Solid-State NMR Investigation of Polymorphism and Stereocomplex Formation in Optically Active Polyesters

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ABSTRACT: Solid-state ^{13}C NMR spectra are reported for samples of poly(α-methyl-α-ethyl-β-propiolactone) (PMEPL) differing in tacticity and thermal history. Two types of spectra are obtained, distinguished primarily by the chemical shifts of the α-methyl and main-chain methylene carbons. These resonances appear at 23.4 and 66.1 ppm, respectively, in the spectrum of melt crystallized isotactic PMEPL, and at 18.1 and 74.1 ppm in a variety of other samples, including films of the isotactic polymer prepared by solution casting. The peak displacements are interpreted in terms of conformational changes, both in the α-ethyl group and the chain backbone. By comparison to the spectrum of oriented films, it is concluded that isotactic PMEPL crystallizes from the melt in the extended chain conformation. This conclusion is supported by infrared spectroscopy. Solid-state NMR spectra are also reported for atactic PMEPL and the stereocomplex that is formed in mixtures of the two isotactic polymers of opposite absolute configuration. These spectra resemble that obtained for solution cast films of the isotactic sample and are attributed to the 2_1 helical conformation. Although NMR spectroscopy indicates that atactic PMEPL and the stereocomplex share similar conformations, X-ray diffraction powder patterns reveal different crystal structures. NMR spectra of poly(α-methyl-α-*n*-propyl-β-propiolactone) (PMPPL) suggest that both the atactic and isotactic polymer crystallize in a helical conformation.

Introduction

The preparation of aliphatic polyesters by the ring opening polymerization of lactones is well known.[1-3] In the specific case of the polymerization of α,α-disubstituted β-propiolactones,[3,4] polyesters of the general formula $(CH_2CR_1R_2COO)_n$ are obtained. Several polymers in this series have been found to be semicrystalline despite their atactic nature and X-ray diffraction studies have revealed two crystal modifications,[5-8] referred to as the α- and β-forms. In general, unoriented films exhibit the α-form and the transformation to the β-form is induced by stretching.

As a consequence of the α- to β-transition which accompanies orientation, fiber patterns of the α-form are difficult to obtain. Melt extruded fibers of poly(α,α-dimethyl-β-propiolactone), known as poly(pivalolactone) (PPL), do, however, crystallize in the α-form and retain their orientation upon high-temperature annealing under tension.[9] Furthermore, oriented samples of poly(α-methyl-α-*n*-propyl-β-propiolactone) (PMPPL) have been prepared which show X-ray layer lines corresponding to the two phases.[8] The α-form of both PPL and PMPPL is characterized by a fiber repeat distance of about 6 Å, which has been identified as the periodicity of a 2_1 helix. Although oriented samples of poly(α-methyl-α-ethyl-β-propiolactone) (PMEPL) in the α-phase have never been reported, X-ray powder data[10] have been fitted with a monoclinic unit cell with c = 6.1 Å.

Studies of the crystalline, thermal, and mechanical properties of PPL[6] and PMPPL[8] indicate that the α–β transformation involves a change in conformation from a 2_1 helix to the fully extended chain. A fiber repeat distance of 4.75 Å, corresponding to the planar zigzag conformation, is evident in the X-ray diffraction patterns of the β-forms of PPL,[6] PMPPL,[8] and PMEPL.[7]

A third polymorph, known as the γ-phase, has been found for PPL crystallized by rapid cooling from the melt.[11,12] From combined electron and X-ray diffraction data, the crystal structure of this phase was determined to be an orthorhombic lattice containing antiparallel 2_1 helices of the same chirality.[13]

Conformational analysis[14] predicts that the general class of polyesters based on the substituted poly(β-propiolactone) backbone will have nearly identical crystalline conformations, that of a 2_1 helix with a periodicity of 6 Å. The planar zigzag conformation is also energetically allowed, with low energy barriers separating the two conformations.[15]

To date, studies concerning the polymorphic behavior of α,α-disubstituted poly(β-propiolactones) have been limited to atactic polymers. Polyesters which contain two different α-substituents, such as PMEPL and PMPPL, possess a chiral center, and optically active polymers can therefore be prepared. Samples of varying degrees of optical purity have been obtained by the polymerization of racemic mixtures of monomer with a stereoselective initiator[16] and from optically pure starting material.[17,18] The stereoregular synthesis of the related poly(β-hydroxybutyrate) has also been investigated.[19,20]

