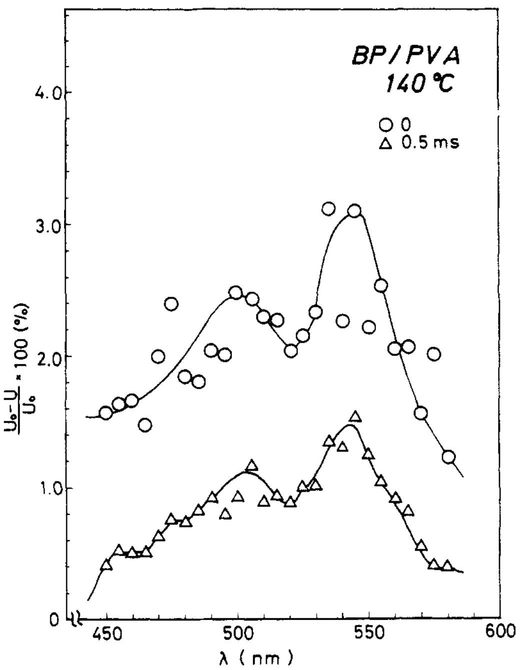

Figure 8. Transient spectra for benzophenone ketyl radical in poly(vinyl alcohol).

inside the cage and k_r is the rate coefficient for escape from the cage resulting in the irreversible reaction product. The reaction scheme is summarized in Figure 6.

Transient Measurements of Benzophenone Ketyl Radicals. Transient spectra and decay lifetime were measured for poly(vinyl alcohol) film containing benzophenone after 337-nm laser pulse irradiation. The transient absorption at 545 nm observed from −120 to +30 °C showed the same decay profile and lifetime as the phosphorescence decay at the same temperature, and so it was attributed to the triplet–triplet absorption of $^3BP^*$. A new transient absorption at 545 nm appeared in the millisecond region for $T > T_g$ (Figure 7). The transient spectrum of this absorption, shown in Figure 8 has peaks at 500 and 545 nm and has been assigned to benzophenone ketyl radical.[16] The concentration of this absorbed species increases with increasing temperature, and its lifetime decreases from 18 ms at 120 °C to 10 ms at 140 °C to 3.0 ms at 160 °C. Thus, the observed absorption at $T > T_g$ is supposed to be due to the benzophenone ketyl radical escaping from the cage in the matrix. The ketyl radical inside the cage for $T > T_g$ could not be observed in the present experiments probably due to its very rapid decay by the backward disproportionation reaction inside the cage.

In conclusion, the phosphorescence decay of benzophenone in poly(vinyl alcohol) shows deviation from a single-exponential type for the temperature range $T_\gamma < T < T_g$ and is attributed to diffusion-controlled hydrogen abstraction by benzophenone triplet from the poly(vinyl alcohol) matrix. Measurements of quantum yield for benzophenone disappearance under continous irradiation as well as transient absorption revealed the existence of a predominant backward disproportionation reaction of ketyl radicals inside the cage of the matrix.

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Conformational Control of Benzylic Radical Bromination in Polymers from Methylstyrenes

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ABSTRACT: Atactic and isotactic poly(3,4-dimethylstyrenes) (poly(3,4-DMSt)) have been subjected to benzylic radical bromination using either the *N*-bromosuccinimide–benzoyl peroxide (NBS–BPO) or the Br_2–K_2CO_3–light systems. Brominated and unbrominated polymers were studied by ^{13}C NMR spectroscopy. A remarkable difference in the chemical reactivity of the methyl groups in positions 3 and 4 of the benzene ring between atactic poly(3,4-DMSt) and isotactic poly(3,4-DMSt) was observed. These results suggest a conformational control of the polymer main chain on the chemical reactivity of the two methyl groups on the benzene ring toward the bromine substitution reaction.

