Table I

M_{calcd}	$\overline{M}_n$(VPO)	$\overline{M}_w/\overline{M}_n$	No. OH/chain
3.100	3.200	1.10	0.97
5.060	5.000	1.12	1.04
9.100	8.500	1.16	1.08

the propagation takes place and a living monodisperse PDMS is obtained.

$$\text{R-[Si (CH}_3)_2\text{-O]}_3\text{-Li} + (n-1)\text{D}_3 \xrightarrow[\text{solvent}]{\text{polar}} \text{R}\!+\!\text{Si (CH}_3)_2\text{-O]}_{3n} - \text{Li}$$

Thus, it was necessary to prepare a solution of the lithioacetal I in a nonpolar solvent. Unfortunately, the synthesis of I in hexane was unsuccessful and its solubility in such a nonpolar solvent was even claimed doubtful.[8] In fact, the lithioacetal I is only formed in polar medium, but a simple solvent exchange allows it to be obtained in benzene or toluene solution.

Then, by adding this benzene solution of I to D_3 in the same solvent, the lithium silanolate II (where R is an acetal group) is obtained. Once the initiation step has occurred, THF is added to the reaction medium and an acetal PDMS with a low polydispersity is formed and finally hydrolyzed into the expected hydroxyl PDMS. Table I summarizes the values of molecular weight, polydispersity index ($\overline{M}_w/\overline{M}_n$), and hydroxyl functionality for different functionally terminated PDMS.

The molecular weights, calculated on the basis of the monomer over catalyst molar ratios, are in excellent agreement with the observed values, while the polydispersity is now satisfying, 1.13 ± 0.03. These results confirm the living character of D_3 anionic polymerization as well as the similar values of the initiation and propagation rate constants. The functionality observed is as good as that mentioned by Schulz[8] in the case of a hydroxyl polybutadiene.

The coupling of living acetal PDMS with $(CH_3)_2SiCl_2$ followed by the hydrolysis of the acetal end groups leads to α–ω dihydroxyl PDMS.

Moreover, thanks to the solubility of the lithioacetal I in benzene, it is also now possible to synthesize hydroxyl polybutadiene with a high 1–4 microstructure.

Conclusions

Lithioalkylacetal derivatives in benzene solution are excellent initiators of D_3 polymerization. They offer an attractive route to the synthesis of ω-hydroxyalkyl polydimethylsiloxanes, $CH_3\text{–}[Si(CH_3)_2\text{–}O]_n\text{–}Si(CH_3)_2\text{–}(CH_2)_6\text{–}OH$ where $n \geq 3$; the coupling of the corresponding living chains leads to dihydroxyl macromolecules. The absence of any Si–O–C bond as well as the distance between the hydroxyl group and the first silicium atom (six carbons) ensure the remarkable hydrolytic stability of such telechelic polymers. Their polydispersity is reduced and their functionality quasi-ideal.

Acknowledgment. P.L. is also indebted to I.R.S.I.A. for a fellowship.

References and Notes

(1) S. C. Wells, *J. Elastoplast.*, **5,** 102 (1973).
(2) N. F. Novikova, V. P. Mileshkevich, A. V. Karlin, and F. B. Novoselok, Patent No. 239560 (1969).
(3) T. L. Magila and D. G. Legrand, *Polym. Eng. Sci.*, **10,** 349 (1970).
(4) D. C. Allport and W. H. Janes, "Block Copolymers", Applied Science Publishers LTD, London, 1973.
(5) K. D. Steffen, *Angew. Makromol. Chem.*, **24,** 1, 21 (1972).
(6) G. Greber, *J. Prakt. Chem.*, **313,** 461 (1971).
(7) K. Kojima, C. R. Gore, and C. S. Marvel, *J. Polym. Sci., Part A-1,* **4,** 2325 (1966).
(8) D. N. Schulz, A. F. Halasa, and A. E. Oberster, *J. Polym. Sci., Polym. Chem. Ed.*, **12,** 153 (1974).
(9) C. L. Ogg, W. L. Porter, and C. O. Willis, *Ind. Eng. Chem., Anal. Ed.*, **17,** 394 (1945).
(10) D. M. French, M. S. Chang, and A. S. Tompa, *J. Appl. Polym. Sci.*, **16,** 1615 (1972).
(11) W. A. Fessler and P. C. Juliano, *Ind. Eng. Chem., Prod. Res. Dev.*, **11,** 407 (1972).

