The Gaussian character of the conformation of the elastic chains has been verified with a high precision.

Further results related to experiments carried out on systems submitted to uniaxial deformation and on swollen networks will be reported in forthcoming publications.

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Crystalline Order in Copolymers of Ethylene and Propylene

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ABSTRACT: Copolymers of ethylene and propylene in which none of the propylene units are reversed have low levels of crystallinity over the entire range of composition. Molecular mechanics calculations indicated that the polyethylene-type planar-zigzag conformation and the polypropylene-type helical conformation would have similar energies in copolymers containing 33–55 mol % ethylene. Measurements by X-ray diffraction and differential scanning calorimetry showed that samples in this range contained both kinds of crystals. When a copolymer of propylene with 36 mol % ethylene was incorporated in a blend of isotactic polypropylene and low-density polyethylene, the polyethylene phase was more finely dispersed, and the interfacial adhesion and notched Izod impact strength were improved. These effects were attributed to the ability of the copolymer to cocrystallize with both homopolymers.

Introduction

Copolymers of ethylene and propylene involve a surprising number of structural variables. First, one is concerned with the fractions of the two monomer units. Then there is the question of their distribution in the polymer chains. A great deal of information about this can be obtained by carbon-13 NMR.[1-3] The propylene units may all add head-to-tail, or some of them may be reversed. Reversals are revealed by the presence of sequences of even numbers of methylene units between branch points. In copolymers made with vanadium-based catalysts, a significant fraction of the propylene units is reversed.[1,4] When a titanium-based catalyst is used, this does not occur at a detectable level.[2,4] Finally, one should consider the tacticity of any sequences of propylene units.

It is well-known that a certain number of methyl side groups can be accomodated in a polyethylene-type crystal through expansion of the unit cell along its *a* axis.[5-9] In this case, the conformation of the chain remains all-trans planar zigzag. On the other hand, in isotactic polypropylene, the conformation is a 3-fold tgtgtg helix, which serves to minimize the interactions between adjacent methyl groups. A copolymer having a low [E]/[P] ratio is equivalent to a polypropylene from which a few methyl groups have been removed. It would not be surprising to find that a polypropylene crystal could tolerate a certain number of defects of this type. However, at some point, the polyethylene-type conformation should become preferred. It is the purpose of this paper to examine the competition between the helical and planar conformations.

Polymer Modeling via Molecular Mechanics

We have addressed the problem outlined above by studying oligomers incorporating the principal features of interest in polypropylene and ethylene–propylene copolymers. (At this point, we are concerned with the energies of various conformations for isolated molecules in the gas phase. The effect of crystal packing will then be addressed experimentally through studies of the properties of copolymers.) Models were generated in various conformations which were then refined with the molecular mechanics program MM1.[10] This program incorporates the 1973 Allinger force field[11] and refines the starting coordinates, seeking the nearest minimum-energy state.

This methodology has been successfully applied to a wide variety of compounds, most notably hydrocarbons of

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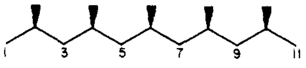
the type we consider here.[12]

The preferred helical structure of isotactic polypropylene is well understood in terms of avoidance of the g^+,g^- sequence in *n*-pentane-like segments.[13] For pentane itself we find a conformational energy of 2.85 kcal/mol for this form. Thus the driving force for helix formation is adequately accounted for.