Introduction

In order to prepare a macromolecular ligand having a diphosphino group system anchored to a stereoregular polymeric matrix and to study the influence of an ordered macromolecular structure on the selectivity in reactions catalyzed by transition-metal complexes bound to the

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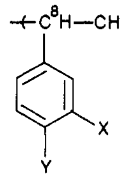
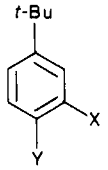
Table I
^{13}C NMR Chemical Shifts (ppm from $(CH_3)_4Si$)[a] of the C^8, C^9, and C^{10} Carbon Atoms of the Polymers and the Model Compounds before and after Bromination

Polymers



unbrominated compounds				brominated compounds					
	C^8	C^9	C^{10}		C^8	C^9	C^{10}	C^9Br	C^{10}Br
X = C^9H_3, Y = H				X = C^9H_2Br, Y = H					
atac[b]	41.6	21.5		atac	41.9			33.9	
isotac[c]	41.8	21.5		isotac	42.1			33.9	
X = H, Y = $C^{10}H_3$				X = H, Y = $C^{10}H_2Br$					
atac	40.9		21.1	atac	41.4				33.7
isotac	41.1		21.0	isotac	41.7				33.7
X = C^9H_3, Y = $C^{10}H_3$				X = C^9H_2Br, Y = $C^{10}H_2Br$					
atac	41.3	19.6	19.2	atac	40.7			30.4	29.8
isotac	41.4	19.5	19.1	isotac	41.9	19.7		32.8	31.9

Model Compounds

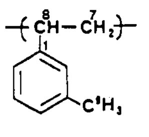


unbrominated compounds			brominated compounds		
	C^9	C^{10}		C^9Br	C^{10}Br
1, X = C^9H_3; Y = H	21.9		4, X = C^9H_2Br; Y = $C^{10}H_3$	33.0	
2, X = H; Y = $C^{10}H_3$		21.3	5, X = C^9H_3; Y = $C^{10}H_2Br$		30.3
3, X = C^9H_3; Y = $C^{10}H_3$	20.1	19.6	6, X = C^9H_2Br; Y = $C^{10}H_2Br$	30.8	30.0

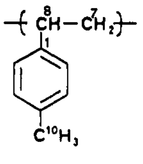
[a] In o-dichlorobenzene at 140 °C. [b] Atactic polymer. [c] Isotactic polymer.

above polymeric support, we approached the synthesis of an isotactic derivative of poly(3,4-dimethylstyrene) containing diphosphino groups in the side chain. The synthetic procedure adopted involved the benzylic radical bromination of isotactic polymer fractions followed by displacement of the bromine by a phosphide anion.

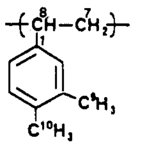
To explore the unknown reactivity of the poly(methylstyrenes) toward benzylic bromine substitution, we reacted samples of atactic and isotactic poly(3-methylstyrene) (poly(3-MSt)), poly(4-methylstyrene) (poly(4-MSt)), and poly(3,4-dimethylstyrene) (poly(3,4-DMSt)) with *N*-bromosuccinimide or the bromine–potassium carbonate–light system.



poly–3MSt



poly–4MSt



poly–3,4DMSt

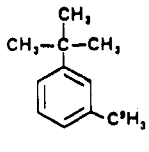
The starting unbrominated polymers and the brominated derivatives were examined by ^{13}C NMR spectroscopy to gain information about the chemical reactivity of the methyl groups in positions 3 and 4 of the pendant benzene rings.

Polymerization and Characterization

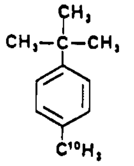
The polymerization of the methylstyrenes was carried out by using known procedures, both with a radical initiator (benzoyl peroxide (BPO)) and with a stereospecific catalyst ($Al(i\text{-}C_4H_9)_3/TiCl_3$ ARA[1]), to obtain samples of polymer with different tacticities. The polymers obtained by BPO were substantially atactic, while those prepared by the $Al(i\text{-}C_4H_9)_3/TiCl_3$ ARA system were highly isotactic.

The microstructure of the polymers was examined by ^{13}C NMR spectroscopy, using the aromatic C^1 carbon absorption. The ^{13}C spectrum of this carbon atom is sensitive to the change of polymer stereoregularity.[2] The isotactic polymer is characterized by a single peak between 145 and 143 ppm, assigned to *mmmm* pentads by Kawamura et al.,[3] reflecting the position of ring methyl substituents. The atactic polymer shows a multiplicity of peaks in the same region (Figure 1), so the former can be easily distinguished from the latter.

