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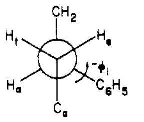
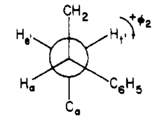
(54) As an example, in the *t,t* conformation (Figure 6a) ϕ_1, ϕ_2 = −20°, 20° because this causes relief from the steric interactions of the phenyl ring and the methyl methacrylate C_α, as can be seen in the Newman projections





Correlation between ^{13}C NMR Chemical Shifts and Conformation of Polymers. 5. Solution and Solid-State Spectra of Poly[(*S*)-3,7-dimethyl-1-octene]

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ABSTRACT: Isotactic poly[(*S*)-3,7-dimethyl-1-octene] (poly[(*S*)-3,7DM1O]) is examined by ^{13}C NMR in solution and in the solid state. The correlation between ^{13}C NMR chemical shifts and conformation of the polymer is studied by calculations based on an empirical scheme that takes into account conformational effects. Comparison between the solid-state spectra of poly[(*S*)-3,7DM1O] and poly[(*S*)-3-methyl-1-pentene] has made it possible to assign a fourfold chain helical conformation to the main chain of poly[(*S*)-3,7DM1O]. The analysis of the observed and computed ^{13}C chemical shifts of the side chain of poly[(*S*)-3,7DM1O] and its model compound 2,6-dimethylheptane has shown that the side chain of poly[(*S*)-3,7DM1O] has a considerable conformational freedom also in the solid state.

High-resolution ^{13}C NMR spectra of solid-state polymers obtained with the magic-angle spinning technique can provide information on the conformation of crystalline or amorphous polymers and on the conformational dependence of the chemical shifts, although the situation may be complicated by crystal packing effects.[1-4] Recently, on the basis of observed solid-state ^{13}C NMR chemical shifts and of conformational considerations we were able to

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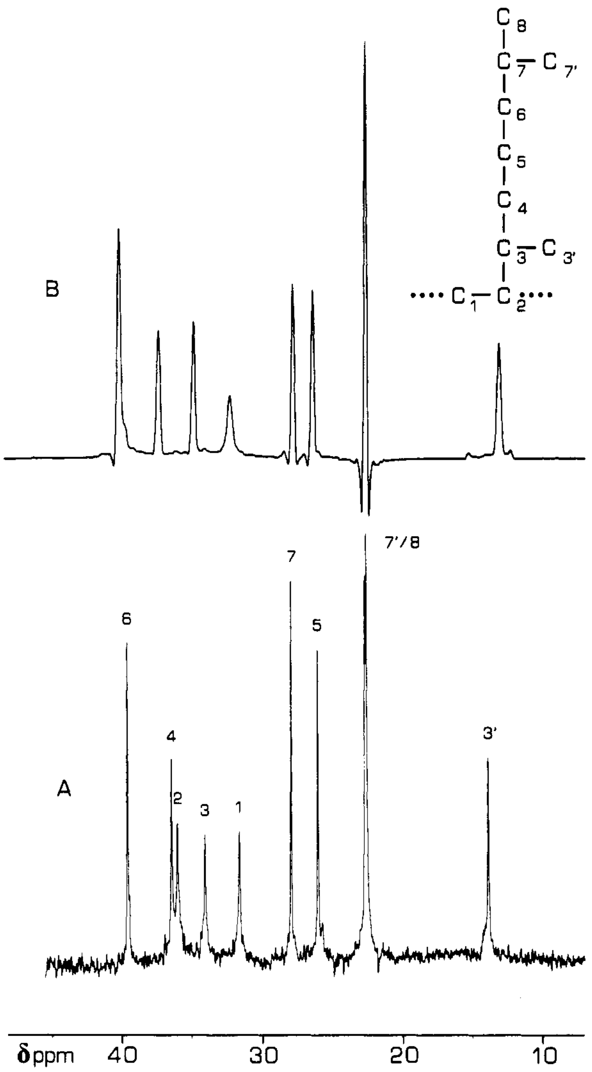


Figure 1. ^{13}C NMR spectra of isotactic poly[(*S*)-3,7-dimethyl-1-octene]: (A) solution spectrum; (B) solid-state spectrum. Chemical shifts downfield from Me_4Si.