Polypropylene. We have studied the isotactic polypropylene models represented by I. The helical form for

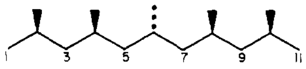


I

$n = 3$ may be represented by the dihedral angle sequence t,g^-,t,g^-,t,g^-,t,g^-, and this is the lowest energy conformer. Other conformational minima have been examined, and the following relative energies found: t,g^-,t,t,t,g^-,t,g^-, 2.0 kcal/mol; t,g^-,t,t,t,t,t,g^-, 4.1 kcal/mol; t,t,t,g^-,t,t,t,g^-, 3.5 kcal/mol; t,g^-,t,t,t,t,t,t, t,t,t,g^-,t,t,t,t, and t,t,t,t,t,g^-,t,t, ~6.0 kcal/mol. The all-trans form has a relative energy of ~8 kcal/mol. In summary, a single ...t,g^- ... to ...t,t... transition costs ~2 kcal/mol. The energetic cost of these transitions appears to be roughly additive. All of the energies given here are for 1 mol of the species shown. In general, each such conformational sequence in a longer chain would contribute a similar energy.

For a structure such as I, a reversed helix may also exist, designated as ...g^+,t,g^+,t..., with a corresponding manifold of states. A more interesting question is the cost of introducing a helix reversal in an isotactic sequence. We have modeled the transition ...$t,g^-,t,g^-,t,g^-,t,g^-,t,g^-$... to ...$g^+,t,g^+,t,t,g^-,t,g^-,t,g^-$... for a monomer model (I, $n = 7$). The energy change for this transition is only 0.6 kcal/mol. The noteworthy feature of the higher energy form is the change in axis direction for the reversed segment. For this reason, helix reversals are not expected to occur in a crystal lattice.

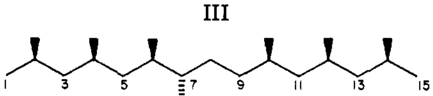
Atactic polypropylene was modeled using the related undecane II. The most stable conformer has the sequence



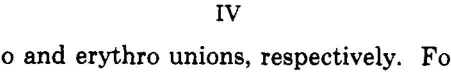
II

t,g^-,t,t,t,t,t,g^-. A g^- to t transition costs ~2 kcal/mol, consistent with the previous results. The destabilization of the helix due to the r,r dyad sequence is 4.0 kcal/mol. A more complete search was conducted, varying th dihedral angles about C5–C6 and C7–C8. Only the states t,g^+ (2.4 kcal/mol) and g^+,t (1.8 kcal/mol) are competitive with those indicated above. The destabilization caused by the r,r dyad sequence is local, indicating a change in the direction of the helix axis.

Finally, we examined the consequences of mer-unit reversal in between two isotactic polypropylene chain segments. The pentadecanes III and IV were chosen to model



III

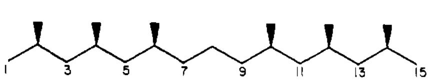


IV

the threo and erythro unions, respectively. For III the helical form was the preferred conformation, although other states were found within 1 kcal/mol. Thus the threo-coupled system will propagate the helix. We find for IV that the global minimum has the sequence $t,g^-,t,g^-,t,t,t,t,t,g^-,t,g^-$, the full helix being 3.5 kcal/mol higher in energy. Clearly, erythro coupling will disrupt the helix.

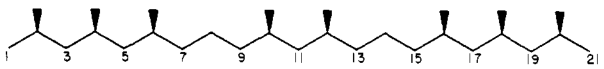
Ethylene–Propylene Copolymers. We have examined three aspects of the copolymer problem: the effect of isolated ethylene incorporation on helix propagation, the isolation of propylene dyads by ethylene incorporation, and the energetics of the planar-zigzag to helix transition in a 1:1 copolymer. We have limited our conformational searches for the models employed. Polypropylene segments are generally constrained to the helical form. The results in the previous section attest to the reasonableness of this restriction.

The pentadecane V was chosen as the model for incorporation of a single ethylene. The first search was based on the sequence $t,g^-,t,g^-,t^*,t^*,t,g^-,t,g^-$. The lowest energy form is ...t,t,t..., adopting a planar-zigzag arrangement in the vicinity of the ethylenic unit. The full helix ...g^-,t,g^-... is, however, only 0.9 kcal/mol higher in energy and should readily occur in the crystal lattice of polypropylene. There are, in fact, several states within ~1 kcal/mol of the lowest one. If the bonds to the unsubstituted central carbon are fixed as trans, the 2 kcal/mol penalty for uncoiling a helical segment still obtains.