In the case of poly(3-MSt) and poly(4-MSt), the carbon atom signal assignments were made from the data reported by Kawamura et al.[3] We have assigned the signals due to C^9 and C^{10} carbon atoms of the methyl groups on the benzene ring in poly(3,4-DMSt) by comparing its ^{13}C NMR spectrum with those of poly(3-MSt) and poly(4-MSt) and also by examining the ^{13}C NMR spectra of low molecular weight model compounds such as 1-*tert*-butyl-3-methylbenzene (1), 1-*tert*-butyl-4-methylbenzene (2), and 1-*tert*-butyl-3,4-dimethylbenzene (3).



1



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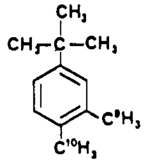


3

The results obtained are reported in Table I. In all the ring monomethyl cases, the chemical shift of C^{10} was observed at a higher field of about 0.4–0.6 ppm with respect

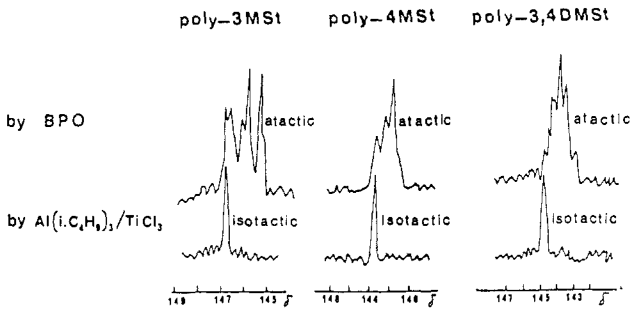


Figure 1. Aromatic C^1 carbon ^{13}C NMR spectra of poly(3-methylstyrene) (poly(3-MSt)), poly(4-methylstyrene) (poly(4-MSt)), and poly(3,4-dimethylstyrene) (poly(3,4-DMSt)).

Table II
Elemental Analysis Data for Atactic and Isotactic Poly(3,4-DMSt) Samples after Bromination

element	calcd % mono-bromination	calcd % di-bromination	found % for polymer atactic	found % for polymer isotactic
C	56.87	41.38	41.01	56.35
H	5.21	3.45	3.32	5.09
Br	37.91	55.17	56.29	38.97

to the chemical shift of C^9. Therefore in the case of 3,4-dimethyl derivatives, the higher field absorption was assigned to C^{10}.

^{13}C longitudinal relaxation time (T_1) measurements were also performed on model compound 3 in order to assign C^9 and C^{10}. A longer relaxation time for C^9 with respect to C^{10} is in fact expected because of the anisotropic tumbling of the molecule.[4] The results obtained are T_1 = 5.8 s for the high-field line (19.6 ppm) and T_1 = 6.8 s for the line at 20.1 ppm, confirming our assignment.

Bromination of the Polymers and Model Compounds

Atactic and isotactic samples of poly(3-MSt), poly(4-MSt), and poly(3,4-DMSt) were radically brominated by using two types of reactions, occurring under different experimental conditions. One reaction was carried out with *N*-bromosuccinimide (NBS), as is usually done for the bromination of allylic and benzylic systems.[5] The following conditions were used: refluxing in anhydrous carbon tetrachloride solution for 2 h in the dark and under a nitrogen atmosphere; NBS/methyl group molar ratio = 1.5:1; 2% by weight BPO. A second type of bromination was carried out at room temperature without initiators in methylene chloride solution using Br_2 and anhydrous K_2CO_3 under exposure to white light. This method has been shown to operate with hydrogen abstraction by bromine atoms and with good scavenging of HBr by K_2CO_3 to avoid reversibility.[6]

The polymers were precipitated by methanol and dried under vacuum before the bromine content was determined by elemental analysis and ^{13}C NMR spectra were obtained. The product composition found was the same from either the NBS–BPO or the Br_2–K_2CO_3–light system; the results obtained in the bromination are reported in the Table I. In no instance did bromination occur at C^7 or C^8 carbon atoms since the ^{13}C absorption for these carbons was essentially unaltered in the brominated polymer products. Polystyrene showed no evidence of bromination in 40 h when the Br_2–K_2CO_3–light method was used.

