Synthesis and Characterization of Racemic and Isotactic Poly(β-alkyl-β-propiolactone)s

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ABSTRACT: Isotactic poly(β-methyl-β-propiolactone) (poly(CH_3-PL)) and poly(β-ethyl-β-propiolactone) (poly(C_2H_5-PL)) with (*S*) and (*R*) configurations, respectively, were synthesized in yields of 70% via the polymerization of optically active β-(trichloromethyl)-β-propiolactone (CCl_3-PL) and β-(dichloroethyl)-β-propiolactone (CH_3CCl_2-PL). The polymerization was conducted in bulk, under vacuum, using the triethylaluminum/water or the diethylzinc/water catalysts. These polymerizations were followed by the dechlorination of the resulting chlorinated polymers, using the tri-*n*-butyltin hydride (Bu_3SnH) reducing agent. ^{13}C NMR spectroscopy shows that all the chlorinated and dechlorinated polymers have a degree of isotacticity of 100%, indicating that little or no racemization occurs during the course of the polymerization. Atactic homologues were also synthesized; these are soluble in the usual organic solvents, contrary to the isotactic polymers. Multiangle laser light scattering analyses of atactic polymers indicate that the dechlorination reaction occurs with some degradation, leading to poly(CCl_3-PL) and poly(CH_3-CCl_2-PL) with molecular weights of about 5000. The variations of the glass transition temperature, melting temperature, and enthalpy of fusion with the dechlorination ratio are discussed. The whole analysis shows that the dechlorination reaction generates statistical copolymers, with the formation of the intermediate homopolymers poly($CHCl_2$-PL) and poly(CH_2Cl-PL) in the case of the dechlorination of poly(CCl_3-PL). X-ray patterns show that each homopolymer has its own crystalline structure and that the semicrystalline copolymers adopt a crystalline structure similar to that of the homopolymer of closest composition.

Introduction

Poly[(*R*)-β-hydroxyalkanoates] (PHA), with the repeat unit ($CHR-CH_2-COO)_n$, are biodegradable polymers and exhibit potential applications in the environmental and biomedical fields.[1,2] They are synthesized by a wide variety of bacteria and function as intracellular carbon and energy storage materials.[3] These natural poly(esters) are highly isotactic and always exhibit the (*R*) stereochemical configuration. They often consist of copolymers containing mainly the β-hydroxybutyrate (HB) and β-hydroxyvalerate (HV) repeating units, where R is CH_3 and C_2H_5, respectively; poly(hydroxybutyrate) (PHB) is the only member of this series that has been observed as a true homopolymer, so far.[4]

The synthesis of such PHAs can also be carried out by the ring-opening polymerization of appropriate β-monosubstituted-β-propiolactones (β-PL).[5] On one hand, synthetic analogues are interesting model systems to investigate the effects of stereochemical and morphological parameters on the physical properties and biological activity of PHAs from bacterial origin which, in many cases, are produced only as copolymers in a limited range of compositions. On the other hand, the ring-opening route to PHB and other PHAs allows the synthesis of homopolymers and copolymers with tailored stereochemical and physical characteristics, which are not currently available from the biosynthetic route.

The β-monosubstituted poly(β-propiolactone)s (poly(β-PL)) are usually prepared by ring-opening polymerization of the corresponding β-PL, using principally anionic or coordination initiators.[5] When anionic initiators are used, a fully atactic polymer is usually formed with high yields[6−10] from racemic monomers, whereas an optically pure monomer leads to a highly isotactic polymer, as in the recently reported case of the polymerization of optically active β-methyl-β-propiolactone (CH_3-PL) using potassium alkoxides/18-crown-6 complex as catalyst.[11]

Coordination initiators have also been widely used. Actually, a series of poly(β-PL) was prepared from the ring-opening polymerization of the corresponding racemic β-PL by means of stereoselective organoaluminum or organozinc catalysts.[12−22] It is generally found that racemic monomers lead to atactic polymers,[17,20] although some initiators promote the formation of an isotactic small fraction.[13−16,21,22] Similar results were obtained with aluminoxane catalysts, $-(AlR-O)_n-$, although these catalysts are believed to be more stereoregulating and have better catalytic activity than the trialkylaluminum/water system.[23−26] Recently, Jesudason and Marchessault[27] reported the synthesis of highly isotactic poly(β-hydroxyheptanoate) and poly(β-hydroxynonanoate) by polymerization of the corresponding racemic monomers, using a trimethylaluminum/water catalyst, but the yields obtained were of the order of 5 and 2%, respectively. The use of tin-based catalysts has been finally investigated[28−31] and a predominantly syndiotactic poly(CH_3-PL), eventually after fractionation, was obtained from the polymerization of racemic CH_3-PL.

Isotactic poly(CH_3-PL) can more easily be obtained from the polymerization of optically active CH_3-PL by means of the $AlEt_3/H_2O$[12,13,32] or $ZnEt_2/H_2O$[32,33] initiators. In this last case, the polymerization proceeded primarily by the cleavage of the acyl−oxygen bond with retention of configuration[32,33] whereas, by using $AlEt_3$/

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H_2O in situ, the reaction proceeded through the cleavage of the acyl−oxygen bond (with retention of configuration) or the alkyl−oxygen bond (with inversion of configuration), depending on the method used for the preparation of the catalyst.[32] These attempts gave much better results than those obtained from the similar polymerization of racemic CH_3-PL, although the synthesis of optically active CH_3-PL with a high enantiomeric excess (ee) represents a difficult task,[13] involving sometimes many steps.[32] More recently, Ohta et al.[34] reported an easier synthesis of optically active CH_3-PL (ee = 92%) by the hydrogenation of diketene catalyzed by ruthenium complexes. Using this method of synthesis, Hori and co-workers[35] reported the polymerization of optically active (*R*)-CH_3-PL with very active distannoxane catalysts, leading to isotactic poly(CH_3-PL) of high molecular weight, in good yields.

Optically active β-PL can also be prepared by a method initially described by Wynberg and Staring[36,37] that involves a reaction between ketene and aldehydes in the presence of a chiral base, as quinidine and quinine. This method was used with success in our laboratory, to prepare, for instance, β-(trichloromethyl)-, β-(dichloroethyl)- and β-(dichloropropyl)-β-propiolactone (CCl_3-PL, CH_3CCl_2-PL, and $C_2H_5CCl_2$-PL, respectively) with a 100% enantiomeric excess and very good yields.[38−42] These monomers were then polymerized, using mainly $ZnEt_2/H_2O$[39] or $AlEt_3/H_2O$[38] as catalysts; crystalline and highly isotactic polymers were obtained, indicating that little or no racemization occurred in the course of the polymerization.

In view of the difficulties to produce high optical purity PHA analogues, in high yields, we propose a new method of synthesis of isotactic poly(CH_3-PL), poly(β-ethyl-β-propiolactone) (poly(C_2H_5-PL)), and poly(β-propyl-β-propiolactone) (poly(C_3H_7-PL)). It involves first the synthesis of optically active CCl_3-PL, CH_3CCl_2-PL, and $C_2H_5CCl_2$-PL, as already described by Prud'homme and co-workers;[39,40] these chlorinated monomers are then polymerized using $AlEt_3/H_2O$ or $ZnEt_2/H_2O$ catalysts, depending on whether inversion or retention is required; the dechlorination of the polymers is then achieved by means of the tri-*n*-butyltin hydride (Bu_3SnH) reductor, as described in the literature in the case of small molecules.[42] Because of the insolubility of these isotactic polymers in usual organic solvents, racemic poly(CH_3-PL) and poly(C_2H_5-PL) are also synthesized using the same strategy, to characterize all intermediates. This procedure presents the additional advantage of generating new polymers, for instance, poly(β-(dichloromethyl)-β-propiolactone (poly($CHCl_2$-PL)) from poly(CCl_3-PL). All polymers were characterized in terms of enantiomeric purity, molecular weight, degree of isotacticity, glass transition, melting temperature, and enthalpy of fusion.