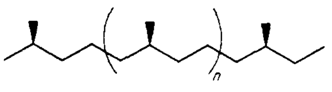
V

It was initially felt that isolation of the propylene dyad by insertion of two ethylene units might diminish the energetic cost for the t,g^- to g^-,g^- transition. Our results for VI suggest that this is not the case. All conformers incorporating a "*cis*-pentane" involving the pendant groups of the central dyad are at least 2 kcal/mol higher in energy than the preferred form. (Hence there is no "buttressing" effect in the pure polypropylene.) This latter form has both ethylenic units incorporated via t,g^-,g^- sequences. Again, the helical form is only 0.9 kcal/mol higher in energy. It should be noted that this cost has not increased over that for V. The lack of additivity was clarified by the study of the 1:1 copolymer model described below.



VI

The constancy of the "*cis*-pentane" effect in these studies led us to believe that a 1:1 alternating copolymer (isotactic) would be more stable in the planar-zigzag form. Surprisingly, calculations on VII($n = 4$) show the *helical* form to be preferred by 1.5 kcal/mol. We examined this in more detail by comparing results for VII($n = 0$) with calculations for *n*-octane (VIII). In VIII the planar-zigzag form is more stable by 1.4 kcal/mol, as expected. Introduction of the two methyl groups to form VII($n = 0$) makes the two forms essentially isoenergetic! This stabilization derives from van der Waals attraction between the pendant methyl group and the third methylene from the tertiary center. This interaction rationalizes the lower "*cis*-pentane" cost in the polymer models, as well as the nonadditivity previously noted for VI. This interaction occurs



VII

Table I
Polymerizations

sample	[E]/[P] feed ratio	temp, °C	yield, g	η_{inh},[a] dL/g	mol % ethylene by ^{13}C NMR
B	1/10	53-71	106	5.8	12.8
C	1/80	50-79	94	7.2	17.9
D	1/10	50-78	49	7.5	29.2
E	1/2.5	46-60	45	5.3	34.4
F	1/2.5	48-70	72	6.1	48.8
G[b]	1/1.3	−24 to −8	30	12.0	96

[a] Inherent viscosities were run at 135 °C at 0.05% in decalin containing 0.2% 4-methyl-2,6-diisobutylphenol. [b] Mitsui $TiCl_3$ on $MgCl_2$ type catalyst.[16]

for each repeat unit, leading to increasing stability for the helical form with increasing chain length.

Summary. We feel that these model studies permit the following conclusions regarding ethylene–propylene copolymers:

(1) Isolated ethylenic units may be incorporated into the helix at small cost. Interchain forces can readily compensate for this cost.

(2) As the [E]/[P] ratio increases, propagation of the helix will be dependent upon the randomness of the copolymer. Blocks of ethylene will hinder helix propagation, but randomness will facilitate it.

(3) Atacticity will induce local helix disruption, which may be overcome by interchain forces.

(4) Copolymers containing 50–70 mol % ethylene apparently can adopt the helical conformation with ease. In this range a chain might be induced to adopt the conformation of its neighbors to facilitate crystallization. Over a broad middle range of compositions, the energies of the planar and helical conformations are sufficiently close to permit crystallization in either form.

(5) Spectroscopic results for copolymers of this type[14] have been interpreted in terms of polypropylene blocks. These results suggest that this analysis is perhaps too restrictive.