The crystalline properties of these optically active polyesters are found to depend, to varying degrees, on tacticity. In the case of poly(α-phenyl-α-ethyl-β-propiolactone), significantly different X-ray diffraction patterns are obtained for isotactic and atactic samples.[18] Although the melting temperature and enthalpy of fusion were found to increase with optical purity for samples of PMEPL and PMPPL of varying tacticity,[16,10] only slight differences in unit cell dimensions were reported between the racemic and optically active products. In the case of PMEPL, however, a new and unusual crystal form was found in mixtures of the two isotactic polymers of opposite absolute configuration.[21,22] Equimolar blends crystallize with a morphology and crystal structure that are distinctly different from those of the individual isotactic components, indicating the formation of a stereocomplex. In nonequimolar blends, stereocomplex formation occurs preferentially over the crystallization of the isotactic polymers and controls the morphology over a wide concentration range. Perhaps most striking is the observation that the stereocomplex melts 40 °C above the melting temperature of the individual isotactic components.

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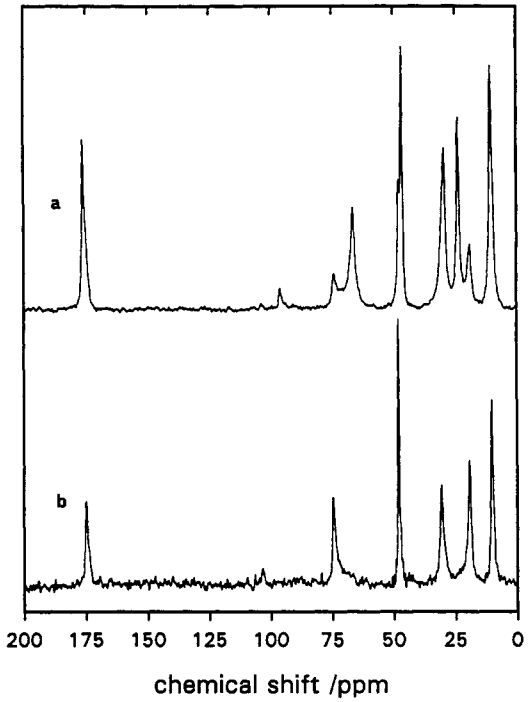


Figure 1. Solid-state ^{13}C NMR spectra of (a) melt crystallized and (b) solution cast isotactic PMEPL.

In the present paper, differences between isotactic PMEPL and the stereocomplex are examined by solid-state nuclear magnetic resonance spectroscopy (NMR). In addition, these studies reveal new polymorphic behavior of the isotactic polymer and differences in crystal structure which depend on tacticity.

Experimental Section

PMEPLs of varying degrees of optical purity were prepared and characterized by Grenier et al.[17] PMPPL samples were synthesized by Ambeault.[23]

All samples were initially prepared as films cast from solution in hexafluoro-2-propanol, the only known solvent for isotactic PMEPL. Melt crystallized samples were obtained by the subsequent heating of these films, under vacuum, to temperatures 20 °C above the melting point, followed by cooling at 1–3 °C/min. Films of the stereocomplex were prepared by casting from solutions containing equal concentrations of the two isotactic polymers of opposite absolute configuration.

Oriented samples of isotactic PMEPL were obtained by stretching solution cast films swollen in 1-butanol. Upon drawing, these films exhibit the phenomenon of "necking in" and thus draw ratios are difficult to estimate. Tension was maintained on the films during the removal of butanol under vacuum.

Solid-state CP/MAS NMR spectra were recorded with a 75-MHz Chemagnetics spectrometer. The standard pulse sequence for cross polarization with bilevel dipolar decoupling was employed with a contact time and recycle delay of 1 ms and 3 s, respectively. Chemical shifts were referenced to hexamethylbenzene at 17.4 ppm.

Infrared spectra were obtained with a Mattson Instruments Sirius 100 FT-IR operated at a resolution of 4 cm^{-1}. Spectra shown are the total of 100 accumulations recorded from thin polymer films (30–50 μm).

X-ray diffraction powder patterns were recorded with a Rigaku Model RU200 rotating anode generator. Diffraction angles reported are for Cu Kα radiation.

Results and Discussion

Poly(α-methyl-α-ethylpropiolactone) (PMEPL). NMR Spectra. Solid-state NMR spectra of isotactic PMEPL prepared by solution casting and melt crystallization are shown in Figure 1. The peak assignments, summarized in Table I, are confirmed by the delayed decoupling spectrum of Figure 2. With delayed decoupling, signals arising from carbon atoms bonded to one or two hydrogen atoms vanish because of dipolar dephasing and, thus, only peaks corresponding to the carbonyl, the tertiary, and the two methyl carbon atoms remain in the spectrum. The delayed decoupling spectrum is of particular interest in the assignment of the peak pair at 23.6 and 18.9 ppm to the α-methyl group. The presence of both peaks in the spectrum of Figure 2 confirms that neither arises from the methylene carbon of the α-ethyl group.