Experimental Section

Materials. All chemicals used in this study were obtained commercially, except anhydrous chloral, ketene, and 2,2-dichloropropanal. Anhydrous chloral was obtained by drying chloral hydrate with concentrated sulfuric acid, separating the two layers, and then distilling. Triethylamine was purified by distillation. Gaseous ketene was prepared by pyrolysis of acetone vapors. Residual acetone vapors were eliminated with a chlorobenzene−dry ice trap maintained at − 40 °C. The generator produced 0.05 mol/h of ketene, as determined by the method described by Vogel.[43] 2,2-Dichloropropanal and 2,2-dichlorobutanal used, respectively, in the synthesis of CH_3CCl_2-PL and $C_2H_5CCl_2$-PL, were prepared by the method described by Verhé et al.[44]

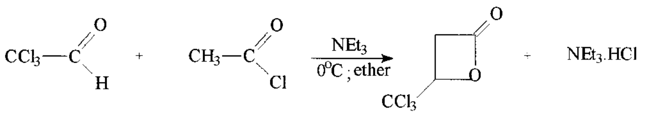
Methods. The purity of the chemicals used was verified with a Beckman IR-4250 spectrophotometer and by NMR spectroscopy. ^1H and ^{13}C NMR spectra of polymers in solution (5−15% w/v) in $CDCl_3$ or C_6D_6 were recorded at 200 MHz on a Varian XL-200 spectrometer, at room temperature, with a 4.5 μs pulse and 3000 Hz spectral width in the case of ^1H NMR and a 12.5 μs pulse and 13 000 Hz spectral width in the case of ^{13}C NMR. TMS was used as the internal reference. These conditions allowed a quantitative analysis.[45] The peaks were assigned to the corresponding atoms by considering data given in the literature.[16,46] Dechlorination ratios (τ) were calculated from ^1H NMR spectra by measuring the relative area of the peak characteristic of a chlorinated group over that of the CH group on the polymer backbone. The peak areas were evaluated using the Spectracalc Software. The dechlorination ratio of each sample was also determined by elemental analysis using a Carlos Erba 1106 analyzer. Cystine or acetanilide was used for calibration. A good correlation (2% variation) was observed between the dechlorination ratios determined by ^1H NMR and elemental analysis. Elemental analysis was sometimes the only method used for the determination of τ when NMR was not appropriate, e.g., in the case of little or no dechlorinated isotactic poly(CCl_3-PL), which is insoluble in usual organic solvents, and in the case of atactic poly(CCl_3-PL) with a τ value lower than 33%, because of the overlap of the peaks characteristic of the $CHCl_2$ lateral group and the CH on the main chain having a CCl_3 in its neighborhood.

Measurements of optical rotation were made with a JASCO DIP 360 polarimeter, at 589 nm and 27 °C, at a concentration of 10 g/L in spectroscopic grade chloroform. Molecular weights were determined by multiangle laser light scattering (MALLS) using a Dawn-F photogoniometer from Wyatt Technologies in the static mode, at 632 nm and 40 °C. Sample concentrations between 2 and 20 g/L, in chromatographic quality butyl acetate, were used. At least 6 mL of the polymer solution was introduced in 25 mm diameter scintillation bottles, which have been washed with sulfochromic acid first and then with acetone vapor, as described in the literature.[47] d*n*/d*c* values were determined using a Wyatt Optilab 903 differential refractometer, at 632 nm. Sample concentrations between 1 and 5 g/L, in chromatographic grade butyl acetate, were used. d*n*/d*c* values that were not experimentally measured, were determined by interpolation.

A Perkin-Elmer DSC-4 apparatus, equipped with a 3600 TADS computer and a cooling accessory, was used for calorimetry measurements. The analyses were made at a scanning rate of 20 °C/min, and indium was used for calibration. The melting temperature (T_m) was recorded from the first scan at the end of the melting peak. For measurements of the glass transition temperature (T_g), atactic poly(CCl_3-PL) and poly(CH_3CCl_2-PL) were heated until 130 °C, then quenched, and scanned again up to 130 °C. With partially dechlorinated poly(β-PL), the same operating procedure was used but the samples were heated until 100 °C only, to avoid a possible decomposition. With isotactic poly(β-PL), the procedure was similar but the scan was usually stopped when the temperature exceeded T_m by 20−30 deg, except in the case of isotactic poly(CCl_3-PL) where the decomposition immediately followed the melting. All T_g's were taken from the second scan at the midpoint of the heat capacity jump.

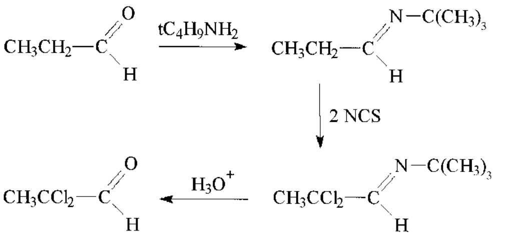
The X-ray diffraction patterns of isotactic poly(β-PL) were recorded at room temperature with a Rigaku RU200B system using the nickel-filtered Cu Kα radiation (λ = 0.154 nm, 40 kV, 190 mA) in the 2θ range 5−50° at a scan speed of 0.80°/min each 0.04°. Samples were usually analyzed in the form of a powder maintained in 1.5 mm diameter Lindemann capillaries.

Synthesis. Synthesis of Racemic β-(Trichloromethyl)-β-propiolactone (CCl_3-PL). The synthesis of racemic β-(trichloromethyl)-β-propiolactone (CCl_3-PL) was carried out from chloral and acid chloride (eq 1) according to the method described by Lavallée et al.,[38] without further modification (yield: 89%):



(1)

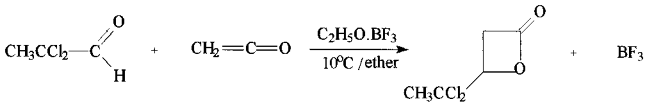
Synthesis of 2,2-Dichloropropanal. The synthesis of 2,2-dichloropropanal was carried out from propanal (eq 2), where NCS is *N*-chlorosuccinimide, according to the method described by Verhé et al.[44] (yield: 60%):



(2)

CH_3CCl_2CHO: $T_b = 78-80$ °C/760 mmHg; IR(NaCl), $\nu_{max} = 1740$ cm^{-1} (C=O); ^{1}H NMR (60 MHz, $CDCl_3$) $\delta_1 = 2.16$ ppm (s, CH_3), $\delta_2 = 9.30$ ppm (s, CHO). The same procedure was used for the synthesis of 2,2-dichlorobutanal used in the synthesis of optically active $C_2H_5CCl_2$-PL.

Synthesis of Racemic β-(Dichloroethyl)-β-propiolactone (CH_3CCl_2-PL). The synthesis of racemic β-(dichloroethyl)-β-propiolactone (CH_3CCl_2-PL) was carried out from 2,2-dichloropropanal and ketene, following eq 3, according to the method described by Knunyants and Cherbukov[48] (yield: 63%):



(3)

The synthesis of optically active CCl_3-PL, CH_3CCl_2-PL, and $C_2H_5CCl_2$-PL was carried out according to the method described by Prud'homme and co-workers,[38,39] without further modification. The addition of an optically active catalyst, like quinidine, to the reaction medium allows the obtention of β-(chloroalkyl)-β-propiolactones with the (*R*) stereochemical configuration and a high optical purity.

