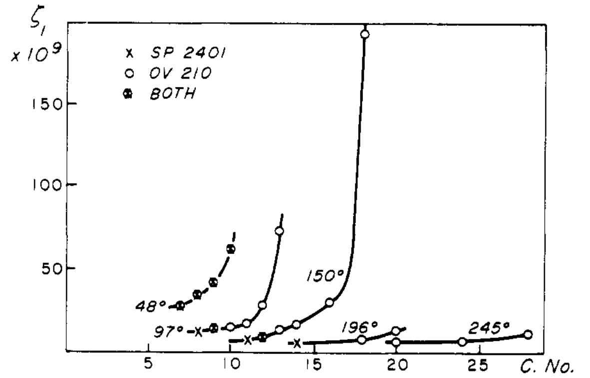

**Figure 6.** Translational friction coefficients of *n*-alkanes in trifluoropropylmethylsiloxane: ×, SP-2401, $\eta$ = 700 cs; o, OV210, $\eta$ = 10,000 cs.

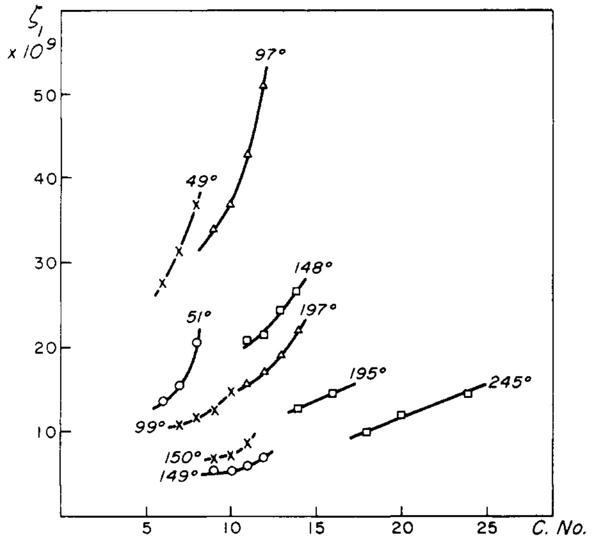

**Figure 7.** Translational friction coefficients of *n*-alkanes in phenylated silicones: o, DC550 = 25% phenyl; Δ, OV225 = 25% phenyl, 25% cyanopropyl; ×, DC710 = 50% phenyl; □, OV25 = 75% phenyl.

Table II
Diffusion Coefficients of Organic Compounds in Silicones ($\times 10^7$ cm$^2$/sec)

| | DC-550 | OV-210 | SP-2401 | DC-710 | OV-225 | OV-25 |
|---|---|---|---|---|---|---|
| *m*-Xylene at 98 ± 2°C | 65 | 52 | 49 | 44 | 17 | |
| *n*-Dodecane at 149 ± 1°C | 85 | 66 | 65 | 60 | 34 | 27 |

viscosity 700 and 10,000 cs had nearly identical diffusional properties (see Figure 6). The latter had a molecular weight of $2 \times 10^5$, but this represents only $1.3 \times 10^3$ monomer units making it comparable to the PDMS with $M = 10^5$ or $1.3 \times 10^3$ monomer units. In PDMS the molecular weight effects are apparent but not well developed at $M \simeq 10^5$. A marginal molecular weight dependence might therefore be expected in the higher fluoropolymer but is not apparent, perhaps because the dipole–dipole interactions between the chains hold it more firmly into a dense structure. It will be interesting to examine a fluoropolymer of still higher molecular weight.

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## References and Notes

(1) J. M. Kong and S. J. Hawkes, *J. Chromatogr. Sci.*, in press
(2) J. E. Tanner, *Macromolecules*, **4**, 748 (1971).
(3) I. Auerbach, S. D. Gehman, W. R. Miller, and W. C. Kuryla, *J. Polym. Sci.*, **28**, 129 (1958).
(4) H. Shih and P. J. Flory, *Macromolecules*, **5**, 758 (1972).
(5) A. J. Barlow, G. Harrison, J. Lamb, *Proc. R. Soc. London, Ser. A*, **282**, 228 (1964).
(6) General Electric Company, commercial literature.
(7) W. Millen, private communication.
(8) A. Weissler, *J. Am. Chem. Soc.*, **71**, 93 (1949).