Comparison of the two spectra of Figure 1 indicates significant differences between the melt crystallized and the solution cast samples. In the melt crystallized spectrum, both C3 and C4 (defined in Figure 3) appear as two well-separated peaks rather than as single resonances. The major components of these peak pairs are located at 66.1 and 23.4 ppm, respectively. The NMR spectrum of the solution cast film contains only one peak for each of C3 and C4, located at 74.1 and 18.1 ppm, respectively.

Table I
Chemical Shifts (in ppm) and Peak Assignments for ^{13}C Spectra of Various Samples of PMEPL[a]

	isotactic			atactic	
	melt crystallized	solution cast	stereocomplex		in $CDCl_3$ solution[35]
C1	175.4	175.5	175.0	175.0	174.2
C2	47.4	47.4	48.1*	48.1*	
	46.1*		46.5	46.5	46.6
C3	73.6	74.1*	73.0*	72.8*	68.7
	66.1*	66.9s	66.6	68.9s	
C4	23.4*		23.4		19.3
	18.7	18.1	19.1*	18.9	
C5	29.2	30.0	30.0	29.8	28.5
C6	10.0	9.6	9.8	10.0	8.5

[a] The numbering of carbon atoms is defined in Figure 3. In cases where two resonances are observed for a single atom the major component is indicated with an asterisk. Shoulders are identified with an s.

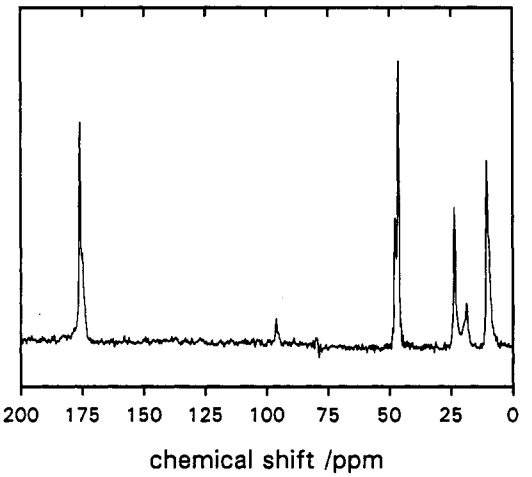


Figure 2. Dipolar-dephased ^{13}C NMR spectrum of melt crystallized isotactic PMEPL.

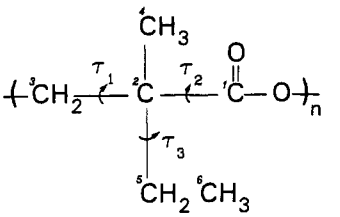


Figure 3. Chemical structure of PMEPL defining carbon atoms and torsion angles referred to in the text.

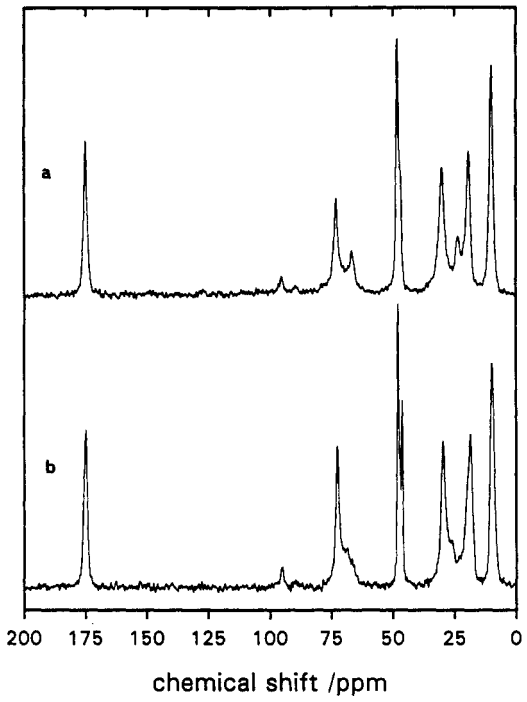


Figure 4. Solid-state ^{13}C NMR spectra of (a) the stereocomplex and (b) atactic PMEPL.

These chemical shifts correspond to those of the minor components of the two peak pairs in the melt crystallized sample. Peak splitting of a lesser magnitude is observed for the tertiary carbon, C2, in the melt crystallized sample, giving rise to peaks at 47.4 and 46.1 ppm. Once again, a single resonance is observed in the solution cast spectrum, occurring at the position of the minor component in the melt crystallized sample.

Spectra obtained for atactic PMEPL and the stereocomplex formed by equal molar mixtures of the two isotactic polymers of opposite absolute configuration are presented in Figure 4. In contrast to the isotactic case, no dependence on thermal history is found. These spectra are unexpectedly similar, and resemble the solution cast isotactic spectrum of Figure 1.