Experimental Section

Synthesis of Copolymers. Copolymers of ethylene and propylene were made using neophylzirconium aluminate on alumina (NZA) as a catalyst.[15] A 1-L stainless steel autoclave equipped with a magnetic stirrer was charged with a slurry of 2 g of Al_2O_3 in 400 mL of cyclohexane under nitrogen. While stirring was maintained at 500 rpm, the autoclave was heated to 50 °C. The system was saturated with a predetermined mixture of ethylene and propylene, with a pressure relief valve set variously at 70–140 psi. A solution of 0.4 mmol of catalyst in 4 mL of toluene was then injected. Throughout the run, which lasted 1 h, ethylene and propylene were fed simultaneously through rotameters to maintain a fixed ratio. An effort was made to maintain a constant overflow rate through the pressure relief valve. In most of the experiments, the ethylene was doped with hydrogen to act as a chain-transfer agent and limit the molecular weight. The pressure of hydrogen was 25 psi in a 1-L storage cylinder containing 200 g of ethylene. Data for representative polymerizations are given in Table I.

Comonomer Sequences. The copolymer structure was examined by carbon-13 NMR spectroscopy using assignments taken from the literature.[1,3] The mole fraction of ethylene was computed from the ratio of methyls to total carbons and is reported in Table I. The number of PP sequences was computed from the concentration of $S_{\alpha\alpha}$ carbons, i.e., methylenes adjacent to two tertiary carbons. As shown in Figure 1, this quantity is close to the values for random copolymers for samples containing 18–49 mol % ethylene. At lower levels of ethylene, the measured number of $S_{\alpha\alpha}$ carbons was not consistent with any distribution of comonomer units. The reason for this is not known.

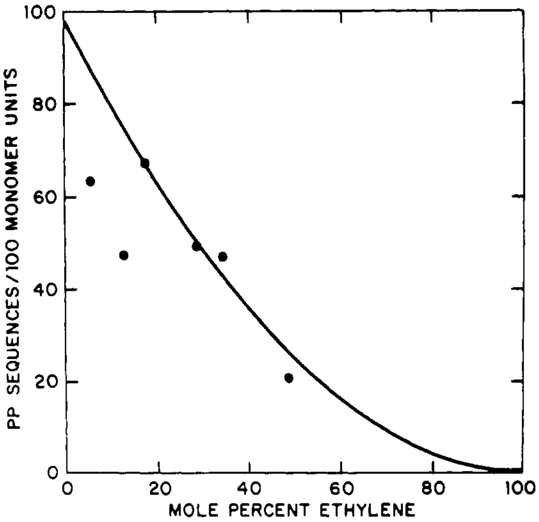


Figure 1. PP sequences in ethylene–propylene copolymers: line, calculated for random copolymers; points, carbon-13 NMR data.

There were no detectable sequences of even numbers of methylene units between tertiary carbons. This means that the NZA catalyst system does not cause any of the propylene units to be reversed. Other workers have shown that propylene reversals occur in ethylene–propylene copolymers made with vanadium-based catalysts[1,4] but not with titanium-based catalysts.[2,4]

Physical Properties. A series of copolymers was run on the Du Pont differential scanning calorimeter (DSC) at a heating rate of 20 °C/min and on the Du Pont dynamic mechanical analyzer (DMA). An X-ray diffractometer scan was obtained for each sample using Cu Kα radiation. All samples were molded in the same way. The possible effects of variations in thermal treatment were not explored. The key observations from these experiments are summarized in Table II.

Copolymers containing up to 29 mol % ethylene are dominated by the properties of isotactic polypropylene. This is reflected in a polypropylene-type X-ray diffraction pattern, a glass temperature seen at −15 to −20 °C by DSC and slightly higher temperatures by DMA, and a melting endotherm at 145–150 °C. From the heat of fusion, it was concluded that these samples contain 9–14% polypropylene-type crystallinity. The fact that the degree of crystallinity is the same for samples containing 6–18 mol % ethylene supports the conclusion that isolated ethylene units do not impede the formation of the polypropylene helix.