# Communications to the Editor

## Model Compounds and $^{13}$C NMR Observation of Stereosequences of Polypropylene

The $^{13}$C NMR spectrum of methyl carbons of stereoirregular polypropylene shows at least nine clearly distinguishable resonance peaks. These have been attributed to the pentad configurational sequences, but complete agreement on the assignment of the spectrum, especially in the region of the *mr*-centered[3] pentads, is still lacking in the literature.[4–7]

We have observed the $^{13}$C NMR spectra of the 9-methyl group of 3(*S*),5(*R*),7(*RS*),9($R_aS$),11(*RS*),13(*R*),15(*S*)-heptamethylheptadecane (compound A) and of a mixture of A with 3(*S*),5(*S*),7(*RS*),9(*RS*),11(*RS*),13(*R*),15(*S*)-heptamethylheptadecane (compound B).[8] The 9-methyl group of the compounds was 93% enriched in $^{13}$C. The spectra are shown in Figure 1.[9]

The structures of the compounds are represented in Fischer projection in Figure 2. Actually, A and B are mixtures of several diastereoisomers. Consideration of the possible structures represented by each shows that the pentad configurational sequences around the 9-methyl of A are *mmmr, mmrm, rrmr,* and *rrrm,* while those in B are *mmmm, rmmr, mmrr, mrmr, mrrm,* and *rrrr.* Although the racemic carbons of A and B are not exactly in a 50:50 ratio owing to the method of preparation, they are nearly so; the populations of the configurational sequences in A are therefore approximately 1:1:1:1 and those in B are 1:1:2:2:1:1.

Nine chemical shifts are observed in the spectra of Figure 1, and these agree with those found, under the same conditions, in the methyl spectra of polypropylene[6] (see Table I). This observation establishes the validity of compounds A and B as models for the pentad configurational sequences in polypropylene.

A unique assignment of the pentad stereochemical shifts can be achieved by comparing the spectra of A and B (chemical shifts and relative intensities) with those of the

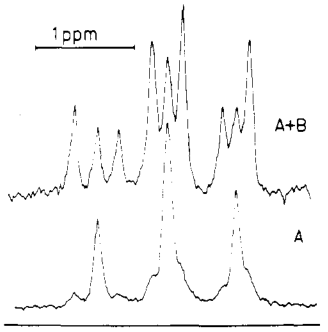

**Figure 1.** Proton decoupled 22.63 MHz $^{13}$C spectra of the 9-methyl carbon (93% enriched in $^{13}$C) of (bottom) compound A; (top) a 1:1 mixture of compound A and compound B.

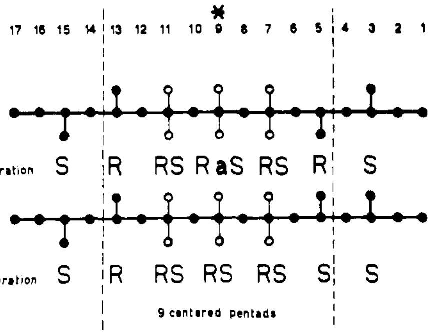

**Figure 2.** Schematic represtation of the Fischer projections of compounds A and B. The enriched 9-methyl carbon is marked by an asterisk. The pentad sequences around the 9-methyl carbon are represented by the vertical dashed lines (configurational differences at C-3 and C-15 are not discriminated).

highly isotactic and the highly syndiotactic polypropylenes already published[6] and by assuming that the methyl pentad stereochemical shifts are grouped according to the central triad sequences *mm*, *mr*, and *rr*, which appear with increasing shielding in this order.[11] By doing so and by considering the diastereoisomers present in A and B and recognizing also that in highly isotactic polypropylene,[6] *mrmr* cannot appear at $21.0_1$, one can easily convince oneself of the following assignments:

| | | |
|---|---|---|
| *mm* | *mmmm* | $21.7_8$ |
| | *mmmr* | $21.5_5$ |
| | *rmmr* | $21.3_3$ |
| *mr* | *mmrr* | $21.0_1$ |
| | *mrmm* and *rmrr* | $20.8_5$ |
| | *mrmr* | $20.7_1$ |
| *rr* | *rrrr* | $20.3_1$ |
| | *rrrm* | $20.1_7$ |
| | *mrrm* | $20.0_4$ |