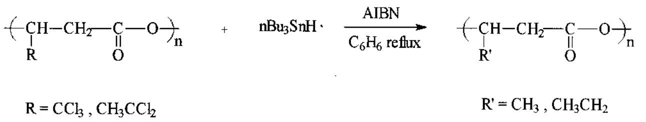
Synthesis of Optically Active β-Methyl-β-propiolactone (CH_3-PL). The synthesis of optically active β-methyl-β-propiolactone (CH_3-PL) was achieved by the dechlorination of optically active (*R*)-CCl_3-PL, according to the procedure already used, in our laboratory, for the dechlorination of α-dichloro-β-ethyl-β-methyl-β-PL:[49] into a 500 mL three-neck flask equipped with a cooler and a magnetic stirrer, 5 g of optically active CCl_3-PL (26.4 mmol) is dissolved, under a nitrogen flow, in 50 mL of benzene (distilled and dried on sodium). 2,2′-Azobis(isobutyronitrile) (AIBN) (28 mg, 0.17 mmol) is then added, and 21.3 mL (79.2 mmol) of tri-*n*-butyltin hydride (Bu_3SnH) is injected. This solution is allowed to stand at room temperature with stirring over 72 h. The excess of Bu_3SnH is eliminated at the end of the reaction by adding a few drops of CCl_4. Benzene is evaporated under reduced pressure (100 mmHg), and the residual mixture is heated in order to isolate (*R*)-CH_3-PL which has a boiling temperature of 100 °C under reduced pressure (100 mmHg). Yields of about 25% were obtained.

Polymerization and Dechlorination. The polymerization was conducted in bulk, at 60 °C, under vacuum (10^{-4}–10^{-5} mmHg), using $AlEt_3/H_2O$ for (*R*)-CCl_3-PL and $ZnEt_2/H_2O$ for (*R*)-CH_3CCl_2-PL and (*R*)-$C_2H_5CCl_2$-PL, as stereoselective catalysts. The procedure described by Lavallée et al.[38] was applied without further modification.

Table 1. Quantities of Polymer, AIBN, and Bu_3SnH Used in the Dechlorination Reaction of Poly(CCl_3-PL), Poly(CH_3CCl_2-PL), and Poly($C_2H_5CCl_2$-PL) and Resulting Polymer Yields

	polymer		AIBN		Bu_3SnH		polymer
polymer	g	mmol	mg	mmol	g	mmol	yield, %
poly(CCl_3-PL)	5	26.4	28	0.17	21.3	79.2	90
poly(CH_3CCl_2-PL)	5	29.2	21	0.13	15.7	58.4	70
poly($C_2H_5CCl_2$-PL)	5	27.3	19	0.12	14.7	54.6	0

The reaction of dechlorination was carried out as follows:

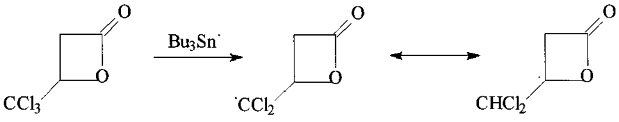


(4)

This procedure is the same as that previously described for the dechlorination of optically active CCl_3-PL but with different polymer/AIBN/Bu_3SnH ratios in order to keep equimolar quantities of chlorine atoms and reducing agent Bu_3SnH. The quantities used for different polymers are given in Table 1. After the required time, aliquots of poly(β-PL) were removed, then isolated by precipitation of the solution into hexane or methanol, and finally dried for 1 week under reduced pressure at 60 °C.

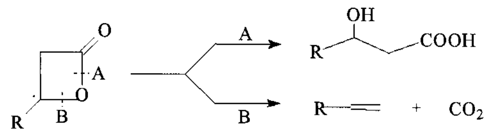
Results and Discussion

Dechlorination Reaction. Synthesis of Optically Active CH_3-PL. The more direct method to obtain poly(β-propiolactones) consists of the polymerization of the corresponding monomer. To synthesize optically active CH_3-PL, we chose to prepare, first, the optically active CCl_3-PL, followed by its dechlorination, since previous results obtained in our laboratory[38,39] indicated that CCl_3-PL can be obtained with a high optical purity in high yields. Several dechlorination attempts were made, varying parameters such as the temperature (10–50 °C), the CCl_3-PL concentration (0.13–0.52 mol/L), and the reaction time (24–168 h). The best results were obtained when the reaction was allowed to stand for 3 days at room temperature. However, the dechlorination reaction also leads to the formation of byproducts and a low 26% yield was obtained. The byproducts were not precisely identified, but it was observed that they contain ester, hydroxyl, carbonyl, and/or ethylenic groups. An attempt to reduce the formation of byproducts was made by carrying out the reaction at 10 °C, but $CHCl_2$ groups were still present after 7 days. These results might be explained if the formation of an initial primary radical on the lateral group is considered. This unstable radical can shift toward the β carbon atom of the ring, leading to a more stable secondary radical:



(5)

The latter and its dechlorinated homologues can lead to an opening of the ring by different types of cleavage and to the formation of byproducts as, for instance, hydroxy-2-butyric acid, or CO_2 and propane derivatives, obtained by the decomposition of the lactone:



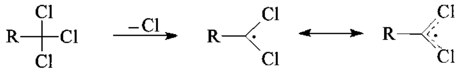
(6)

The yield obtained (26%) is lower than that of the dechlorination of α-dichloro-β-ethyl-β-methyl-β-propiolactone (62%), from which this reaction is based.[49] In this second case, the formation of byproducts might occur to a lesser extent because of the direct formation of a secondary radical. Considering the results, we then chose to proceed to the direct dechlorination of poly(CCl_3-PL) instead of its monomer.

Poly((chloroalkyl)-β-propiolactone)s. Dechlorination ratios (τ) of 100% were obtained for atactic and isotactic poly(CCl_3-PL) and poly(CH_3CCl_2-PL). However, it appeared that the synthesis of poly(C_3H_7-PL) by dechlorination of the chlorinated corresponding polymer was impossible.

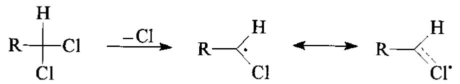
The evolution of τ versus time, at 80 °C, for isotactic and atactic poly(CCl_3-PL), and atactic poly(CH_3CCl_2-PL), is given in Figure 1. It is observed that dechlorination rates are initially rapid, but they decrease after 1 h, whatever the nature of the poly(β-PL). However, the reaction time required for a complete reduction depends on the nature of the polymer: it requires 48 h for atactic poly(CCl_3-PL) and only 24 h for atactic poly(CH_3CCl_2-PL). It is also seen that the dechlorination rate of atactic poly(CCl_3-PL) is higher than that of atactic poly(CH_3CCl_2-PL).

The decrease of the reaction rate at longer time can be explained by two phenomena. On one hand, the number of chlorine atoms and the concentration of reducting agent decrease with time; on the other hand, the stability of the intermediate radical influences the reaction rate: the more stable the radical, the easier the cleavage of the C−Cl bond, and the higher the reaction rate. Actually, in the case of poly(CCl_3-PL), the first chlorine atom leads to the formation of a dichloromethyl radical stabilized by resonance:



(7)

The chloromethyl radical generated by the departure of the second chlorine atom is also stabilized by resonance, but to a lesser extent:



(8)

In contrast, when there is no more chlorine atom on the methyl radical, no stabilization occurs. Consequently, the substitution of the first chlorine atom is easier than that of the second, which is, in turn, easier than that of the third one. In the case of poly(CH_3CCl_2-PL), the intermediate radical produced by the departure of the first chlorine atom is less stable than that of poly(CCl_3-PL), which could explain a lower initial reaction rate. Moreover, the presence of a bulky CH_3 group can make the approach to the active site more difficult and, then, reduce the reaction rate. However, the dechlorination of poly(CH_3CCl_2-PL) is achieved more rapidly than that of poly(CCl_3-PL) because only two chlorine atoms are replaced, against three in the case of poly(CCl_3-PL).