Mesomorphic Order in Polymers with Side Groups Containing Elements of Mesogenic Structure

ALEXANDRE BLUMSTEIN

Polymer Program, Department of Chemistry, University of Lowell, Lowell, Massachusetts 01854.

Received February 9, 1977

Recent industrial developments in the field of high modulus fibers have generated a lively interest in polymers with liquid crystalline organization. Such polymers can be roughly divided into three categories: polymers in which the mesogenic element of structure is contained in the backbone of the macromolecule, polymers in which such elements are in the side group, and block and graft copolymers.

The correlation between molecular structure and nature of the liquid crystalline order has been a subject of intensive study in the case of block and graft copolymers.[1] However, such correlations have been little discussed for the first two categories of polymers mentioned above. The object of this note is to discuss such correlations for polymers in which the side groups contain elements of mesogenic structure. This discussion will be based on existing literature data.

It has been pointed out on several occasions[2–5] that the molecular organization of a mesomorphic monomer can be "locked in" if rapid polymerization were accompanied by extensive cross-linking of the polymer. In such cases the molecular organization prevailing within the mesophase of the monomer was found preserved in the polymeric network down to the minute detail of textural disclinations.[5] The situation is, however, entirely different in the absence of cross-linking at lower polymerization rates. Under such circumstances relaxation occurs and this often leads to phase separation and formation of an amorphous polymer. In some cases a directional (nematic) or layered (smectic) order is developed in the polymer. Rapid precipitation from dilute solution in good solvents of such ordered polymers leads invariably to an amorphous polymer, whereas skillful annealing, swelling, and casting bring back the mesomorphic order.[6–8] This order is not necessarily identical with the order of the initial monomeric mesophase.

A sizable body of information concerning the molecular organization of polymers derived from mesogenic monomers has recently emerged. Statements found in the literature are often confusing and not always reliable. A critical albeit qualitative discussion of well-established data appears to be justified at this point in providing some understanding of correlation between the structure of the mesogenic monomer and the nature of the order in the polymer.

A compendium of monomers and polymers for which the nature of molecular and segmental order has been reliably established by x-ray diffraction is given in Table I. As one can easily see from this table, the majority of polymers assume layered arrangements. In most cases bilayers of macromolecules are formed in which the "mesomorphic" side group is oriented at an angle to the plane of the stratum containing the convoluted backbone. The side group may or may not be arranged into a regular array.

Table I
Organization of Mesomorphic Monomers and Their Polymers

	Monomer		Polymer[a]			
	Molecular structure	Transition °C[b]	d, Å	D, Å	Organization	Ref
1.	$CH_2{=}CHPhN{=}CHPhC{\equiv}N$	K 113 N 140.5 I		4.9	Nematic	9
2.	$CH_2{=}CHPhN{=}CHPhCH{=}NPhCH{=}CH_2$	K 180 N polymer		5.1	Nematic	7
3.	$CH_2{=}CHCOOPhCH{=}N{-}N{=}CHPhOO$-$CCH{=}CH_2$	K 140 N polymer		5.3	Nematic	7
4.	$CH_2{=}CHPhN{=}CHPhOC_4H_9$	K 88.3 N 120.6 I	26 (b, i)	5.0	Intermediate $l \sim 19$ Å	6
5.	$CH_2{=}CHPhN{=}CHPhOC_6H_{13}$	K 94.5 S 97.5 N 116 I	28.5 (b, i)	5.0	Intermediate $l \sim 22$ Å	
6.	$CH\ {=}CHCOOC_{27}H_{45}$	K 118.7 I 127 (78 C)	33.4 (b, i)	6.4	Intermediate $l \sim 18$ Å	13
7.	$CH_2{=}CHCOOPhCH{=}NPhOC_2H_5$	K 78 N 136 I	32 (s, i)	4.9	Smectic $l \sim 18$ Å	11
8.	$CH_2{=}CHCOOPhCH{=}NPhN{=}CHPh$-$OOCCH{=}CH_2$	K 180 S polymer	22.2 (s, i)	5.0	Smectic $l \sim 22$ Å	7
9.	$CH_2{=}CHCOOPhPh$	K 65 I	23.2 (s, i)	5.2	Smectic $l \sim 11$ Å	12
10.	$CH_2{=}C(CH_3)COOC_{27}H_{45}$	K 109 I (103 C 85 K)	36.5 (s, i)	6.3	Smectic $l \sim 18$ Å	13
11.	$CH_2{=}CHCOOPhCOOC_{27}H_{45}$	K 128 C polymer	45.2 (s, i)	6.1	Smectic $l \sim 23$ Å	13
12.	$CH_2{=}CHCOOPhCOOH$	K 201 I	17.7 (vs, i)	4.7; 5.1	(Form II) $l \sim 11$ Å	8
13.	$CH_2{=}C(CH_3)COOPhCOOH$	K 182 I	19 (vs, i)	4.4	Smectic (C) $l \sim 11$ Å	6
14.	$CH_2{=}C(CH_3)COOPhCH{=}NPhCOOH$	K_1 182 K_2 201 S 205 N polymer	32 (s, i)	5.1	Smectic $l \sim 16.5$ Å	15