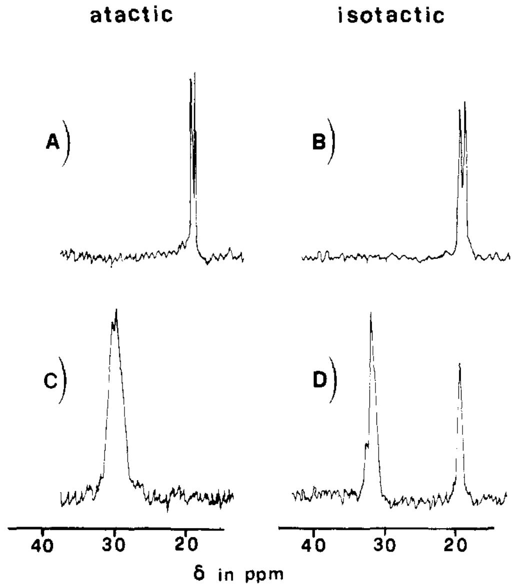
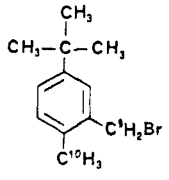


Figure 2. ^{13}C NMR chemical shifts of C^9 and C^{10} carbons of poly(3,4-DMSt) (A, B) and of brominated poly(3,4-DMSt) (C, D).

The assignment of the signals due to C^9 and C^{10} bonded to bromine atoms was made by comparing the spectra of the brominated polymers and the spectra of the model compounds 1-(bromomethyl)-2-methyl-5-*tert*-butylbenzene (4), 1-(bromomethyl)-2-methyl-4-*tert*-butylbenzene (5), and 1,2-bis(bromomethyl)-4-*tert*-butylbenzene (6) (Table I). As was the case for the unbrominated model compounds, the C^9 chemical shifts for the brominated ones were always observed at lower field with respect to the chemical shifts of C^{10}.



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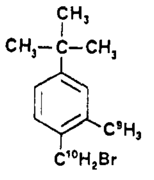

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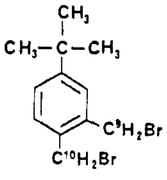

6

In the case of both atactic and isotactic poly(3-MSt) and poly(4-MSt), the methyl group was quantitatively monobrominated, as shown by the appearance of the signals at δ 33.9 and 33.7 due respectively to the carbons C^9 and C^{10} of the bromomethyl groups and by the simultaneous disappearance of the signals at δ 21.5 and 21.1 of the carbons C^9 and C^{10} of the unbrominated methyl groups (Table I).

In the case of atactic poly(3,4-DMSt), using the same molar ratio between the brominating agent and methyl groups (1:1) yields the monobromination of both methyl groups, whereas for isotactic poly(3,4-DMSt) the ^{13}C NMR spectra show that one of the two methyl groups is preferentially brominated. This is also in good agreement with the bromine elemental analysis data (Table II). In the ^{13}C NMR spectra of brominated isotactic poly(3,4-DMSt), a signal at δ 31.9 is present and the signal at δ 19.1 is absent (Table I), showing a quantitative monobromination on C^{10}.

For the methyl group in the 3 position a small signal at δ 32.8, attributed to the C^9 carbon of the brominated group C^9H_2Br, appears and, in addition, an intense signal at δ 19.7 is present due to the C^9 carbon of the unbrominated group C^9H_3 (Figure 2).

A tentative evaluation from the ratio of the values for the peak intensities gives an estimate for isotactic poly(3,4-DMSt) that only about 20% of the polymer structural units show bromination at the methyl groups in both the 3 and 4 positions and about 80% are brominated only on the methyl group in the 4 position.

It is reported that isotactic polystyrene[7] and poly[(*S*)-*p*-*sec*-butylstyrene][8] can assume a helical conformation in solution; analogously such a conformational order can