Figure 1 also shows that the dechlorination rate of isotactic poly(CCl_3-PL) is lower than that of the atactic corresponding polymer. This is probably due to its low solubility in organic solvents. Actually, isotactic poly(CCl_3-PL) is insoluble in benzene even at high temperatures. However, the dechlorination increases the solubility of the polymer that becomes soluble after a reaction time of about 10 min, at 80 °C, when τ is about 47%. In contrast, a value of τ of 61% is obtained in the case of atactic poly(CCl_3-PL) after the same reaction time. Moreover, unlike atactic polymers, the reduction reaction does not go to completion when equimolar quantities of chlorine atoms and reducing agent are used, and τ's remain between 76 and 81% even after 120 h. Nevertheless, values of τ of 100% can be obtained when a partially dechlorinated polymer ($\tau = 84\%$) is dechlorinated for a second time, at 80 °C, for 96 h. The fact that the dechlorination reaction, using equimolar quantities of chlorine atoms and reducing agent, is not possible, in this case, can be explained by considering that a fraction of the reducing agent reacts with the ester groups, at the very beginning of the reaction, leading to some degradation of the polymer. This degradation leads to a decrease of the polymer molecular weight, which increases the solubility of the polymer. The reduction that is experimentally observed at the beginning of the reaction, seems to occur simultaneously with the degradation reaction. When the polymer becomes soluble, the dechlorination can proceed without simultaneous degradation. It was unfortunately impossible to verify this assumption because of the insolubility of the isotactic poly(CCl_3-PL) in usual organic solvents.

Isotactic poly(C_2H_5-PL) was obtained from the dechlorination of isotactic poly(CH_3CCl_2-PL), after 24 h, at 80 °C. In this case, unlike the case of isotactic poly(CCl_3-PL), equimolar quantities of chlorine atoms and reducing agent lead to a complete dechlorination. This result can be understood if the molecular weight of isotactic poly(CH_3CCl_2-PL) is lower than that of the isotactic poly(CCl_3-PL), leading to a better solubility of the former at the very beginning of the reaction. It could also be due to the fact that the repeat unit of poly(CH_3CCl_2-PL) contains one chlorine atom less than poly(CCl_3-PL), which could lead to a decrease of the polymer−polymer interaction.

The synthesis of isotactic poly(C_3H_7-PL) by the dechlorination of the corresponding chlorinated polymer leads to maximum values of τ of 67% when the reaction occurred at 80 °C, after 24 h. Moreover, the polymer yields are low: 6 and 18% when the reaction occurs at, respectively, 80 and 50 °C. No reaction occurred at room temperature. This low reactivity could be due to the steric hindrance of the dichloropropyl group on the lateral chain, which limits the reduction reaction in favor of the chain degradation. In addition, it is possible that the initial MW of poly(C_3H_7-PL) is low and that the degradation leads to oligomers with MW much lower, which cannot be easily recovered by precipitation, as will be verified, later, by the determination of the molecular weight of the initial polymer that is soluble in the usual organic solvents.

NMR Analyses. ^{1}H NMR spectra of poly(CCl_3-PL), poly(CH_3-PL), and partially dechlorinated intermediates are shown in Figure 2. The spectrum of poly(CCl_3-PL) shows two peaks characteristic of the methine (6.1 ppm, C_1) and methylene (3.3 ppm, C_2) groups. The spectrum of partially dechlorinated poly(CCl_3-PL) with a τ value

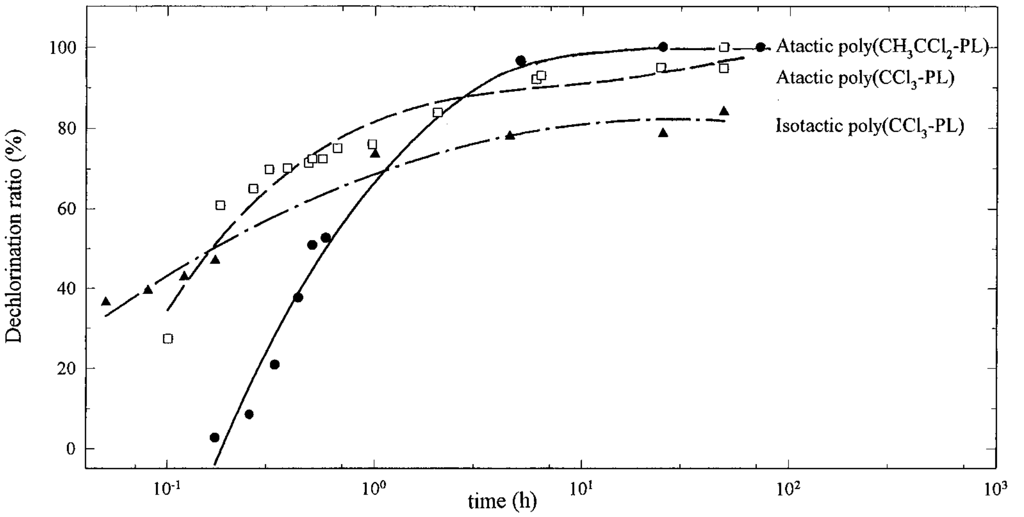


Figure 1. Dechlorination ratio of atactic and isotactic poly(CCl_3-PL) and atactic poly(CH_3CCl_2-PL) as a function of reaction time at 80 °C.

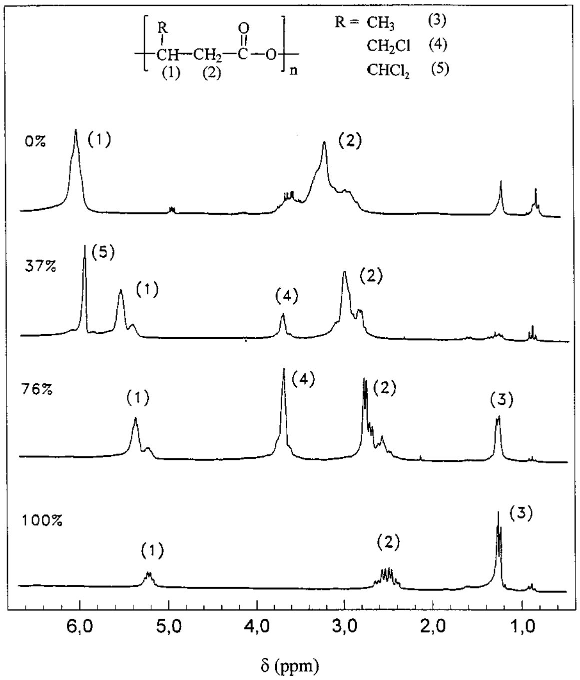


Figure 2. ^{1}H NMR spectrum of partially dechlorinated poly(CCl_3-PL).