NMR spectra were also recorded for polymers of intermediate tacticity. PMEPL of optical purity 75% shows the same dependence on sample preparation as is found for the isotactic polymer whereas samples of optical purity 25% behave as the atactic case. Similar observations were made by Grenier and Prud'homme[21] by the comparison of other properties, including X-ray patterns, solubility, and morphology.

The presence of two peaks for a single carbon atom in a given NMR spectrum indicates the existence of two different environments for that atom within the sample. The separations of the peak pairs assigned to C3 and C4 are too large (7.5 and 4.7 ppm, respectively) to be solely the result of variations in chain packing, and thus indicate the presence of two different polymer conformations. As outlined in the introduction, conformational calculations and structural studies of similar polyesters suggest that the probable conformations for PMEPL are the 2_1 helix and the planar zigzag. These two conformations differ in the torsion angles labeled τ_1 and τ_2 in Figure 3. The Newman projections of the possible corresponding rotational isomers are sketched in Figure 5. Both right-handed and left-handed helices must be considered, since isotactic PMEPL contains a chiral center and the two helices are thus not equivalent.

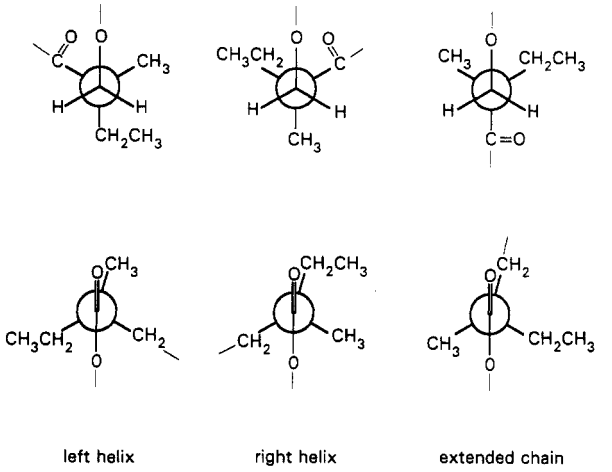


Figure 5. Newman projections illustrating the differences in torsion angles τ_1 and τ_2 between the helical and extended chain conformations of isotactic PMEPL of absolute configuration *R*.

Chemical shift displacements of the magnitude observed for C3 and C4 are frequently attributed to changes in the number of γ-substituents occupying gauche positions relative to the carbon atom of interest.[24] In addition to γ-gauche substituents, the rotational isomers in Figure 5 also involve conformations in which a carbon atom is eclipsed by the oxygen of the carbonyl group (for example, the α-methyl carbon in the left-handed helix). Therefore, any prediction of the shifts in peak position expected to accompany a given change in conformation requires the evaluation of the sign and magnitude of this interaction.

The γ-eclipsed interaction is, in general, found to be shielding.[25] In 1-butanal, the carbon atom located in the β-position respective to the aldehyde functionality is shifted upfield, by −0.4 ppm, despite the normally deshielding effect of substituents at the β-position.[26] This apparent anomaly has been attributed to the presence of substantial concentrations of rotational isomers in which the carbonyl oxygen eclipses the β-carbon, resulting in shielding sufficient to cancel the normal deshielding β-effect, estimated at 5 ppm.[27] This rationale leads to a shielding effect by the eclipsed carbonyl oxygen of at least −5 ppm.

A similar estimate can be derived from a NMR investigation of conformational changes in a series of polyamides.[28] A transition in conformation involving the removal of a methylene carbon atom from an eclipsed position relative to a carbonyl oxygen atom to a gauche position relative to a nitrogen atom was found to be deshielding. This implies that the shielding effect of the γ-eclipsed oxygen exceeds that of the γ-gauche nitrogen, estimated as −7 ppm.[27] It should, however, be pointed out that, for the particular polyamide considered, chemical shift contributions from δ-effects may also be important.

By considering the shielding effects of γ-substituents, the anticipated relative peak positions for the various conformational isomers of Figure 5 are qualitatively discussed below.

i. Differences between Right- and Left-Handed Helices. As shown in Figure 5, right- and left-handed helices of isotactic PMEPL differ in the environments of the α-methyl and α-ethyl groups. The α-methyl carbon (C4) of the isotactic polymer of absolute configuration *R* occupies a gauche position relative to an oxygen atom in the right-handed helix. In the left-handed helix, the same carbon atom, C4, remains gauche to the oxygen, but, in addition, is eclipsed by the carbonyl oxygen atom. Similar differences are found for the α-ethyl group, but in this

case the additional γ-eclipsed oxygen occurs in the right-handed helix. Therefore the NMR spectrum of an isotactic sample composed of equal numbers of left and right helices should exhibit two peaks of equal intensity for both C4 and C5, separated by the shift anticipated for the introduction of an eclipsing oxygen atom.