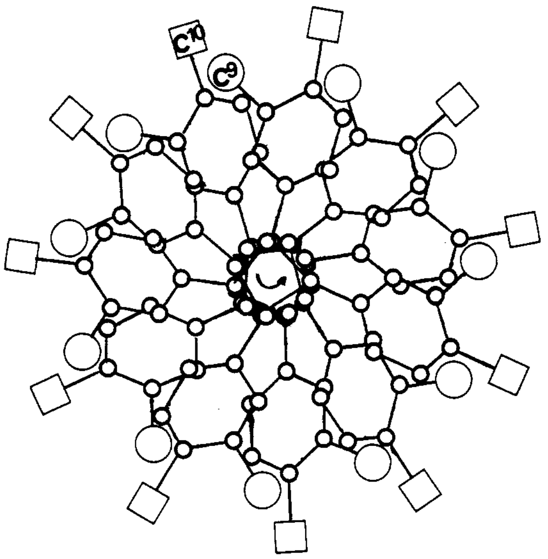

Figure 3. End view of the trial model of the chain of the isotactic poly(3,4-DMSt).

be reasonably assumed also for isotactic poly(3,4-DMSt). This statement seems to be supported by circular dichroism measurements carried out on a sample of isotactic poly[(*R*)-3,7-dimethyl-1-octene-*co*-3,4-dimethylstyrene]. The circular dichroism spectrum is essentially the same as the poly[(*R*)-3,7-dimethyl-1-octene-*co*-styrene] one, for which the circular dichroism behavior in the spectral region of the ^1B transition was related to the electrostatic dipole–dipole interaction between aromatic chromophores disposed in a fixed dissymmetric geometry as in the one-screw helix.[9]

Differences observed in the benzylic bromine substitution of atactic and isotactic poly(3,4-DMSt) can be reasonably attributed to the conformational control of the polymer main chain on the chemical reactivity of the two methyl groups in positions 3 and 4 of the aromatic ring toward the bromination. Indeed, in accordance with that reported for the structures of the isotactic polystyrene and poly(3-methylstyrene)[10] in the crystalline state, we can draw the trial model for the isotactic poly(3,4-DMSt) reported in Figure 3. This picture accounts for the regioselectivity found for the methyl group in the 3 position of the benzene ring being much more hindered to the bromine attack than is the methyl group in the 4 position. Lacking the above ordered structure in the atactic polymer, no regioselectivity is observed in the model compounds as well. However, the importance of a bulky structure on the occurrence of the radical bromination is pointed out by the observation that the benzylic hydrogen on the main chain remains unsubstituted under the bromination conditions in both the isotactic and atactic polymer fractions. On the contrary, the bromination easily occurs with a tertiary benzylic hydrogen atom of low molecular weight compounds.[11]

Experimental Section

Monomers. 3-Methylstyrene and 4-methylstyrene were commercial products (Fluka, puriss. grade) purified by distillation under vacuum. 3,4-Dimethylstyrene was obtained by a procedure adopted for the preparation of some alkylstyrenes:[12] 185 g (1 mol) of 4-bromo-*o*-xylene, prepared[13] from the reaction of 132.3 g (1.25 mol) of *o*-xylene with 3.5 g of iron turnings and 195 g (1.2 mol) of bromine, was converted by reaction with magnesium in dry ether into the corresponding Grignard reagent. A solution of 52.8 g (1.2 mol) of freshly distilled acetaldehyde dissolved in 500 mL of dry ether was added at 0 °C, and the mixture was refluxed for 4 h. From the reaction mixture treated in the usual manner was isolated 87 g (0.58 mol) of (3,4-dimethylphenyl)methylcarbinol, having bp 123–124 °C (15 mmHg) (lit.[14] bp 113–114 °C (9 mmHg)). The latter was dehydrated according to the directions of Sianesi[14] with fused potassium bisulfate by adding *p*-*tert*-butylcatechol as an inhibitor to give 52.2 g (0.44 mol) of gas chromatographically pure 3,4-dimethylstyrene. The product boiled at 83–84 °C (15 mmHg) (lit.[14] bp 74–75 °C (10 mmHg)).

Model Compounds. 1-*tert*-Butyl-4-methylbenzene (2) was a pure grade commercial product.

1-*tert*-Butyl-3-methylbenzene (1). Using the Serijan et al.[15] procedure, we reacted 115 g (1.25 mol) of toluene with 18.5 g (0.25 mol) of *tert*-butyl alcohol in the presence of 33 g (0.25 mol) of $AlCl_3$; 18.5 g (0.125 mol) of a mixture of **1** (70%) and **2** (30%) was obtained. By use of a spinning-band distillation apparatus, 12.8 g (0.086 mol) of **1**, chemically pure by gas chromatographic analysis was isolated (bp 187–188 °C; lit.[15] bp 189.3 °C).