X-ray scans from copolymers containing 34 and 49 mol % ethylene exhibited crystalline peaks of both polyethylene and polypropylene. This is confirmed by the presence of two melting endotherms in the DSC scans at 121–122 and 147–148 °C, respectively. The height of the DMA peak for the β relaxation or glass transition in polypropylene is reduced. In a sample containing 96 mol % ethylene, X-ray and DSC data reflect only polyethylene-type crystals. These observations agree with the predictions from the molecular mechanics calculations that both the helical and planar-zigzag conformations are energetically accessible in copolymers containing 33–50 mol % ethylene.

A polyethylene-type γ relaxation was found in all copolymers containing at least 18 mol % ethylene. This relaxation is thought to reflect local motions of segments of at least four methylene units.[17]

Many of the copolymers have properties which have been reported for EP and EPDM rubbers. These include a T_g at −53 to −34 °C by DSC and DMA and an endotherm at 57–60 °C. The observation of two glass transitions in some samples suggests that there may be two amorphous phases.

Blends. In view of the evidence that certain copolymers of ethylene and propylene can adopt either a planar or a helical conformation, it was thought that these materials might be effective interfacial blending agents based on cocrystallization for mixtures of polyethylene and isotactic polypropylene.

Seventy parts of isotactic polypropylene (iPP) were blended with 30 parts of low-density polyethylene (LDPE). In a second blend, one third of the polyethylene was replaced with a copolymer of propylene and 36 mol % ethylene (EP). Scanning electron

Table II
Properties of Ethylene-Propylene Copolymers[a]

	sample						
	A	B	C	D	E	F	G
mol % ethylene by ^{13}C NMR	6.2	12.8	17.9	29.2	34.4	48.8	96
crystal type by X-ray diffraction	PP	PP	PP	PP	PE, (PP)	PE, PP	PE
DSC data							
T_g, °C	−15	−18	−39, −13	−46, −12	−52	−53	−45
T_m, °C [peaks]	58, 150	60, 145	59, 147	60, 145	57, 121, (147)	57, 122, (148)	(60), 132
ΔH_f, cal/g	6.3	6.5	7.0	4.5	9.1	10.5	23.0
% crystallinity	13	13	14	9	13	15–21	33
DMA data							
PE γ relaxation							
T, °C			−120	−101	−107	−109	
tan δ_{max}			s	0.040	0.057	0.049	
E/P β relaxation							
T, °C	−53	−34	−40	−36	−35	−35	
tan δ_{max}	0.053	0.118	0.06	0.067	0.2	0.2	
PP β relaxation							
T, °C	−19	−3	5	2	−13	−8	
tan δ_{max}	1.07	0.924	0.982	0.979	0.488	0.387	

[a] Parentheses indicate properties suggesting minor components. s = shoulder.