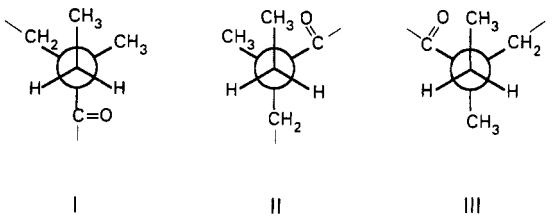
Neither of the spectra in Figure 1 shows evidence of peak splitting at C5, suggesting that crystal forms containing equal numbers of helices of opposite chirality are not found for isotactic PMEPL. Furthermore, the differences between the two spectra in Figure 1, and the doubling of peaks in the melt crystallized spectrum cannot be accounted for in this way.

It is significant to note that a similar discussion is relevant to the stereocomplex, with the important difference that, in this case, the absence of peak splitting at C5 indicates the presence of equimolar quantities of right and left helices—with one handedness occurring for the isotactic component of absolute configuration *S*, the other for the isotactic component of absolute *R*. The environments of C4 and C5 would differ in polymers of opposite absolute configuration but the same helical sense.

ii. Differences between the 2_1 Helix and the Planar Zigzag. A conformational transition from the 2_1 helix to the planar zigzag influences the proximity of γ-substituents for C1, C3, C4, and C5. The main-chain methylene carbon (C3) has one γ-gauche substituent in the helical conformation and is eclipsed by the carbonyl oxygen atom in the extended zigzag conformation. The relative position of this peak in the two conformations thus depends on which of these two substituents produces the greater shielding. A solid-state NMR study of the α- and β-forms of PPL[29] found that the methylene carbon atom (equivalent to C3 in PMEPL) is shielded by 1.5 ppm in the extended chain relative to the helical conformation, signifying that the eclipsed substituent in more shielded than the gauche one. Direct comparison with the observed shift in peak position for C3 in the two spectra of Figure 1 implies that isotactic PMEPL exists as a planar zigzag when melt crystallized and as a 2_1 helix in solution cast films. It must be noted, however, that the shift observed in the present case is significantly larger than that reported for PPL.

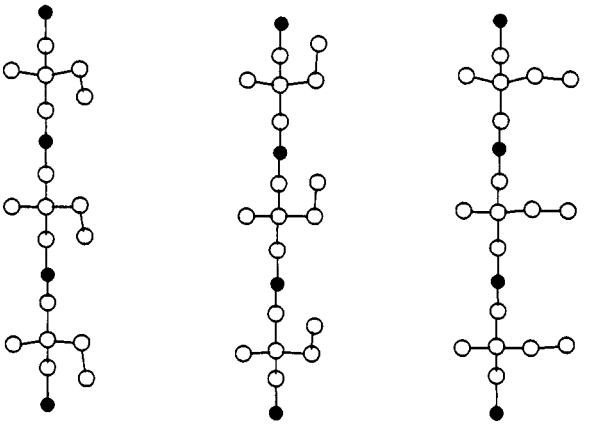
The carbonyl carbon, C1, possesses a gauche substituent in the 2_1 helix that is absent in the planar zigzag, and the corresponding resonance may therefore be expected to appear at different positions in the two conformations. However, since shielding by gauche substituents is known to be minimal for carbons not directly bonded to hydrogen atoms,[24] the absence of peak splitting at C1 does not preclude the possibility that the two spectra of Figure 1 do in fact correspond to the helical and extended chain conformations.

The shielding experienced by carbons C4 and C5 differs in helices of opposite handedness, and consequently, the change in chemical shift predicted for these atoms upon the transition from a helical conformation to the extended chain depends on the chirality of the initial helix. For example, for the isotactic polymer of absolute configuration *R*, C4 would be expected to be more highly shielded in the planar zigzag than in the right helix, but deshielded relative to the left helix. If indeed isotactic PMEPL crystallizes from the melt as an extended chain and from solution as a helix, the observation that C4 is more highly shielded in the solution cast sample implies that the helical conformation adopted by the *R* isomer is left-handed. The corresponding effect for C5 is, however, not observed.



I II III

Figure 6. Newman projections illustrating the possible rotational isomers of the α-ethyl group of isotactic PMEPL of absolute configuration *R*.