1-*tert*-Butyl-3,4-dimethylbenzene (3). To 169.6 g (1.6 mol) of *o*-xylene and 14.6 g (0.09 mol) of $FeCl_3$ was slowly (2 h) added, at 0 °C, 28.7 g (0.31 mol) of *tert*-butyl chloride. The reaction mixture was stirred for 6 h and then hydrolyzed with ice–HCl (1:1). The organic layer, extracted with *n*-pentane, was dried over Na_2SO_4. The solvent was removed, and the residue was distilled at reduced pressure to give 34.6 g (0.22 mol, 70% yield) of pure **3** having bp 57–58 °C (0.07 mmHg) (lit.[16] bp 83–85 °C (3 mmHg)).

1,2-Bis(bromomethyl)-4-*tert*-butylbenzene (6). Into a 250-mL round-bottomed flask, equipped with a magnetic stirrer and condenser, were placed 8.6 g (0.053 mol) of **3**, 19.2 g (0.11 mol) of NBS, 0.17 g of BPO, and 50 mL of dry carbon tetrachloride. The reaction mixture was refluxed with stirring in the dark under a nitrogen atmosphere for 3 h and then maintained at room temperature for 12 h. The mixture was filtered and the solvent removed. The residue was fractionated at reduced pressure by a spinning-band column to give 22.2 g (0.069 mol, 63% yield) of **6**, chemically pure by VPC analysis: bp 116–118 °C (0.12 mmHg); ^1H NMR (CCl_4) δ 7.4 (m, 3 H, aromatic protons), 4.7 (s, 2 H, *m*-CH_2Br), 4.6 (s, 2 H, *p*-CH_2Br), 1.4 (s, 9 H, *tert*-butyl group).

1-(Bromomethyl)-2-methyl-5-*tert*-butylbenzene (4) and 1-(bromomethyl)-2-methyl-4-*tert*-butylbenzene (5) were prepared by the same procedure previously reported for **6**: 8.6 g (0.053 mol) of **3** was reacted with 9.6 g (0.053 mol) of NBS and 0.09 g of BPO in 25 mL of anhydrous carbon tetrachloride. A mixture formed by **4** (56%) and **5** (44%), as shown by VPC analysis, was obtained. By distillation at reduced pressure with a spinning-band column, the two products were separated into gas chromatographically pure compounds giving boiling points of respectively 64 (0.015 mmHg) and 58 °C (0.015 mmHg). Isomers **4** and **5** were distinguished and then characterized by ^1H NMR analysis on the basis of that reported[17] for the corresponding monochlorinated compounds: for **4**, ^1H NMR (CCl_4) δ 7.2 (m, 3 H, aromatic protons), 4.4 (s, 2 H, *m*-CH_2Br), 2.3 (s, 3 H, *p*-CH_3), 1.3 (s, 9 H, *tert*-butyl group); for **5**, ^1H NMR (CCl_4) δ 7.1 (s, 3 H, aromatic protons), 4.4 (s, 2 H, *p*-CH_2Br), 2.4 (s, 3 H, *m*-CH_3), 1.3 (s, 9 H, *tert*-butyl group).

Polymers. All polymerizations were carried out by using standard techniques. Radical polymers were prepared by benzoyl peroxide initiated polymerizations in anhydrous deaerated toluene at 70–80 °C and were purified by multiple precipitation from toluene into methanol. Stereoregular polymers were obtained with an $Al(i\text{-}C_4H_9)_3/TiCl_3$ system in anhydrous degassed isooctane (monomer/$TiCl_3$ molar ratio = 40:1 and $Al(i\text{-}C_4H_9)_3/TiCl_3$ molar ratio = 3:1) by extracting the crude products with boiling acetone to remove the amorphous fractions.

Bromination of Polymers. The bromination of both radical and stereoregular polymers was carried out by following two procedures.

Procedure A: The polymers were reacted with NBS (NBS/methyl group molar ratio = 1.5:1) in anhydrous carbon tetrachloride solution in the dark under a nitrogen atmosphere in the presence of 2% by weight BPO at the boiling point of the solvent for 2 h. The solutions were filtered to eliminate the insoluble succinimide produced and purified by passing through an Al_2O_3 column. The polymers were precipitated by methanol and dried under vacuum.