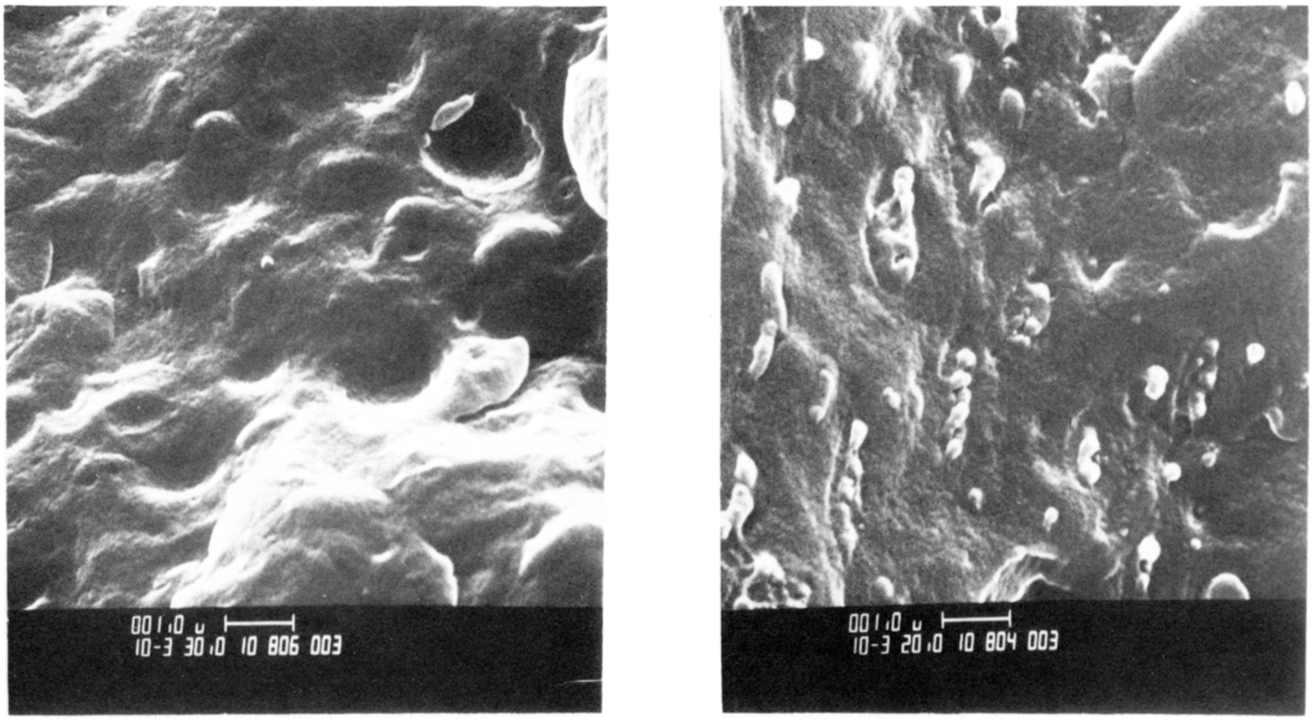


Figure 2. Scanning electron micrographs from liquid nitrogen fracture surfaces: (left) 70% iPP, 30% LDPE; (right) 70% iPP, 20% LDPE, 10% EP.

micrographs at 1000× from liquid nitrogen fracture surfaces are shown in Figure 2. In the binary blend, the dispersed polyethylene phase appears to consist of particles mostly 1–1.5 μm in diameter, with very poor adhesion to the polypropylene matrix. When the EP copolymer is incorporated, the particle size is reduced to 0.2–0.3 μm, and the adhesion to the matrix is markedly improved.

Associated with the changes in morphology are improvements in the notched Izod impact strength. Incorporating the EP copolymer in the polypropylene–polyethylene blend increased the impact strength from 0.55 to 2.23 (ft lb)/in. at room temperature and from 0.23 to 0.56 (ft lb)/in. at 0 °F.

It appears that the copolymer functions in two ways. As a surface-active agent, it lowers the interfacial free energy and makes the domains of the dispersed polyethylene phase smaller and more uniform. As an adhesive, it is anchored in both the polyethylene and polypropylene phases, presumably through cocrystallization.

Registry No. iPP, 25085-53-4; LDPE, 9002-88-4; EP, 9010-79-1.

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Simultaneous Static and Dynamic Light Scattering

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ABSTRACT: A modified photon correlation spectrometer that allows the simultaneous recording of dynamic and static light scattering is described. Details for a precise alignment are given. The utility of the equipment is demonstrated with four well-characterized polystyrene samples and two polystyrene latices. Excellent agreement with literature values is obtained for the linear, monodisperse polystyrene samples. The apparent diffusion coefficient, D_{app}, of the large latex particle (481 nm) exhibits no angular dependence up to an angle of 120°. At larger angles a drastic drop of D_{app} is observed, which is shown to be caused by 2% reflection of the primary beam at the solution-glass boundary and at the refractive index matching bath-air boundary. For the smaller latex (91 nm) the back-scattering has a somewhat different influence on D_{app}, which is almost negligible.