I II III

Figure 7. Models of the extended chain conformation of isotactic PMEPL illustrating the three rotational isomers of the α-ethyl group sketched in Figure 6. Oxygens atoms are indicated by shading and hydrogens atoms have been omitted for reasons for clarity. The carbonyl oxygens, located directly behind the corresponding carbon atoms, are not visible.

iii. Rotational Isomerism of the α-Ethyl Group. The two carbon atoms which show large shifts in peak position, i.e. C3 and C4, both occupy positions γ to the terminal methyl group of the α-ethyl side chain, suggesting that the differences observed between the NMR spectra of the various PMEPL samples may be related to conformational changes involving this substituent. The three possible rotational isomers differing in the torsion angle τ_3 are shown in Figure 6. A consideration of the number of gauche substituents in each isomer indicates that the observed peak displacements (i.e. the upfield shift of C3 and the downfield shift of C4 in melt crystallized PMEPL relative to the solution cast sample) can be explained by a change from conformer II to conformer III. This interpretation does not, however, exclude the possibility of concurrent changes in backbone conformation; that is, side-chain rotational isomer II may be preferred in the 2_1 helix, whereas isomer III predominates in the extended chain. Elementary molecular models, as sketched in Figure 7, do indeed indicate that this conformation is sterically favored in the planar zigzag conformation where the α-ethyl groups are all located along the same side of the polymer chain.

The hypothesis of an extended chain conformation for isotactic PMEPL when crystallized from the melt is confirmed by comparison with the NMR spectrum obtained for oriented samples, shown in Figure 8. Such samples were prepared by initial solution casting, and thus, before drawing, are characterized by the NMR spectrum of Figure 1b, with C2, C3, and C4 appearing at 47.5, 74.1, and 18.1 ppm, respectively. Upon drawing, the relative intensities of these resonances decrease and additional peaks appear at 46.1, 66.5, and 23.4 ppm, chemical shifts

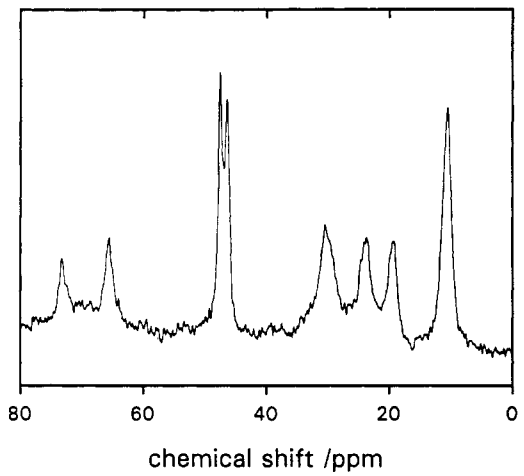


Figure 8. Solid-state ^{13}C NMR spectra of oriented isotactic PMEPL.

identical to those observed for C2, C3, and C4 in melt crystallized samples. Clearly, the conformation induced by stretching is the same as that present in samples crystallized from the melt.

The X-ray diffraction fiber pattern of oriented isotactic PMEPL is the same as that previously reported[7] for the atactic polymer and contains layer lines corresponding to a fiber repeat unit of 4.7 Å, the periodicity of the planar zigzag conformation.

The above interpretation of the solid-state NMR spectra assumes that the observed signals arise uniquely from the crystalline phase. The degree of crystallinity of melt crystallized isotactic PMEPL can be, however, estimated from differential scanning calorimetry as 40%, and therefore the apparent absence of signals from the amorphous phase must be explained. Carbon-13 spin–lattice relaxation times (T_1) were measured and found to be of the same order of magnitude (5–20 s) for carbons C1, C2, C3, and C5, and somewhat shorter (0.5–2 s) for the methyl carbons C4 and C6. These values are typical of crystalline polymers.[30] No significant variation in relaxation times was noted among the various samples and, more importantly, in instances where two peaks are observed for a single carbon, no differences were found between the two components. This observation confirms that although these atoms exist in two distinct environments, they experience similar motional constraints. Clearly neither component of such peak pairs corresponds to the amorphous phase, for which shorter relaxation times are expected. The absence of signals from the amorphous phase can be presumably attributed to extreme peak broadening resulting from both the distribution of conformations and environments found in the disordered phase, and other broadening mechanisms related to polymer motions.[31]

Infrared Spectroscopy

As illustrated in Figure 9, the infrared spectrum of isotactic PMEPL depends on the method of sample preparation. Spectra of melt crystallized films contain peaks located at 1318, 1135, 1013, and 789 cm^{-1} that are of diminished intensity or completely absent in spectra of the solution cast samples. The IR spectrum of an oriented sample of isotactic PMEPL, known from X-ray diffraction to be comprised of molecules in the extended chain conformation, is also shown (Figure 9c). Although peak assignments are not known, the similarities between the spectra of the melt crystallized and the oriented sample,