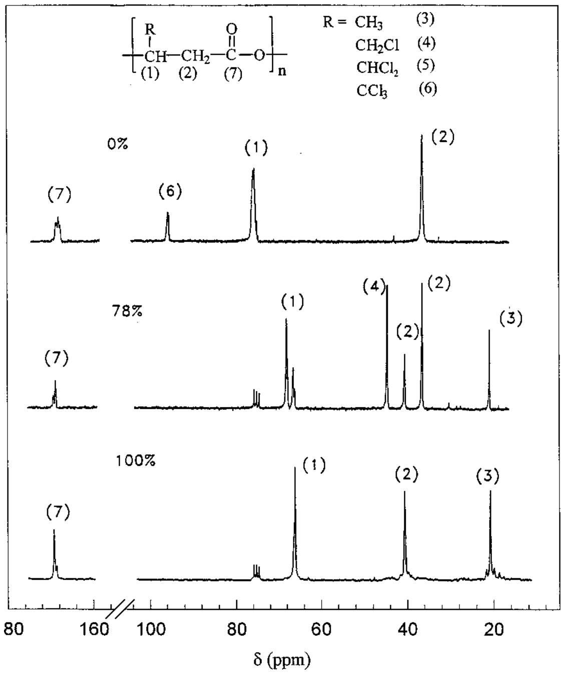


Figure 3. ^{13}C NMR spectrum of partially dechlorinated poly(CCl_3-PL).

of 37% shows two additional peaks corresponding to the $CHCl_2$ (5.98 ppm, C_5) and CH_2Cl (3.71 ppm, C_4) groups. Moreover, the peaks characteristic of the methine (C_1) and methylene (C_2) groups of the main chain are found at lower chemical shifts, indicating the disappearance of CCl_3 groups. They are also split into two peaks at, respectively, 5.57 and 5.41 ppm for C_1 and 3.02 and 2.80 ppm for C_2, indicating the appearance of two types of neighboring groups, e.g., $CHCl_2$ and CH_2Cl. The spectrum of the partially dechlorinated poly(CCl_3-PL) with a τ value of 76% (Figure 2) shows that the lateral groups mainly consist of CH_2Cl groups (3.71 ppm, C_4) with a few CH_3 groups (1.26 ppm, C_3). The peaks characteristic of the methine (C_1) and methylene (C_2) groups continue to decrease in chemical shift at 5.41 and 5.21 ppm for C_1, and 2.80 and 2.50 ppm for C_2, indicating a smaller amount of chlorinated groups in their neighborhood. Finally, the dechlorinated poly(CCl_3-PL) with a τ value of 100% perfectly fits with that of natural PHB reported by Doi et al.[46]

Figure 3 shows the ^{13}C NMR spectra of poly(CCl_3-PL), poly(CH_3-PL), and a partially dechlorinated intermediate. The spectrum of poly(CCl_3-PL) shows the presence of the three carbon atoms of the main chain, characteristic of the methylene (78 ppm, C_1), methine (36 ppm, C_2), and carbonyl (169 ppm, C_7) groups and that of the CCl_3 lateral group (98.9 ppm, C_6). The latter disappears on the spectrum of the dechlorinated intermediate with a τ value of 78%, proving the total disappearance of these groups, in agreement with the chemical shift of the methine and methylene groups observed on the corresponding ^{1}H NMR spectrum. The appearance of the peaks characteristic of the CH_2Cl (45 ppm, C_4) and CH_3 (20 ppm, C_3) groups is also observed, and the peaks characteristic of the methylene and the methine groups are split into two peaks because of the presence of these two groups in their neighborhood. The spectrum of poly(CH_3-PL) with a τ value of 100%

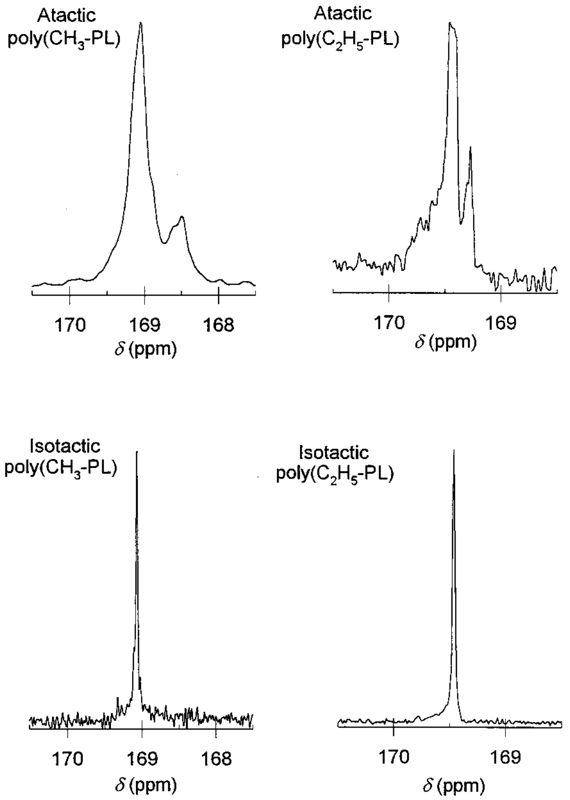


Figure 4. Enlargement of the ^{13}C NMR spectra of atactic and isotactic poly(CH_3-PL) and poly(C_2H_5-PL) in the carbonyl carbon region.

perfectly fits with that of natural PHB reported by Doi et al.,[46] confirming a complete dechlorination.

Both series of NMR spectra indicate that the chlorine atoms on the lateral group do not leave randomly, but one by one. Actually, each lateral group loses one chlorine atom after about 10 min of reaction, at 80 °C, and, therefore, it is possible to isolate poly($CHCl_2$-PL). Similarly, poly(CH_2Cl-PL) can be isolated after 30 min of reaction, at the same temperature. The departure of the last chlorine atom occurs much later, and poly(CH_3-PL) can be obtained after 48 h only, at 80 °C. Similar observations were made from the ^1H and ^{13}C NMR spectra of poly(CH_3CCl_2-PL). Dechlorination also occurs with a one by one departure of the chlorine atoms, but it takes about 30 min of reaction, at 80 °C, before the first chlorine atom could not be observed anymore, more than in the case of poly(CCl_3-PL).

The isotacticity of polypropiolactones is usually calculated from their ^{13}C NMR spectrum by using the peaks characteristic of the carbonyl group at 169 ppm. In the case of poly(CH_3-PL), Gross et al.[23] assigned the peaks at 169.12 and 169.22 ppm to isotactic and syndiotactic diads, respectively, whereas Bloembergen et al.[24] reported chemical shifts at 169.05 and 169.16 ppm for the same diads. For poly(CH_3CH_2-PL), these peaks are reported to be at 169.43 and 169.55 ppm, respectively.[24] In both cases, isotactic diads are located at higher fields than syndiotactic diads. Figure 4 shows an enlargement of the isotactic and atactic poly(CH_3-PL) and poly(CH_3CH_2-PL) ^{13}C NMR spectra in the carbonyl group region. The presence, on one hand, of two peaks at 169.04 ppm (syndiotactic diads) and 168.93 ppm (isotactic diads) for atactic poly(CH_3-PL) and, on the other hand, at 169.44 ppm (syndiotactic diads) and 169.30 ppm (isotactic diads) for atactic poly(CH_3CH_2-PL) shows that the atactic polymers consist of a partial stereoregularity, that is 18% for poly(CH_3-PL) and 23% for poly(CH_3CH_2-PL). This observation confirms the partially stereoselective character of $AlEt_3/H_2O$, which was used as an initiator in the polymerization of these two polymers, as already observed for the polymerization of other β-lactones.[16,23,24] In the case of isotactic poly(CH_3-PL) and poly(CH_3CH_2-PL) obtained from optically pure precursors, only one peak, characteristic of the carbonyl group, is observed at 169.07 and 169.45 ppm, respectively (Figure 4), proving that these polymers are fully isotactic. This observation indicates that the use of $AlEt_3/H_2O$ and $ZnEt_2/H_2O$ as catalysts in the polymerization of the optically active CCl_3-PL and CH_3CCl_2-PL, leads to little or no racemization. The slight differences in chemical shift of the peaks corresponding to the isotactic diads of atactic and isotactic polymers, probably comes from a solvent effect; actually, deuterated chloroform was used for the NMR characterization of the isotactic polymers, whereas the atactic polymers were dissolved in deuterated benzene.