Other resonances observed in the methyl region of atactic and syndiotactic polypropylene, and particularly a peak more shielded than that of *mrrm* in the spectrum of isotactic polypropylene,[6] are most probably to be attributed to the presence of irregularly arranged units, i.e., head-to-head and tail-to-tail. Attempts are being made to test this hypothesis by model compounds. Although the sum rules are fairly well obeyed, deviations here may also be attributed to the same cause.

**Table I**
**Stereochemical Shifts[10] Observed in Polypropylene and in A and B for the Central Methyl Carbon**

| Polypropylene | Compd A | Compd B | Approximate relative intensity A | Approximate relative intensity B |
|---|---|---|---|---|
| $21.8_2$ | | $21.7_8$ | | 1 |
| $21.5_8$ | $21.5_5$ | | 1 | |
| $21.3_8$ | | $21.3_3$ | | 1 |
| $21.0_6$ | | $21.0_1$ | | 2 |
| $20.8_5$ | $20.8_5$ | | 2 | |
| $20.7_0$ | | $20.7_1$ | | 2 |
| $20.3_2$ | | $20.3_1$ | | 1 |
| $20.2_0$ | $20.1_7$ | | 1 | |
| $20.0_7$ | | $20.0_4$ | | 1 |

The mechanisms of steric control that have already been established by proton NMR analysis of isotactic and syndiotactic polymers of propylene[12] and by $^{13}$C NMR analysis of ethylene–propylene copolymers[12–14] are in agreement with the present assignment of steric pentads, although the values recently attributed[15] to syndiotactic steric control forces must necessarily be revised.

**Synthesis of A and B.** A was prepared by methylation of 3(*S*),5(*R*),7(*RS*),11(*RS*),13(*R*),15(*S*)-hexamethylheptadecan-9-one (I) with $^{13}CH_3Li$ followed by catalytic C–O hydrogenolysis of the resulting carbinol. I was prepared starting from 2(*RS*),4(*R*),6(*S*)-trimethyloctanoic acid[16] via the following steps: 2(*RS*),4(*R*),6(*S*)-trimethyloctanoic acid → 2(*RS*),4(*S*),6(*S*)-trimethyloctyllithium (II) → lithium 3(*RS*),5(*R*),7(*S*)-trimethylnonanoate (III). The reaction of II and III yields I. B was prepared in an entirely analogous manner. The structures of A and B were checked by mass spectrometry.

A more detailed account of the synthesis and characterization of A and B will be published in subsequent papers.

It should be noted that concordant $^{13}$C chemical shift assignments have been reported in a preliminary fashion by Stehling and Knox employing an entirely different approach.[17]

