilibration in the presence of epimerizing catalysts.[1-3] Methyl resonance has been found to be particularly sensitive to the stereochemical environment, and the microstructure of the polymer has been determined in terms of pentads and in some cases of heptads.

In this paper we wish to illustrate a new stereoisomer of polypropylene having a particular type of order and characterized by a ^{13}C NMR spectrum markedly different from those reported in the literature. The high-field region of the ^{13}C NMR spectrum of our sample, recorded at 137 °C in 1,2,4-trichlorobenzene at 50.3 MHz (Varian XL 200), is shown in Figure 1 and compared with that predicted for a purely atactic sample. The spectrum shows only the signals of seven of the ten pentads—pentads mrmr, mrmm, and rrmr are missing. Furthermore, the intensity of the signals centered on the mm triad is practically identical with that of the signals centered on the rr triad. The arrangement of the intensity of the signals can be expressed as follows, starting from the low-field signals: 3:2:1:4:0:0:3:2:1 as compared with the sequence 1:2:1:2:4:2:1:2:1 of a Bernoullian sample with m = 0.5. Peaks are very sharp and in some cases we find evidence of resolution at the heptad level, especially when the spectrum is run at room temperature. In the region of the spectrum between 45 and 47 ppm from Me_4Si, typical of methylene groups, the distribution of the signals is far narrower than in conventional atactic polymers: in particular, the low-field and high-field signals, due, respectively, to the hexads mrmrm, rrmrm, and rrmrr and rmrmr, rmrmm, and mmrmm, are not detectable. As a general rule, all the successions containing closed odd sequences of m or r dyads are missing.

An explanation of all these facts is forthcoming if we take into consideration the method of preparation of our polypropylene sample. This was obtained by reduction of poly(2-methylpentadiene), which, in turn, had been obtained by inclusion polymerization of the monomer in perhydrotriphenylene.[4] The structure of this high-melting, scarcely soluble product was found to be head-to-tail 1,4-trans-isotactic on the basis of IR, X-ray, and ^1H NMR spectra. In the polymer no defects of the 1,2- or 1,4-cis type was found; the degree of isotacticity has not yet been determined accurately because of the low solubility, but, as can be seen from the experiments described here, it can reasonably be expected to be very high. Reduction of the polymer with diimide produced in situ starting from tosylhydrazide[5,6] takes place slowly because of the heterogeneity of the system and of the degree of substitution on and around the double bond. By repeated treatments a polymer is obtained with a degree of unsaturation below 3–5% and free from aromatic impurities.

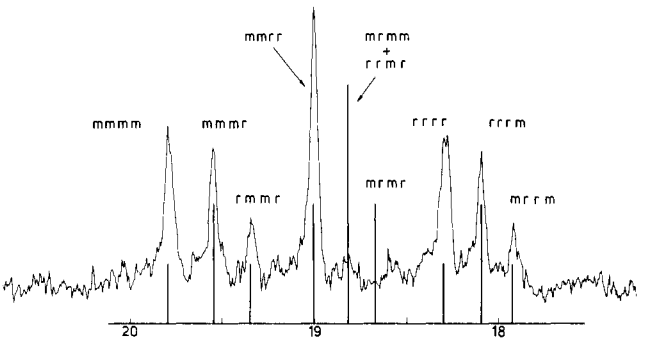
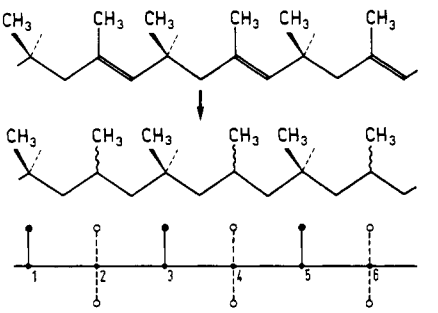


Figure 1. ^{13}C NMR spectrum of the methyl region of "hemitactic" polypropylene.

Scheme I



The structures of the unsaturated and of the saturated polymer are given in Scheme I. From a constitutional point of view the hydrogenated polymer must be considered as a head-to-tail polypropylene. As concerns the stereochemical point of view, it is necessary to make a distinction between the tertiary atoms of the odd series and those of the even series. If we assume the polymer to contain initially 100% isotactic dyads, atoms 1, 3, 5, etc. all have the same relative configuration because they reflect the regularity of the unsaturated polymer. The configuration of atoms 2, 4, 6, etc. is, on the other hand, determined at the moment of hydrogenation, which is largely nonspecific.

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