Optical Rotation. Specific rotation values of +3.7 and −9.5 were determined, at 589 nm and 27 °C, in chloroform, for, respectively, isotactic poly(CH_3-PL) and poly(CH_3CH_2-PL). All monomers being in the (*R*) stereochemical configuration, the sign of the measured angles can indicate if there is a retention or an inversion of the configuration during the polymerization and, consequently, the stereoselectivity of the catalyst used. The configuration of dextrorotatory poly(CH_3-PL) is known to be (*S*);[22,35b] thus, the polymerization of optically active (*R*)-CCl_3-PL using $AlEt_3/H_2O$ as catalyst leads to an isotactic polymer in the (*S*) configuration, indicating that the polymerization occurred with an inversion of the configuration. This result is in agreement with that obtained by Zhang et al.[32] for the polymerization of (*S*)-CH_3-PL. For optically active (*R*)-CH_3CCl_2-PL, it is difficult to conclude if its polymerization occurred with a retention or an inversion of configuration because no value of optical rotation of the optically pure CH_3CH_2-PL or of the isotactic poly(CH_3CH_2-PL) is available in the literature. Nevertheless, the negative sign of poly(CH_3CH_2-PL) as compared to the positive sign of poly(*S*)-CH_3-PL could suggest that this polymer is in the (*R*) configuration and, consequently, that the polymerization of (*R*)-CH_3CH_2-PL using $ZnEt_2/H_2O$ as catalyst, occurred with a retention of configuration, as obtained by Zhang et al.[32] for the polymerization of (*S*)-CH_3-PL. However, the studies of Kobayashi et al.[35b] about the copolymerization of (*R*)-CH_3-PL and (*R*)-CH_3CH_2-PL suggest that the configuration of levorotatory poly(CH_3CH_2-PL) could be (*S*); if this result is confirmed, there would be an inversion of the configuration during the polymerization of (*R*)-CH_3CH_2-PL.

Refractive Index Increment. The determination of the refractive index increment (d*n*/d*c*) of the polymers in solution was necessary to calculate molecular weights. d*n*/d*c* values depend on the polymer/solvent interactions, temperature, and wavelength of the incident light and are considered independent of the polymer molecular weight above 1000. The evolution of the d*n*/d*c* of atactic poly(CCl_3-PL) as a function of dechlorination ratio is given in Figure 5. A linear increase is first observed until a dechlorination ratio of 65%, followed by a linear decrease. This variation can be explained if the partially dechlorinated poly(CCl_3-PL) are considered as statistical copolymers in which the repeat units differ

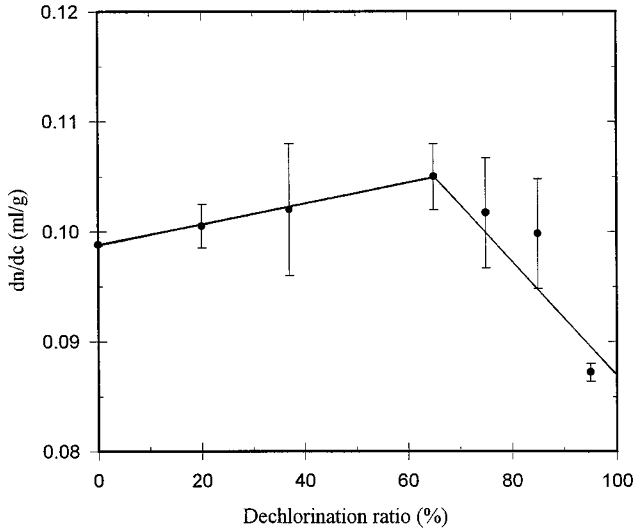


Figure 5. Refractive index increment (d*n*/d*c*) of atactic poly(CCl3-PL) as a function of dechlorination ratio in butylacetate.

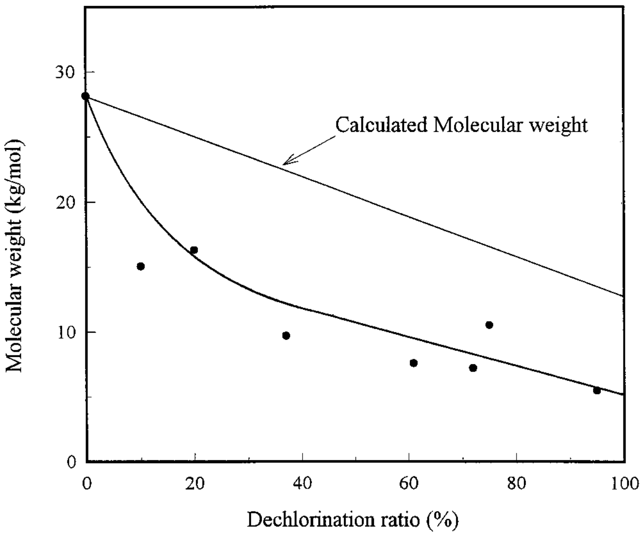


Figure 6. Molecular weight (M_w) of atactic poly(CCl_3-PL) as a function of dechlorination ratio.

depending on the nature of the lateral group. As observed from NMR spectra, the chlorine atoms leave one by one, leading to the successive appearance of poly($CHCl_2$-PL), poly(CH_2Cl-PL), and finally, poly(CH_3-PL). We can then consider that binary copolymers are formed during the dechlorination reaction. The d*n*/d*c* of a copolymer varies as follows with composition:

$$\mathrm{d}n/\mathrm{d}c = w_A(\mathrm{d}n/\mathrm{d}c)_A + w_B(\mathrm{d}n/\mathrm{d}c)_B \qquad (9)$$

where $(\mathrm{d}n/\mathrm{d}c)_A$ and $(\mathrm{d}n/\mathrm{d}c)_B$ are, respectively, the refractive index increment of homopolymers A and B, and w_A and w_B, are the weight fractions of the A and B units in the copolymer. Equation 9 is based on the additivity of the polarizability of each copolymer constituent and involves a linear variation of d*n*/d*c* between the corresponding homopolymers, i.e., between poly(CCl_3-PL) and poly($CHCl_2$-PL), poly($CHCl_2$-PL) and poly(CH_2Cl-PL), and poly(CH_2Cl-PL) and poly(CH_3-PL). Figure 5 shows, within the experimental uncertainty, this behavior but without a distinct break at a dechlorination ratio of 33%. However, a sudden decrease of d*n*/d*c* appears above 66%, as the last chlorine atom of poly(CH_2Cl-PL) is replaced by a hydrogen atom to form poly(CH_3-PL). This behavior suggests that the departure of the last chlorine atom leads to an important modification of the polarizability of the polymer, in contrast with the departure of the first and second chlorine atoms, for which smaller variations were observed. This sort of behavior has already been reported in the case of small molecules. For instance, the d*n*/d*c* of acetone is 1.359, whereas chloroacetone, dicholoro-1,1-acetone, and trichloro-1,1,1-acetone d*n*/d*c* values are, respectively, 1.435, 1.446, and 1.461. Similar results were obtained for poly(CH_3CCl_2-PL).[50]

Molecular Weights. The evolution of the molecular weight (MW) of poly(CCl_3-PL) with dechlorination ratio is shown in Figure 6. First, it is observed that the MW of poly(CCl_3-PL) (28 k) is in good agreement with the 10−40 k values obtained by Lavallée et al.[38] for the same polymer using similar conditions of polymerization. In addition, all the experimental MW fall below the calculated ones that consider only the dechlorination reaction. This result proves that chain degradation also occurs, especially at the beginning of the reaction. Since the experimental slope becomes equal to the calculated slope beyond a dechlorination ratio of about 20%, it is suggested that the degradation reaction becomes nonimportant in that region. Actually, the decrease of the $\overline{DP}_n$ of the polymer from 149 (MW = 28k) for poly(CCl_3-PL) to about 63 (MW = 5k) for poly(CH_3-PL), means that each chain undergoes approximatively 2.4 cuts.