Procedure B: The anhydrous deaereated methylene chloride polymer solutions containing Br_2 (Br_2/methyl group molar ratio = 1:1) and anhydrous potassium carbonate (K_2CO_3/polymer molar ratio = 6:1) were degassed at 10 mmHg by cooling at −60 °C. The stirred solutions were exposed at room temperature to white light. The time of exposure was between 3 and 30 h; if the reaction proceeded to completion, a discoloring of the solutions took place. The solutions were filtered to eliminate the inorganic salts insoluble in the reaction solvent, and the polymers were precipitated by methanol and dried under vacuum.

Characterization of Products. VPC was carried out on a Perkin-Elmer F30 A instrument equipped with 200 × 0.29 cm dual columns packed with 20% silicone gum rubber (SE-30) on 80–100-mesh Chromosorb W. ^1H NMR spectra were recorded on a Varian 60-MHz instrument. ^{13}C NMR monomer and model compound spectra were recorded at 30 °C in $CDCl_3$ on a Varian XL-100 instrument. ^{13}C NMR polymer spectra were registered at 140 °C on approximately 10 wt % solutions (2% for isotactic polmers) in 1,2-dichlorobenzene (126.8 ppm) and converted to the tetramethylsilane scale.

Registry No. **1**, 98-51-1; **2**, 1075-38-3; **3**, 7397-06-0; **4**, 104807-56-9; **5**, 104807-57-0; **6**, 60070-04-4; 2-$H_3CC_6H_4CH_3$, 95-47-6; atactic-poly(3-MSt), 25037-62-1; isotactic-poly(3-MSt), 54190-45-3; atactic-poly(4-MSt), 24936-41-2; isotactic-poly(4-MSt), 54190-46-4; atactic-poly(3,4-DMSt), 61420-50-6; isotactic-poly(3,4-DMSt), 104807-58-1.

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Helical Conformations in a Polyamide of the Nylon-3 Family

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ABSTRACT: We have studied the conformation of poly(α-isobutyl L-aspartate), which is a nylon-3 derivative with a side chain attached to each monomer unit. Alternatively it can be considered as a polypeptide in which an additional CH_2 group has been included in the main chain of each residue. The polymer conformation is thus characterized by the usual torsional angles (ϕ,ψ), plus a ξ angle for the additional carbon atom. Analysis of fiber X-ray diffraction patterns reveals two helical conformations for this polymer, which bear structural similarity to the ubiquitous α-helix in proteins. They respectively have 3.25 and 4 residues per turn of helix. We have determined the coordinates of each helix and studied the helix–coil transition in this polymer by NMR.

Introduction

Bragg et al.[1] investigated with molecular models the various helices that can be made from polypeptide chains, which contain two carbon atoms in the polymeric backbone and therefore may be considered as derivatives of nylon-2. Some of these postulated helical structures have been experimentally observed, as reviewed, for example, by Lotz and Brack,[2] although it appears that the α-helix is the structure most frequently observed in polypeptides and proteins.

With the same hydrogen-bonding schemes used by Bragg et al.[1] it is possible to build helical structures that contain a different number of carbon atoms in the main polymer chain. In our laboratory we are investigating several polymers of this type. In this paper we report our studies on the structure of poly (α-isobutyl L-aspartate) (PAIBLA), which contains three carbon atoms in its main polymer chain, i.e., one carbon more per monomer unit than in polypeptides. We have found two different helical structures in this polymer, one of which was preliminarily described elsewhere.[3] It was the first time that helical conformations of this type were described. Yuki et al.[4] had already studied this polymer, but they suggested that it had the extended β-conformation.

Materials and Methods

The polymer was prepared by a slight modification of the method described by Yuki et al.[4]. The reactions were carried out as shown in Scheme I, where the following abbreviations have been used: Z = benzyloxycarbonyl, DCCI = dicyclohexylcarbodiimide, Pcp = pentachlorophenyl, i-Bu = $CH_2CH(CH_3)_2$, and PAIBLA = poly(α-isobutyl L-aspartate).

All intermediates were recrystallized and their structures