[a] Structural information: d = low-angle spacing; D = wide-angle spacing; vs = very sharp; b = broad; i = intense; l = approximate length of the side group (from molecular models). [b] Transition temperatures: I = isotropic; N = nematic; C = cholesteric; K = crystal; ( ) = monotropic transition; polymer = polymerization ensues.

From a phenomenological point of view one can qualitatively explain these effects by extending to the case of polymers some simple structural considerations initially developed by Gray for low molecular weight thermotropic liquid crystals.[14] Nematic phases are as a rule obtained through strong terminal and weak lateral interactions between molecules. Smectic phases are the result of weak terminal and stronger lateral attraction forces. Thus, one can state very schematically that dipoles operating across the long molecular axes (transverse dipoles) enhance smectogenic tendencies, while dipoles operating along these axes weaken these tendencies through mutual electrostatic repulsion. One should, however, beware of oversimplification and keep in mind that the precise part of a given dipole in the establishment of the mesophase depends on the overall balance of terminal to lateral interactions. For example, a terminal dipole acting at an angle can have a nematogenic effect by strengthening the terminal attraction between molecules. Removed from the end of the molecule the same dipole will strengthen the lateral attractions. This is the pattern of behavior of many homologous series in which lower members display nematic behavior whereas the higher members (long paraffinic chains) are smectogenic. If a structural element weakens the cohesion of molecules in the smectic layers, a nematic or isotropic phase results. Thus, branching weakens lateral cohesion and also weakens the smectogenic tendencies.

These considerations are still qualitatively valid in the case of polymers in which the mesomorphic side groups are placed in the vicinity of each other by their attachment to the backbone of the macromolecule.

It is apparent from Table I that the presence of two strong transversal dipoles (carboxy group) leads in the overwhelming majority of cases to polymers with a well-defined lamellar (smectic) organization. Acrylic and diacrylic derivatives are good examples of this tendency. Polymers prepared from acrylic or methacrylic esters of benzoic acids give well defined smectic arrangements.[6,8] Conversely, the absence of strong transversal dipoles and the presence of one or several strong longitudinal dipoles in a rigid and polarizable side group will decrease the tendency of the polymer to organize into well-defined layered arrangements, possibly by pushing the macromolecular backbone out of the confining planes. Poly[*N*-(*p*-cyanobenzylidene)-*p*-aminostyrene] and poly[*p*-phenylenebis(*N*-methylene-*p*-aminostyrene)] are examples of such exclusively nematic structures (monomers 1 and 2).

In all cases, the presence in the side group of a long linear paraffinic chain or a cholesterol moiety increases the tendency to form layered structures.