Introduction

Quasi-elastic or dynamic light scattering (QLS) has become in recent years a powerful technique for the characterization of polymers.[1] It favorably supplements the now long and well established static or frequency-integrated light scattering (ILS). Measurements of the weight-average molecular weight M_w, the mean square radius of gyration $\langle S^2\rangle_z$, the second virial coefficient A_2, the diffusion coefficient D_z or the corresponding hydrodynamic radius $\langle R_h^{-1}\rangle_z$, and the coefficient k_d of the concentration dependence of the diffusion coefficient have become routine, and in some cases where the molecules have dimensions on the order of the wavelength of the light, information on the shape and architecture of the molecules can be gathered from the angular distribution of the particle scattering factor $P_z(q)$ and the reduced first cumulant Γ/q^2 of the scattering intensity correlation function ($q = (4\pi/\lambda)\sin(\theta/2)$). Recently, it has been shown that a combination of data from both light scattering techniques produces two parameters of particular value.[2] These are the ratio

$$\rho = \langle S^2\rangle_z^{1/2}\langle R_h^{-1}\rangle_z \tag{1}$$

and the coefficient C in the general relationship

$$\Gamma/q^2 = D_z(1 + C\langle S^2\rangle_z q^2 - \ldots) \tag{2}$$

Both quantities are significant parameters for the extent of branching, chain rigidity, the existence of loops, and the molecular polydispersity. A third quantity, k_{f0}, is obtained by combination of several parameters in the following equations:[3-6]

$$k_f + k_d = 2A_2M_w + \bar{v}_2 \tag{3}$$

$$k_f = k_{f0}(N_A V_h/M_w^3) \tag{4}$$

$$V_h = (4\pi/3)R_h^3 \tag{5}$$

In these equations k_f is the coefficient of the concentration dependence of the frictional coefficient f, given by

$$f = f_0(1 + k_f c + \ldots) \tag{6}$$

The amplitude factor k_{f0} depends on the extent of coil interpenetration. In the theory of Pyun and Fixman,[4] $k_{f0} = 7.16$ for hard spheres and 2.23 for fully interpenetrating coils, i.e., the Θ state.

To date, the parameters from static and dynamic light scattering have been determined separately using different instruments, and in order to evaluate the quantity ρ, one had to use measurements from different laboratories. The combination of such data for $\langle S^2\rangle_z$ and $\langle R_h^{-1}\rangle_z$ for PMMA[7] and polystyrene (PS)[8] in Θ solvents led to ρ ratios that were 16-23% lower than predicted theoretically,[3] and similar deviations have been found for both polymers in a good solvent.[7,9] These deviations raise the question to what extent they may be caused by systematic errors introduced by different instruments and different authors. The relative errors in both techniques are fairly low (8% for $\langle S^2\rangle_z$ and 3% for D_z or $\langle R_h^{-1}\rangle_z$), and ρ should be measurable to an accuracy of ±5% or better, provided the systematic errors could be avoided. In principle, this should be possible since with most autocorrelators the ILS intensity is also recorded.

In general, the rule holds true that a real optimization can only be achieved with one instrument and for only one quantity of measurement. The two light scattering techniques are no exception to this. For instance, in QLS the choice of a rather small scattering volume (not larger than 0.2^3 mm^3) is imperative for a good signal-to-noise ratio,[10] whereas ILS can be more easily carried out with precision if the scattering volume is large. Nevertheless, we have adapted our photon correlation spectrometer to ILS, which has involved us in a series of painfully precise adjustments of our spectrometer. We are now able to perform combined static and dynamic light scattering measurements to a high precision with the same instrument at the same time, and this has promoted us into a position where we can measure the properties of slowly changeable systems, e.g., the coagulation of micelles or a change of properties with temperature.

Meanwhile the combined static and dynamic light scattering has become routine in our laboratory and a number of different systems have been studied, including

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