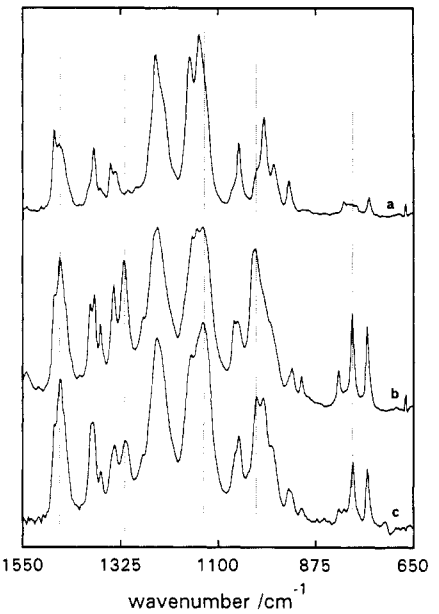


Figure 9. Infrared spectra of (a) solution cast, (b) melt crystallized, and (c) oriented films of isotactic PMEPL.

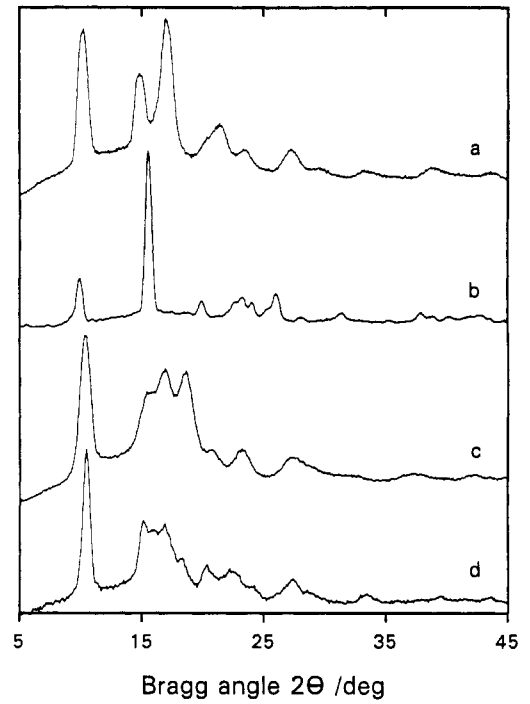


Figure 10. X-ray powder patterns of (a) atactic, (b) isotactic melt crystallized, (c) isotactic solution cast, and (d) the stereocomplex of PMEPL.

supports the conclusion drawn from the NMR experiments, namely, that isotactic PMEPL exists in the extended conformation in melt crystallized samples.

The IR spectra of melt crystallized and oriented isotactic PMEPL also differ from that of the solution cast sample in the relative intensity of the two peaks at 1476 and 1465 cm^{-1}, which can be assigned as CH_2 deformations. Doubling of this vibration has been previously reported for polyethylene, and attributed to interactions between adjacent molecules in the crystalline phase.[32]

X-ray Diffraction

The X-ray diffraction patterns of the various samples of PMEPL are presented in Figure 10. For melt crystallized samples, the same pattern is obtained regardless

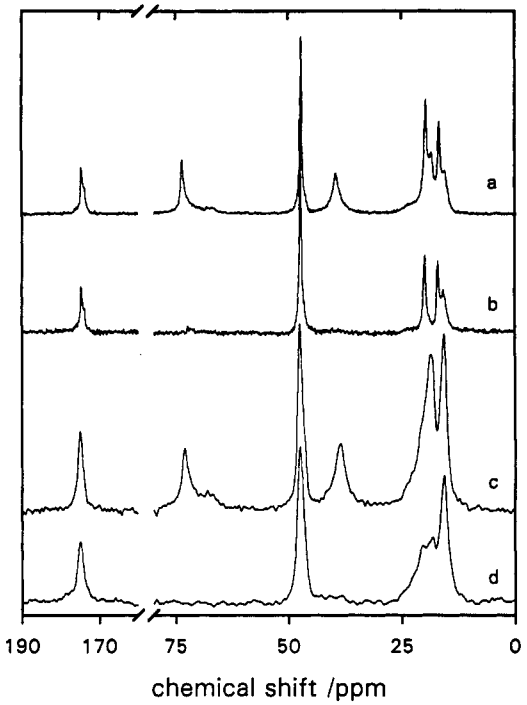


Figure 11. Solid state ^{13}C NMR spectra of (a) isotactic PMPPL, (b) isotactic PMPPL recorded with dipolar dephasing, (c) atactic PMPPL, and (d) atactic PMMPL recorded with dipolar dephasing.