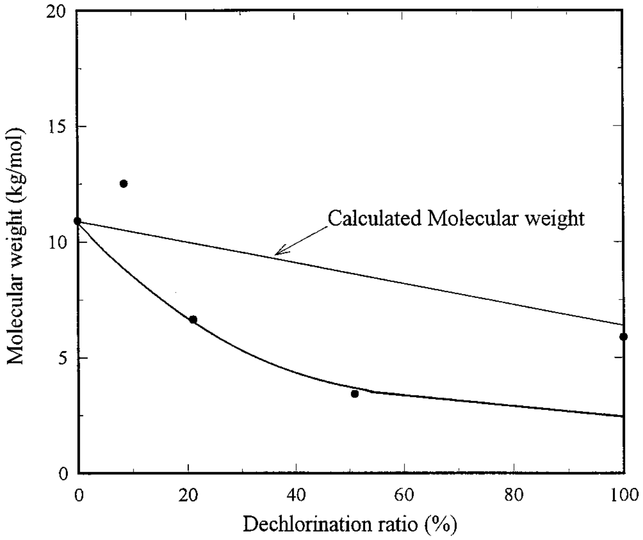


Figure 7. Molecular weight (M_w) of atactic poly(CH_3CCl_2-PL) as a function of dechlorination ratio.

Figure 7 shows similar results concerning the evolution of the MW of poly(CH_3CCl_2-PL) with dechlorination ratio with, however, a large uncertainty for each of the data points. Nevertheless, the MW of poly(CH_3CCl_2-PL), equal to 11k, is close to the 5−10k values obtained by Lavallée et al.[38] for the same polymer under similar conditions of polymerization. If the extrapolated value of 2500 of Figure 7 is used, it leads to a decrease of $\overline{DP}_n$ from 64 (MW = 11k) for poly(CH_3CCl_2-PL) to 25 for poly(C_2H_5-PL), involving about 2.5 cuts per chain, as in the previous example.

The molecular weight of isotactic poly(CCl_3-PL) and poly(CH_3CCl_2-PL) could not be determined because of the insolubility of these polymers in the usual organic solvents. However, for isotactic poly($C_2H_5CCl_2$-PL), which is soluble in butyl acetate, a MW of 28k was

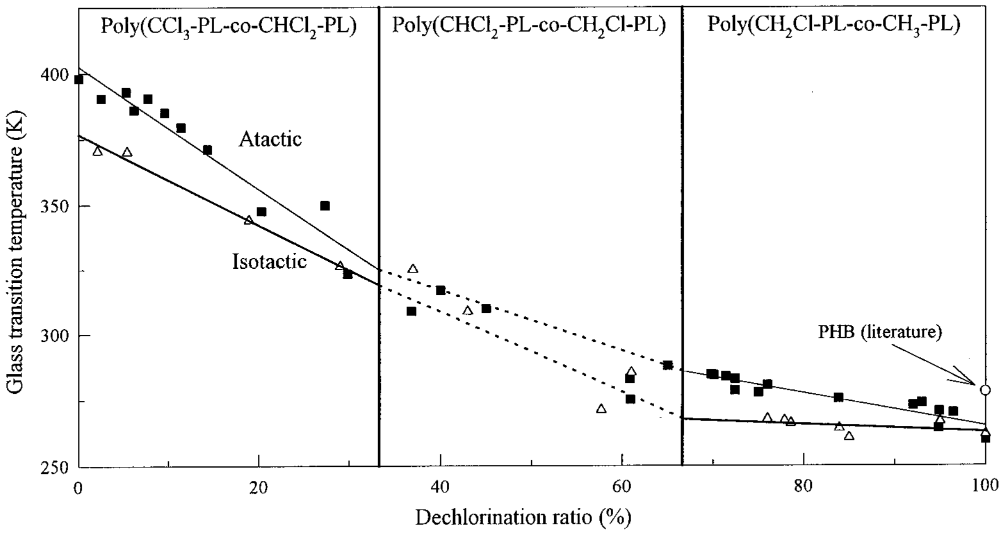


Figure 8. Evolution of the glass transition temperature (T_g) of atactic and isotactic poly(CCl_3-PL) with dechlorination ratio.

determined. The calculated MW of poly($C_2H_5CH_2$-PL), considering only the dechlorination reaction, is then 17.4k. Such a MW should lead to a polymer that can be recovered by precipitation but, since the polymer could not be precipitated, it is suggested that there was a large amount of degradation, involving the transformation of the polymer into oligomers that are soluble in hexane. This degradation could be promoted by the presence of the bulky alkyl group that slows down the dechlorination reaction.

Calorimetric Measurements. Figure 8 shows the T_g of atactic and isotactic poly(CCl_3-PL) as a function of the dechlorination ratio (τ). It is observed that T_g decreases with τ, in agreement with the theory of the free volume:[51] the progressive substitution of chlorine atoms of poly(CCl_3-PL) by smaller hydrogen atoms leads to an increase of the free volume, because the polar and bulky chlorine atoms increase the lateral intermolecular forces and diminish the chain motions, so that the free volume of poly(CH_3-PL) is higher than that of poly(CCl_3-PL). The decrease in T_g observed in Figure 8 is also partially due to the decrease of the MW with dechlorination ratio, as reported in Figure 7. In addition, it is observed that the decrease of T_g with τ is not linear; actually, each of the curves can be separated in three distinct portions with limits for τ values of 0 and 33%, 33 and 66%, and 66 and 100%. A least-squares analysis was applied to the first and third areas, between τ values of 0 and 33% and 66 and 100%, respectively. However, it could not be applied to the middle area because the number of data points is too small and the scatter too large; the dashed lines shown in Figure 8 simply join the interpolated values at 33 and 66% and should be considered as a guide to the eye. The overall result shown in Figure 8 is believed to indicate the generation of copolymers. According to the observations made from the NMR spectra concerning the one by one departure of the chlorine atoms, we can suggest that poly(CCl_3-PL), poly(CCl_3-PL-*co*-$CHCl_2$-PL), poly($CHCl_2$-PL), poly($CHCl_2$-PL-*co*-CH_2Cl-PL), poly(CH_2Cl-PL), poly(CH_2Cl-PL-*co*-CH_3-PL) and finally poly(CH_3-PL) successively appear as the dechlorination reaction of poly(CCl_3-PL) occurs.

The T_g's of atactic and isotactic poly(CCl_3-PL), of partially dechlorinated intermediates, and of poly(CH_3-PL), determined from Figure 8, are given in Table 2.

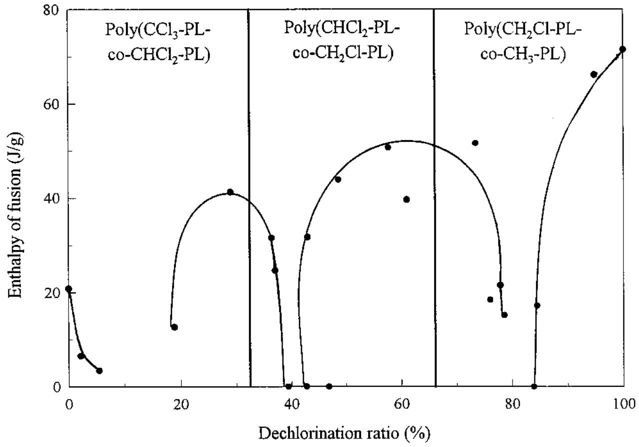


Figure 9. Evolution of the enthalpy of fusion (ΔH_m) of isotactic poly(CCl_3-PL) with dechlorination ratio.