Some polymers given in Table I develop arrangements of side groups intermediate between a well-defined lamellar organization and a nematic organization. Monomers 4, 5, and 6 give polymers characterized by such an intermediate structure. The x-ray patterns of this group of polymers have in common a rather broad but intense low-angle reflection and a diffuse ring at 4–5 Å. This is compatible with a more fluid layered structure of side groups and can perhaps be considered as a special case of nematic arrangements of higher order. It is possible to see from the table that the corresponding monomers have a structure intermediate between that of smectic and exclusively nematic monomers. For example, the replacement of the strong longitudinal terminal $C{\equiv}N$ dipole in monomer 1 by the weak, transverse dipole of an alkoxy group in monomer 4 produces a polymer with such an intermediate structure. Similarly, the replacement of one or more transverse dipoles (carboxy group) by a longitudinal dipole may impair the well-defined smectic organization in the polymer.

Di(*N*-*p*-acryloyloxybenzylidene)hydrazine (monomer No. 3) gives a polymer with a nematic organization of side groups in spite of two strong transverse dipoles. This apparent discrepancy can be rationalized: the relatively free rotation around the $=N{-}N=$hydrazine bond unsettles the rigidity of the side group. This point was confirmed experimentally by x-ray measurements of the average distance D between side groups. This distance was found to be substantially larger in polymer 3 than for other polymers with a Schiff-base structure (see Table I).

This last example shows the danger of predicting the nature of the order in polymers with mesomorphic side groups from qualitative structural considerations. The combined influence of geometry, polarizability of structural elements, and distribution of polar interactions in the side group on the balance of lateral terminal interactions is often difficult to estimate. Structural data available to date support the view that the ordering of side groups in polymers with side group structure related to mesogenic behavior is subjected to laws similar to those governing the mesophase formation in low molecular weight thermotropic liquid crystals.

Acknowledgment. The author wishes to acknowledge the support of the National Science Foundation under Grant DMR75-17397.

References and Notes

(1) A Skoulios, *Adv. Liq. Cryst.*, **1**, 169 (1975).

(2) J. Herz, F. Reiss-Husson, P. Rempp, and V. Luzzati, *J. Polym. Sci., Part C*, 1275 (1963).

(3) L. Liebert and L. Strzelecki, *Bull. Soc. Chim. Fr.*, 603 (1973).

(4) L. Strzelecki and L. Liebert, *Bull. Soc. Chim. Fr.*, 597 (1973).

(5) Y. Bouligand, P. E. Cladis, L. Liebert, and L. Strzelecki, *Mol. Cryst. Liq. Cryst.*, **25**, 233 (1974).

(6) A. Blumstein, R. Blattberg-Blumstein, S. B. Clough, and E. C. Hsu, *Macromolecules*, **8**, 73 (1975).

(7) S. B. Clough, A. Blumstein, and E. C. Hsu, *Macromolecules*, **9**, 123 (1976).

(8) A. Blumstein, S. B. Clough, L. Patel, R. Blattberg-Blumstein, and E. C. Hsu, *Macromolecules*, **9**, 243 (1976).

(9) E. C. Hsu and A. Blumstein, *J. Polym. Sci., Lett. Ed.*, in press.

(10) E. C. Hsu, unpublished results.

(11) E. Perplies, H. Ringsdorf, and J. H. Wendorff, *Makromol. Chem.*, **175**, 553 (1974).

(12) B. Z. Newman, V. Frosini, and P. L. Magagnini, *J. Polym. Sci., Part A-2*, **13**, 87 (1975).

(13) E. C. Hsu, S. C. Clough, and A. Blumstein, *J. Polym. Sci., Lett. Ed.*, in press.

(14) G. W. Gray, "Molecular Structure and the Properties of Liquid Crystals", Academic Press, New York, N.Y., 1962.

(15) A. Blumstein, S. B. Clough, L. Patel, L. K. Lim, E. C. Hsu, and R. Blattberg-Blumstein, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **16**, 241 (1975).

Communications to the Editor

Correlation between ^{13}C NMR Chemical Shifts and Conformation of Polymers. I. The Methyl Spectrum of 3,5,7,9,11,13,15-Heptamethylheptadecane[1]

The ^{13}C NMR spectrum of the central methyl carbon of 3,5,7,9,11,13,15-heptamethylheptadecane (compound I) was interpreted by Zambelli et al.[2a] The nine chemical shifts observed at high temperature were assigned to the ten possible pentad configurational sequences of I. Since the nine peaks coincide with those found in stereoirregular polypropylene, that work allowed pentad assignments in the methyl spectrum of polypropylene.