## References and Notes

(1) Istituto di Chimica delle Macromolecole del CNR.
(2) Bell Laboratories.
(3) The stereochemical notation is that of H. L. Frisch, C. L. Mallows, and F. A. Bovey, *J. Chem. Phys.*, **45**, 1565 (1966).
(4) L. F. Johnson, *Anal. Chem.*, **43**, 28A (1971).
(5) Y. Inoue, A. Nishioka, and R. Chûjô, *Makromol. Chem.*, **152**, 15 (1972).
(6) A. Zambelli, D. E. Dorman, A. I. R. Brewster, and F. A. Bovey, *Macromolecules*, **6**, 925 (1973).
(7) J. C. Randall, *J. Polym. Sci., Polym. Phys. Ed.*, **12**, 703 (1974).
(8) The notation for the asymmetric carbons is that of R. S. Cahn, C. K. Ingold, and V. Prelog, *Angew. Chem., Int. Ed. Engl.*, **5**, 385 (1966); *a* signifies an achiral group.
(9) The spectra were obtained in 1,2,4-trichlorobenzene solution at 410°K using hexamethyldisiloxane (HMDS) as internal reference; a Bruker HX-90 spectrometer, operating at 22.63 MHz for carbon, was employed.
(10) The chemical shifts are expressed on the TMS scale, i.e., as ppm downfield relative to the internal standard (HMDS) with a correction of $+2.0_0$ ppm. They can be compared with the chemical shifts of polypropylene published in ref 6 by subtracting them from $193.5_5$.
(11) See, for instance, F. A. Bovey, "High Resolution NMR of Macromolecules", Academic Press, New York, N.Y., 1972, and references therein.
(12) A. Zambelli in "NMR Basic Principles and Progress", P. Diehl, E. Fluck, and K. Kosfeld, Ed., Springer-Verlag, Berlin, 1971, pp 101–108.
(13) A. Zambelli, G. Gatti, C. Sacchi, W. O. Crain, Jr., and J. D. Roberts, *Macromolecules*, **4**, 475 (1971).
(14) A. Zambelli and C. Tosi, *Adv. Polym. Sci.*, **15**, 31 (1974).

(15) A. Zambelli, C. Wolfsgruber, G. Zannoni, and F. A. Bovey, *Macromolecules*, **7**, 750 (1974).
(16) G. Odham, *Ark. Kemi*, **26**, 367 (1967).
(17) F. C. Stehling and J. R. Knox, *Macromolecules*, *8*, 595 (1975), ref. 30.

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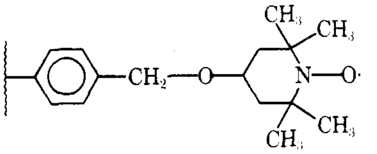
## Motion of Molecules within Solvent Channels of Polystyrene Matrices[1]

Polystyrene matrices show considerable promise as support material for transition-metal catalysts, photochemical sensitizers, organic substrates, and organic reagents.[2] At present, the precise physical and chemical nature of molecules covalently bound to polystyrene resins remains poorly defined. In addition, it is not clear how molecules contained within the solvent channels differ from those residing in the liquid phase outside the lattice. We have recently applied the spin-labeling technique to this problem and have demonstrated that the degree of swelling of polystyrene resins, as determined by the swelling solvent and cross-link density, has a substantial influence on the mobility of a nitroxide covalently attached to the resin.[3,4]

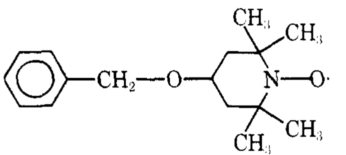
We now wish to report data which establish (1) the degree of swelling of cross-linked polystyrene beads (200–400 mesh) in benzene has a significant influence on the rotational motion of a nitroxide *imbibed* in the solvent channels of the polymer and (2) the magnitude of the effect is nearly equivalent to that observed for the same spin label incorporated into the polymer backbone.

The nitroxide 2,2,6,6-tetramethyl-4-piperidinol-1-oxyl (1) was covalently attached to cross-linked polystyrene yielding 2.[5] The benzyl ether 3 of nitroxide 1 was prepared using procedures similar to that described previously.[7] Benzene solutions of 3 were imbibed into unfunctionalized polystyrene resins; excess solution was then removed by rapid suction filtration. Rotational correlation times, $\tau$, were calculated from observed room-temperature electron paramagnetic resonance (EPR) spectra.[8,9] The degree of swelling values, $q$ (swelled volume/dry volume), was determined from the measured density of the dry resin and the weight of the imbibed benzene.[10]



nitroxide polystyrene
(<0.02% ring substitution)

2



3

Table I
Motion Within Solvent Channels of Polystyrene Matrices[a,f]

| Resin[5] | **2**[b] $10^{10}$ $\tau$, sec | **3**[c] $10^{10}$ $\tau$, sec | $q$ | $\eta$"internal", cP |
|---|---|---|---|---|
| | | 0.19[d] | | 0.6[e] |
| S-X1 | 2.9 | 0.22 | 5.4 | 0.7 |
| S-X2 | 3.1 | 0.31 | 3.7 | 1.0 |
| S-X4 | 5.5 | 0.49 | 2.8 | 1.5 |
| S-X8 | 15.0 | 1.3 | 2.0 | 4.1 |
| S-X12 | 17.0 | 1.9 | 1.9 | 6.0 |