Table I
^{13}C Chemical Shifts[a] of Isotactic Poly[(*S*)-3,7-dimethyl-1-octene] and Poly[(*S*)-3-methyl-1-pentene]

	solution	solid	
C atom	poly[(*S*)-3,7DM1O]	poly[(*S*)-3,7DM1O]	poly[(*S*)-3M1P]
C_1	32.1	32.4	32.5
C_2	36.5	37.6	38.0
C_3	34.5	35.0	36.7
$C_{3'}$	14.1	13.2	14.1
C_4	36.8	37.6	29.0
C_5	26.3	26.6	14.1
C_6	40.0	40.4	
C_7	28.2	28.0	
$C_{7'/8}$	22.8	22.8	
$C_{7'/8}$	22.9	22.8	

[a] Referred to Me_4Si.

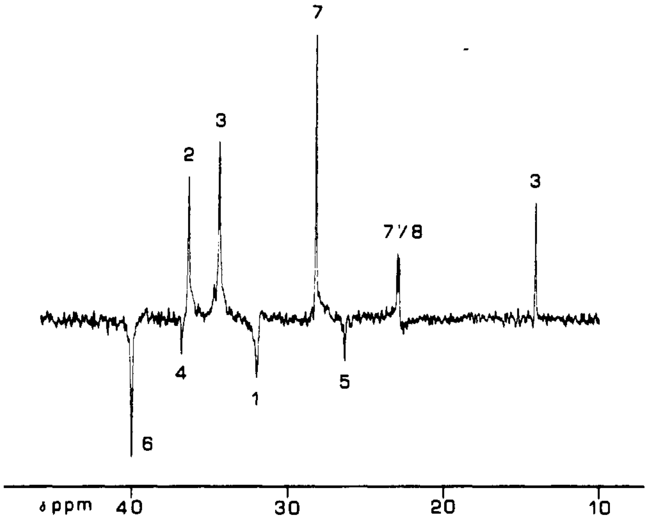


Figure 2. ^{13}C NMR solution spectrum of poly[(*S*)-3,7-dimethyl-1-octene] obtained by using DEPT sequence. The carbon signals of odd multiplicity (C_1, C_4, C_5, and C_6) appear 180° opposite in phase with respect to the carbon signals of even multiplicity (C_2, C_3, $C_{3'}$, C_7, and $C_{7'/8}$).

present evidence of the presence in isotactic poly[(*R*,*S*)-3-methyl-1-pentene] (poly[(*R*,*S*)-3M1P] of *R* (or *S*) monomer units randomly distributed in chains mainly composed of *S* (or of *R*) monomer units.[5,6] Such conclusions could not be reached from the analysis of the solution ^{13}C NMR spectra, due to the signal broadening associated with the configurational (and related conformational) disorder of the chains.[7]

We are at present interested in the study of isotactic polymers of more hindered C_3-branched α-olefins, e.g., 3,7-dimethyl-1-octene (3,7DM1O).[8] Here we report solution and solid-state ^{13}C NMR results concerning isotactic poly[(*S*)-3,7DM1O] whose crystal structure is as yet unknown.

Figure 1 shows (A) the solution spectrum of the diisopropyl ether soluble, diethyl ether insoluble fraction of poly[(*S*)-3,7DM1O] and (B) the solid-state spectrum of the annealed sample of the same fraction. Table I collects the chemical shifts of the resonances of the solution and solid-state spectra of poly[(*S*)-3,7DM1O] of Figure 1, together with the chemical shifts previously observed[5] in the solid-state spectrum of poly[(*S*)-3-methyl-1-pentene] (poly[(*S*)-3M1P]). The signal assignment of the solution spectrum of Figure 1A was performed by means of additivity rules accounting for conformational effects[6,9] and was checked by using the DEPT sequence, after which carbon signals of even and odd multiplicity appeared 180° opposite in phase (Figure 2). A previous assignment[8] based on the additivity rules of Lindeman and Adams[10] was incorrect in regard to the C_3 and C_4 resonances.