Table II
Chemical Shifts (in ppm) and Peak Assignments for ^{13}C Spectra of Various Samples of PMPPL[a]

	isotactic		atactic		
		dipolar dephased		dipolar dephased	in $CDCl_3$ solution[35]
C1	174.7	174.5	174.9	174.8	174.3
C2	47.2	47.0	47.4	47.3	46.4
C3	73.5*		72.9*		69.0
	67.6		68.1		
C4	19.8	19.6	18.6	21.0	19.9
				18.2*	
C5	39.7		38.4		38.2
C6	18.8		18.6		17.6
C7	16.9*	16.8*	15.7	15.9	14.5
	15.9	15.7			

[a] The numbering of carbon atoms is defined in Figure 12. In cases where two resonances are observed for a single atom the major component is indicated with an asterisk.

of the cooling rate employed. Although the solid-state NMR spectra of the atactic polymer, isotactic solution cast samples and the stereocomplex are essentially identical, variations in their X-ray powder patterns indicate that these samples do not share a common crystal structure. Evidently, the NMR spectra are not sensitive to the differences in chain packing that must exist. A detailed electron diffraction study of the various crystal modifications of PMEPL and PMPPL has therefore been undertaken.[33]

Poly(α-methyl-α-propylpropiolactone) (PMPPL)

Solid-state ^{13}C NMR spectra of both atactic and isotactic PMPPL are presented in Figure 11. Peak assignments, summarized in Table II, were made on the basis of literature values from solution spectra[34] and with the assistance of dipolar dephasing. The main-chain methylene carbon (C3) appears near 73 ppm with a minor component at 68 ppm for both the isotactic and atactic polymers. By analogy to the discussion for PMEPL

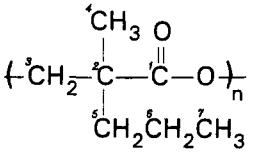


Figure 12. Chemical structure of PMPPL defining carbon atoms referred to in the text.

presented above, it can be concluded that PMPPL exists as a 2_1 helix in the two samples. This is in agreement with the fiber repeat distance of 6 Å reported for the α-phase of this polyester. Although peak overlap hinders the direct assignment of the resonances corresponding to C4, C6, and C7 (defined in Figure 12), these signals can be identified from information obtained with dipolar dephasing. Integration of the dipolar dephased spectra of both the atactic and isotactic polymers reveals that signals arising from only two carbon atoms are present in the region from 15 to 20 ppm, despite the fact that three peaks can be discerned. The methylene carbon, C6, has thus vanished completely, and only the two methyl carbons C4 and C7 remain, one of which appears as two peaks. In the dipolar dephased spectrum of isotactic PMPPL, it is the terminal methyl carbon, C7, of the α-propyl group that occurs as two components, located at 16.9 and 15.9 ppm. In the case of the atactic sample, it is the signal corresponding to the α-methyl carbon, C4, that seems to be split. Although the reason for the difference between the two samples is not obvious, a tentative explanation can be offered: since the atactic polymer contains equal numbers of repeat units of absolute configuration *R* and *S*, two different environments for C4 are expected in a helical conformation of a given handedness. In the isotactic case, however, all repeat units are identical and similar peak doubling would not be anticipated. The splitting of the signal attributed to C7 in spectrum of isotactic PMPPL may be the result of rotational isomerism of the α-propyl group, which is manifested as unresolved peak broadening in the atactic sample because of greater conformational disorder.

No dependence of NMR spectra on thermal history was found for PMPPL.

Conclusions

The solid-state ^{13}C NMR spectrum of poly(α-methyl-α-ethyl-β-propiolactone) shows high sensitivity to changes in polymer conformation. The spectra reveal that isotactic PMEPL crystallizes in two different forms which can be easily distinguished by the chemical shifts of the α-methyl and main-chain methylene carbon atoms. These resonances appear at 23.4 and 66.1 ppm, respectively, in the spectrum of melt crystallized isotactic PMEPL. By comparison to the spectrum of oriented samples, it is concluded that these peak positions are characteristic of the extended-chain conformation. The second crystal form of isotactic PMEPL is obtained on solution casting and is identified by a NMR spectrum in which the α-methyl and main-chain methylene carbons are located at 18.1 and 74.1 ppm, respectively. Similar spectra are also obtained for atactic PMEPL and the stereocomplex and are attributed to the 2_1 helical conformation. The chemical shift differences observed between the planar zigzag and helical conformations can be explained satisfactorily in terms of rotational isomerism of the α-ethyl group.

Although NMR spectroscopy indicates that atactic PMEPL and the stereocomplex share similar conformations, X-ray diffraction powder patterns reveal different crystal structures.

NMR spectra of poly(α-methyl-α-n-propyl-β-propiolactone) (PMPPL) suggest that both the atactic and isotactic polymer crystallize in a helical conformation.

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