[a] Rotational correlation times, $\tau$, are accurate to ±10%; degree of swelling values, $q$ (swelled volume/dry volume), are accurate to ±5%. [b] Nitroxide 1 covalently bound to chloromethylated supports which were swelled with benzene at room temperature. [c] Benzene solutions of 3 ($1.22 \pm 10^{-4}$ *M*) imbibed in unfunctionalized polystyrene resins. [d] Benzene solution of 3 in the absence of polystyrene. [e] Viscosity of benzene at 25°. [f] NOTE: The extent of chloro methylation for S-X1, S-X2, S-X4, S-X8, and S-X12 was 0.75, 1.0, 0.90, 0.80, and 0.75 mmol of chlorine/g of resin as determined by established procedures; J. M. Stewart and J. D. Young, "Solid Phase Peptide Synthesis", W. H. Freeman, San Francisco, Calif., 1969, p 55.

In order to ensure the absence of any specific binding of 3 to cross-linked polystyrene, we measured the nitroxide concentration in the liquid phase above one of the swelled resins. After swelling 0.35 g of Bio-Rad S-X2 with 2.5 ml of a benzene solution of 3 ($1.22 \times 10^{-4}$ *M*) for 24 hr, analysis of the external liquid phase indicated a slight *increase* in concentration of the label ($1.31 \times 10^{-4}$ *M*).[11] Based on the external concentration and degree of swelling of the resin, the calculated concentration of the nitroxide in the solvent channels was $1.08 \times 10^{-4}$ *M*. These results show that 3 prefers to reside outside the lattice.

Data obtained for a benzene solution of 3 imbibed in S-X1, S-X2, S-X4, S-X8, and S-X12, along with data for the corresponding benzene-swelled nitroxide polymers, are presented in Table I. Examination of the observed rotational correlation times reveals two important facts. First, the imbibed nitroxide has approximately ten times more motional freedom than the same label incorporated into a resin having the identical cross-link density. Second, both the imbibed and the "immobilized" labels have correlation times that span almost one order of magnitude for the range of swelling investigated. It is evident from the results cited here that the degree of swelling of the polystyrene matrix in benzene, as defined by the cross-link density, influences not only the mobility of bound molecules, but also the motion of molecules located within the solvent channels. In order to obtain a crude estimate of the "internal viscosity" of the various benzene-swelled resins, we have used the relationship: $\tau \simeq \eta/T$, where $\eta$ is the macroscopic solution viscosity and $T$ is the temperature.[12,13] At constant temperature, a change in $\tau$ corresponds to a proportional change in $\eta$. Based upon the measured values of $\tau$ and $\eta$ for 3 dissolved in benzene and the values of $\tau$ for 3 imbibed in the various supports at 25°, $\eta_{\text{"internal"}}$ values have been obtained and are included in Table I.

## References and Notes

(1) Supported by the Research Corporation, the donors of the Petroleum Research Fund, administered by the American Chemical Society, and the Marquette University Committee on Research.

(2) For recent reviews, see: C. G. Overberger and K. N. Sannes, *Angew. Chem., Int. Ed., Engl.*, **13**, 99 (1974); C. C. Leznoff, *Chem. Soc. Rev.*, **3**, 65 (1974).
(3) S. L. Regen, *J. Am. Chem. Soc.*, **96**, 5275 (1974); S. L. Regen, *ibid.*, **97**, 3108 (1975).
(4) For a related spin label investigation, see: Z. Veksli and W. Miller, *Macromolecules*, **8**, 248 (1975).
(5) Commercially available resins (S-X1, S-X2, S-X4, S-X8, and S-X12, Bio-Rad Laboratories) were chloromethylated[6] and the spin label was then attached using procedures previously described.[3] The number following the letter, X, indicates the percent of divinylbenzene incorporated into the polymer beads. Although we have found that this displacement reaction proceeds quantitatively for much higher percent