Inspection of Figure 1 and of the chemical shift values of Table I shows a strong similarity between the solution and solid-state spectra of poly[(*S*)-3,7DM1O]. Small differences are observed concerning (i) the splitting (0.1 ppm) of the diastereotopic $C_{7'}$ and C_8 methyl carbons, absent in the solid-state spectrum, and (ii) the coincidence of the chemically nonequivalent C_2 and C_4 carbons in the solid-state spectrum (a splitting (0.3 ppm) is observed in the solution resonances, which furthermore are shifted upfield by about 1 ppm). Since shifts of the order of a few ppm, mainly arising from changes in the so-called γ-gauche effects, are generally associated with conformational changes, the comparison between the two spectra of Figure 1 suggests that poly[(*S*)-3,7DM1O] has a similar conformational structure in solution and in the solid state, the similarity being particularly close with regard to the side chain.

The comparison between the solid-state ^{13}C NMR chemical shift values reported in Table I for poly[(*S*)-3,7DM1O] and poly[(*S*)-3M1P] shows nearly coincident values for C_1 and C_2 and close values for $C_{3'}$. As a consequence, it appears that the annealed poly[(*S*)-3,7DM1O] adopts a main-chain conformation close to the fourfold helix found for poly[(*S*)-3M1P][11] (Figure 3). In order to

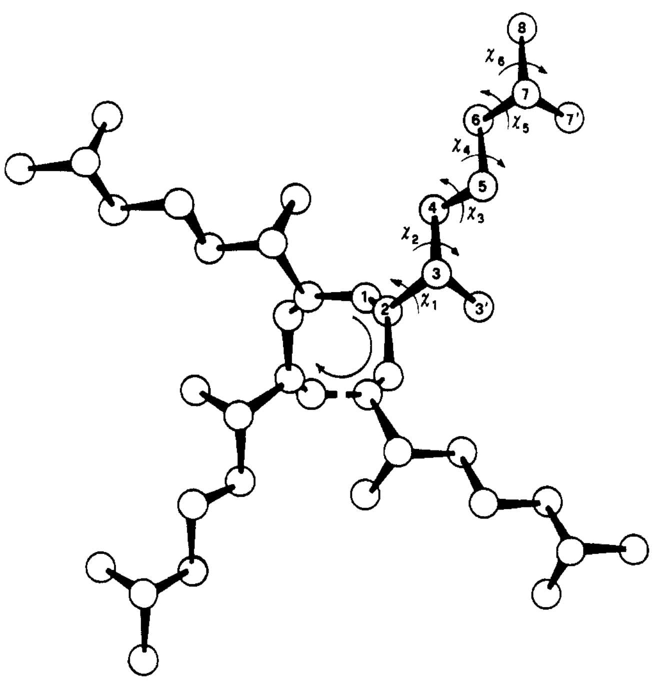


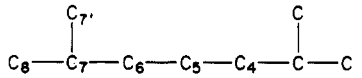
Figure 3. View of the poly[(*S*)-3,7-dimethyl-1-octene] structure along the helix axis. The lateral chains are represented in the all-trans conformation.

Table II
Observed and Calculated ^{13}C Chemical Shifts[a] of the Side Chain of Poly[(*S*)-3,7-dimethyl-1-octene] and Its Model Compound 2,6-Dimethylheptane

	2,6DMH		poly[(*S*)-3,7DM1O]	
C atom	calcd	exptl[b]	calcd	exptl
$C_{7'/8}$	22.5	22.4	22.5	22.8
C_7	28.3	28.1	28.3	28.2
C_6	39.9	39.5	39.7	40.0
C_5	26.2	25.2	26.8	26.3
C_4			36.7	36.8

[a] Referred to Me_4Si. [b] Reference 3.

study the conformational structure of the side chains of poly[(*S*)-3,7DM1O], 2,6-dimethylheptane (2,6DMH) was considered as a suitable model compound:



$$C_8—\overset{\overset{\displaystyle C_{7'}}{|}}{C_7}—C_6—C_5—C_4—\overset{\overset{\displaystyle C}{|}}{C}—C$$

In Table II the values of the chemical shifts of the model compound and of the polymer computed according to the method and the parameter set reported in ref 6 and 9 are listed together with the experimental values. This model compound is one of the paraffins earlier studied by Lindeman and Adams[10] and utilized by us for deriving the parameters of our empirical scheme of computation of hydrocarbon chemical shifts.[6]