The purpose of this work is to investigate whether the stereochemical shifts in the resonance peaks can be ascribed to differences in the conformations of the various stereoisomers. If this is the case, then conformational statistics could be employed to interpret the spectra of other (similar) systems or, vice versa, the NMR spectra could provide information on the conformational (not only configurational) characteristics of polymers. The correlation between ^{13}C chemical shifts and conformer populations in polymers was first suggested by Carman[2b] for poly(vinyl chloride) and then by Bovey[3] for poly(vinyl chloride) and polypropylene.

It is well known[4,5] that the gauche arrangement of a carbon atom with respect to a nonhydrogen substituent in the γ position produces an upfield shift relative to the shielding of the same carbon atom in the trans-planar arrangement. The magnitude of this effect varies significantly in different systems,[5] probably because of distortions from a "normal" gauche conformation in some cases, or because of lack of additivity when several gauche interactions affect the observed atom. Also corrections included to account for distortions are unable to determine a unique value for the γ effect, ranging approximately from -6.5 to -3.5 ppm per gauche contact.[3,5] By adopting a value of -4.3 ppm and taking quantitative account of the gauche interactions, Bovey[3] has approximately reproduced the triad structure of the methyl spectrum of atactic polypropylene. However, he has not attempted to predict the fine structure of the spectrum.

The interaction of a methyl carbon with a substituent in the δ position and in the syn-axial (i.e., GG′) conformation has been found[6] to produce a downfield shift of about 2–3 ppm relative to the other conformations, in contrast to the upfield γ effect. In flexible molecules such as polypropylene, syn-axial interactions, being more repulsive than gauche interactions, have low probability of occurrence, so that it is reasonable to expect that the δ effect will give a minor contribution to the chemical shifts of compound I.

Since the various conformers are separated by relatively low energy barriers, the chemical shift for a carbon atom of a given stereoisomer is the Boltzmann average over all the conformations. We base the calculation of the methyl chemical shifts of a chain molecule such as I on the following two assumptions: (a) each torsional angle can assume three conformations T, G, and G′ (three-state model); (b) the chemical shift of a given conformer is a linear function of the numbers of gauche γ interactions and syn-axial δ interactions in which the observed carbon is involved. The calculated chemical shift for a stereoisomer is then given by

$$\nu = \nu_0 + \gamma P_G + \delta P_\omega \qquad (1)$$

where ν_0 depends on the chemical constitution, not on the configuration of the stereoisomer, and corresponds to the chemical shift of any stereoisomer in a conformational arrangement such that $P_G = P_\omega = 0$. The parameters $\gamma = \nu_G - \nu_T$ and δ represent respectively the γ and δ effects per interaction; P_G and P_ω are the sums of the probabilities that the observed carbon is respectively in the conformations gauche with respect to the carbons three bonds apart and syn-axial relative to the carbons four bonds apart.

The probabilities P_G and P_ω are calculated with the usual methods of the rotational isomeric state theory, using the simple three-state model. Results of nonbonded energy calculations[7,8] have shown that the conformational energy of the polypropylene chain can be expressed approximately as the sum of simple interactions, namely chain–chain and methyl–chain gauche interactions (E_g and E_{SK}, respectively) and syn-axial interactions (E_ω). We have followed Boyd and Breitling[7] in their statistical treatment of the polypropylene chain, with the minor exception that we do not exclude conformational sequences of the type XG|G′Y for two adjacent dyads unless either XG or G′Y imply another ω (syn-axial) interaction within either dyad. Therefore our treatment, which is more rigorous but consistent with Boyd and Breitling's energy calculations, requires statistical weights which are functions of three adjacent torsional angles. The partition function is then given by the expression

$$Z = \sum_{\chi_1}\sum_{\chi_2} \ldots \sum_{\chi_N} W(\chi_1,\chi_2,\chi_3)W(\chi_2,\chi_3,\chi_4) \ldots W(\chi_{i-2},\chi_{i-1},\chi_i) \ldots W(\chi_{N-2},\chi_{N-1},\chi_N) \qquad (2)$$