We first note a close resemblance between the chemical shifts observed for the corresponding carbon atoms of 2,6DMH and of the polymer side chain, the latter showing rather small relative downfield shifts, larger for the atoms closer to the main chain. In turn, the observed chemical shifts of the model compound are reasonably well reproduced by the calculation, which describes the conformational structure as the Boltzmann equilibrium between various conformers. More precisely, on the basis of molecular energy calculations, the following populations were assigned to the rotational states of the four bonds of the chain: for the two external bonds (dihedral angles χ_5 and χ_2 in the notation used for the polymer side chain) a probability of 0.12 is given to the least stable conformer having both methyl groups gauche with respect to C_5, while the other two staggered conformations have equal probabilities and very small populations are assigned to distorted states; for the two central bonds, the antiplanar (trans) conformer has a probability of 0.74, most of the remaining being assigned to the two equivalent gauche conformers. The fact that all the calculated resonances are shifted downfield with respect to the observed ones seems to indicate that gauche interactions are slightly underestimated.

The major conclusion of the above considerations is then that the side chain of poly[(*S*)-3,7DM1O] is also disordered both in solution and in the solid state. This is obvious in the case of the χ_5 rotation, since the quasi-equivalence of carbons $C_{7'}$ and C_8 implies nearly equal populations of the two asymmetrical conformers, while we discard the hypothesis that only the symmetrical conformer is present, both on energetical grounds and with regard to the expected chemical shift. Equilibrium between various conformers must be invoked also for other bonds of the side chain of poly[(*S*)-3,7DM1O] (dihedral angles χ_4, χ_3, and χ_2). Indeed we found no single conformer that could lead to calculated chemical shifts in agreement with experiment. On the contrary, the computed values given in Table II and based on conformational equilibrium show a rather good agreement with the observed chemical shifts. No conformational energy calculations were actually performed on poly[(*S*)-3,7DM1O] for obtaining the Boltzmann conformer population. The chemical shifts were computed by assuming for χ_5 and χ_4 the same equilibrium as for 2,6DMH, by giving a probability of 0.7 to the trans conformer of χ_3, and finally by assuming the conformation observed[11] in poly[(*S*)-3M1P] with regard to χ_2 and χ_1 (i.e., two equiprobable states for χ_2 and a single preferred state for χ_1).

Thus, the conformational model proposed here for poly[(*S*)-3,7DM1O] is a combination of the solid-state conformation observed for poly[(*S*)-3M1P][11] and the solution conformation of 2,6DMH. Such a model also reproduces the resonance of carbon C_4 successfully. Moreover, the upfield shift of the C_3 resonance with respect to poly[(*S*)-3M1P] can be approximately accounted for by the (partial) occurrence of a γ-gauche interaction with C_6. Finally, as far as atoms C_1, C_2, and $C_{3'}$ are concerned, which present resonances close to those found for poly[(*S*)-3M1P], we recall that our previous calculations on the latter[6] predicted resonances significantly shifted upfield with respect to the observed ones. We ascribed the discrepancies to the effects of the distortions from staggered conformations arising in a fourfold helix. This qualitative explanation is in agreement with the upfield shifts connected with the transition from a fourfold helix to a threefold helix observed by Belfiore et al.[4] in their CP-MAS study of the various crystalline forms of poly(1-butene).

The present picture of the solid-state structure of poly[(*S*)-3,7DM1O], derived from NMR and X-ray experiments, is quite unusual, as it implies the presence of ordered helices in spite of a large portion of the side chains (from atom C_5 on, i.e., half of the total mass) being conformationally disordered and in rapid motion. This situation might explain why, as far as we know, attempts to obtain a model from X-ray fiber diffraction have failed up to now. The driving force to pack the chains in a crystalline structure should lie in the strong tendency of optically active isotactic C_3-branched poly(α-olefins) to form helices, even in solution and in the molten state.[14,15] Conformational disorder in the side chains was revealed by X-ray analysis of several isotactic polymers with branched side chains.[11,16] The crystal structure proposed by Petraccone et al.[11] for poly[(*S*)-3M1P] shows two equiprobable conformations of the side-chain end (methyl C_5 only). In this case flippings from one conformation to the other in neighboring chains are interrelated; however, ^{13}C CP-MAS NMR analysis of this polymer[5,6] shows unique resonances, indicating that the exchange rate between the two conformations at room temperature is fast with respect to the NMR time scale. In the present case of poly[(*S*)-3,7DM1O] the disorder should involve a much larger part of the side groups. It is conceivable that low-temperature ^{13}C CP-MAS NMR measurements may help one to further elucidate the structure of this polymer.

Experimental Section

(*S*)-3,7-Dimethyl-1-octene was synthesized in three steps from (*S*)-citronellol according to the literature.[12] Purified (*S*)-3,7DM1O (5 mL) in 10 mL of anhydrous toluene was polymerized at 80 °C in the presence of δ-TiCl$_3$ (3.2 mmol) and Al(CH$_3$)$_3$ (1.7 mmol). After 4 days the polymerization was stopped by adding HCl-acidified methanol; then the polymer was collected, washed, and dried under vacuum. Yield: 1.06 g. The crude polymer was then fractioned with boiling solvents.[8] An annealed sample of the boiling diisopropyl ether soluble, diethyl ether insoluble fraction, obtained by heating at 250 °C for 2 h and slow cooling (1 °C/5 min) showed a highly crystalline X-ray pattern.

The ^{13}C CP-MAS NMR spectrum of annealed poly[(*S*)-3,7DM1O] was obtained on a Bruker CXP-300 spectrometer operating at 75.46 MHz, with a magic-angle rotation speed of 4.3 kHz. Free induction decays were generated by cross polarization using a single contact pulse of 1 ms per ^{1}H spin locking and a recycle of 5 s. The chemical shifts were referred to external Me$_4$Si.

The ^{13}C NMR spectrum of the diethyl ether soluble, diisopropyl ether insoluble fraction of the same polymer was obtained at 94 °C on a Bruker AM-270 spectrometer operating at 67.9 MHz in the PFT mode. The sequence τ_1–90°–τ_2–180°, 90°–τ_2–135°, 180°–τ_2–BB–acquire was used for the DEPT experiment[13] with a delay τ_2 of 3.6 ms and 90° pulse widths of 7.3 and 1.9 μs for ^{13}C and ^{1}H, respectively. A sweep width of 3600 Hz was used with 16K of computer memory for the interferogram. The sample was prepared by dissolving the polymer in 1,2,4-trichlorobenzene and by adding 1% hexamethyldisiloxane (HMDS) as an internal standard. The chemical shifts were converted to the Me$_4$Si scale.

Registry No. Isotactic poly[(*S*)-3,7-dimethyl-1-octene], 29407-49-6; 2,6-dimethylheptane, 1072-05-5.

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Transient Spectroscopy and Kinetics of Poly(1-(4-substituted-phenyl)-2-propen-1-ones)[†]

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ABSTRACT: The transient absorption spectra of 1-(4-substituted-phenyl)-2-propen-1-one chromophores in model compounds, homopolymers, and copolymers with styrene and methyl methacrylate were examined in chloroform at room temperature using laser flash photolysis techniques. Most triplets showed maxima in the 350-nm region with the exception of methoxy-substituted derivatives, where the maxima at ~390 nm, characteristic of the π,π^* triplet, were observed. Spectra are quite similar for the model compounds and homopolymers. When the polymers can undergo the Norrish type II reaction we observe a drastic decrease in triplet lifetime as compared with the model compounds, where this is not possible. Quenching rate constants for small molecules (e.g., conjugated dienes) normally follow the order k_q(model) > k_q(copolymer) ≥ k_q(homopolymer). Polymer-bound quenchers show similar efficiency to free ones, when local concentration effects are taken into consideration.

Introduction

Carbonyl chromophores in polymer systems continue to attract attention even though their photochemical behavior has been extensively studied during the last decade.[1a] Poly(1-phenyl-2-propen-1-one), also known as poly(phenyl vinyl ketone) or poly(acrylophenone), and its derivatives have been investigated rather thoroughly.[2] Not surprisingly, many aspects of the photochemistry and photophysics of carbonyl groups in polymers in solution parallel closely the behavior of their monomeric analogues. There are, however, specific effects, related either to the polymeric structure and/or to the ability of the excitation energy to migrate along the chain of chromophores.

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