Table 2. T_g of Atactic and Isotactic Poly(CCl_3-PL), Poly($CHCl_2$-PL), Poly(CH_2Cl-PL), and Poly(CH_3-PL) Determined from Figure 8 and T_g of Natural PHB

polymer	T_g (K) atactic	T_g (K) isotactic
poly(CCl_3-PL)	402	377
poly($CHCl_2$-PL)	325	319
poly(CH_2Cl-PL)	286	268
poly(CH_3-PL)	265	263
natural PHB[57]		278

The T_g value of 402 K of atactic poly(CCl_3-PL) is similar to the 397−416 K values obtained by Lavallée et al.[38] for the same polymer. However, the T_g of isotactic poly(CCl_3-PL) is lower than that of its atactic homologue, contrary to Lavallée et al's. observation. This behavior might be due to the MW of isotactic poly(CCl_3-PL), which is lower than that of atactic poly(CCl_3-PL), i.e., lower than 28 000. The difference observed between the T_g of isotactic poly(CH_3-PL) (263 K) and that of natural PHB (278 K) could also be explained by the 5000 MW of poly(CH_3-PL) as compared to the 6 × 10^5 value of PHB.

Figure 9 shows the variation of the enthalpy of fusion (ΔH_m) as a function of dechlorination ratio. The evolution of the polymer from poly(CCl_3-PL) to poly(CH_3-PL), in three different steps, is clearly seen. A maximum in ΔH_m is found for each of the four "pure" polymers, and

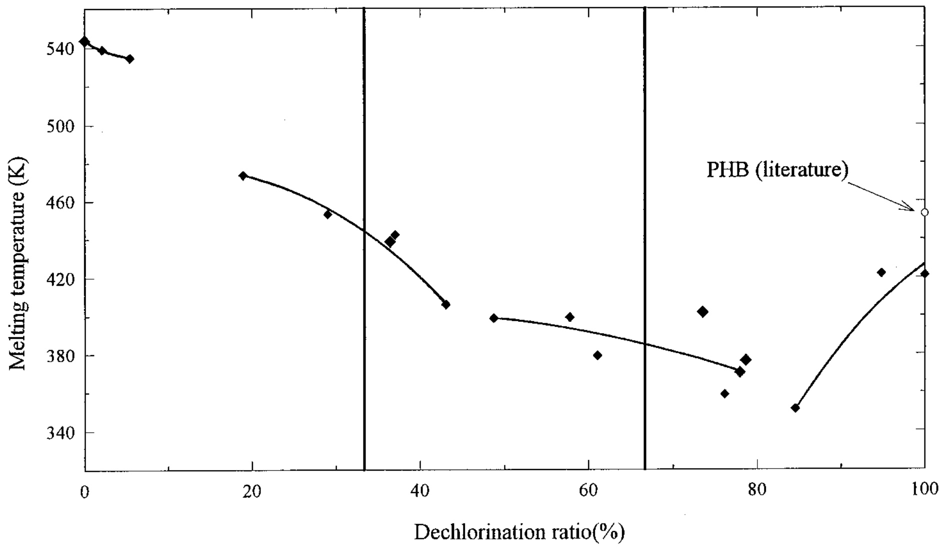


Figure 10. Evolution of the melting temperature (T_m) of isotactic poly(CCl_3-PL) with dechlorination ratio.

lower values occur at intermediate compositions. In fact, in each of the three sections of the figure, at intermediate compositions, an amorphous zone is found. Moreover, the maximum in ΔH_m tends to increase when going from poly(CCl_3-PL), to poly($CHCl_2$-PL), to poly(CH_2Cl-PL) and, finally, to poly(CH_3-PL), for the specific crystallization conditions used here: the corresponding values are 21, 42, 53, and 72 J/g. This behavior is typical of statistical copolymers containing two A and B units, both of them being able to crystallize with incompatible crystalline phases. Similar examples were given in the literature,[52,53] for instance, in the case of poly(caprolactone-*co*-lactide).[53] The incompatibility of the crystalline phases means that the crystalline structures of the two reference homopolymers are too different to allow the insertion of one kind of unit into the crystalline structure of the other one, and inversely. The units of the minority phase act then as a diluent. Other systems are semicrystalline for all compositions. For instance, two crystalline structures can be observed, that of the polyA for compositions high in A and that of polyB for compositions high in B, with a clear minimum in ΔH_m and, often, in T_m, at some intermediate compositions. This kind of behavior, called isodimorphous, has been observed for poly(hydroxybutyrate-*co*-hydroxyvalerate).[54]

The influence of dechlorination ratio on the melting temperature (T_m) is shown in Figure 10. At both ends of the figure, a decrease of T_m is observed with composition, which is the typical copolymer behavior expected.[52,53] However, for the two poly($CHCl_2$-PL) and poly(CH_2Cl-PL) homopolymers, the experimental behavior is more ambiguous: there is a net decrease of T_m at τ values in the ranges 33−50% and 66−80%, but a significant increase in the 20−33% and 50−66% ranges. This behavior can be attributed to a simultaneous decrease of MW with τ, especially between 20 and 33%, which gives the opposite trend. For the isotactic poly(CCl_3-PL), T_m and ΔH_m of 540 K and 21 J/g, respectively, are obtained, according to the values given by Lavallée et al.[40] for a similar polymer (548 K and 28 J/g, respectively). For the isotactic poly(CH_3-PL), T_m and ΔH_m are equal to 421 K and 72 J/g, respectively. This T_m value is much lower than those of natural PHB (452 K) and synthetic PHB ([i] = 0.85) (443 K) reported by Bloembergen et al.,[24] but this difference is attributed to a MW effect. Actually, Marchessault et al.[55] obtained a similar T_m (419 K) for a PHB with a MW of about 5000. This suggests that the MW of the isotactic poly(CH_3-PL) reported in this article should be around 5000, not far from that of its atactic homologue. The ΔH_m value of poly(CH_3-PL) of 72 J/g agrees with the values of the literature for natural PHB, which vary between 75 and 105 J/g[23,24,33,45] depending on the crystallinity of the polymer. The interpolated T_m values of poly($CHCl_2$-PL) and poly(CH_2Cl-PL) are, respectively, 447 and 391 K.

As shown in Figure 11, the evolution of T_g with dechlorination ratio for atactic poly(CH_3CCl_2-PL) is similar to that of poly(CCl_3-PL). There is a regular decrease of T_g when going from poly(CH_3CCl_2-PL) to poly(CH_3CH_2-PL). This decrease is linear at dechlorination ratios between 50 and 100% but appears to be nonlinear at low dechlorination ratios. As seen previously, T_g is also influenced by the polymer molecular weight, which, here, decreases from 11 000 to 5900 between the initial polymer and its dechlorinated homologue. The T_g of the atactic poly(CH_3CCl_2-PL) is 352 K, which is lower than the value of 374 K obtained by Lavallée et al.[38] for the same polymer with similar MW. The reason for this difference is unknown. T_g values of isotactic poly(C_2H_5-PL) and its atactic homologue (251 and 260 K, respectively), are similar to the 253 K value obtained by Bloembergen et al.[24] for a synthetic PHV with a presumably low MW. T_g of poly(CH_3CHCl-PL) is approximatively 291 K.

The T_m of poly(C_2H_5-PL) at 381 K is found to be similar to the value of 385 K obtained by Bloembergen et al.[24] for a synthetic isotactic PHV, whereas its ΔH_m is higher at 113 J/g against 84 J/g for PHV, possibly due to the presence of more syndiotactic diads in the PHV.

X-ray Diffraction Patterns. Figure 12 shows the X-ray diffraction powder patterns of isotactic poly(CCl_3-PL) and its partially dechlorinated homologues. For dechlorination ratios of 0 and 2%, the crystal patterns are found to be similar with three major peaks at 17, 25, and 32°. For τ values of 19, 29, and 37%, the appearance of new well-defined peaks at 22 and 29° is observed while the peaks previously observed at 17 and 25° become more intense. For τ values of 49, 61, and 79%, additional peaks are found at 11, 19, and 27°

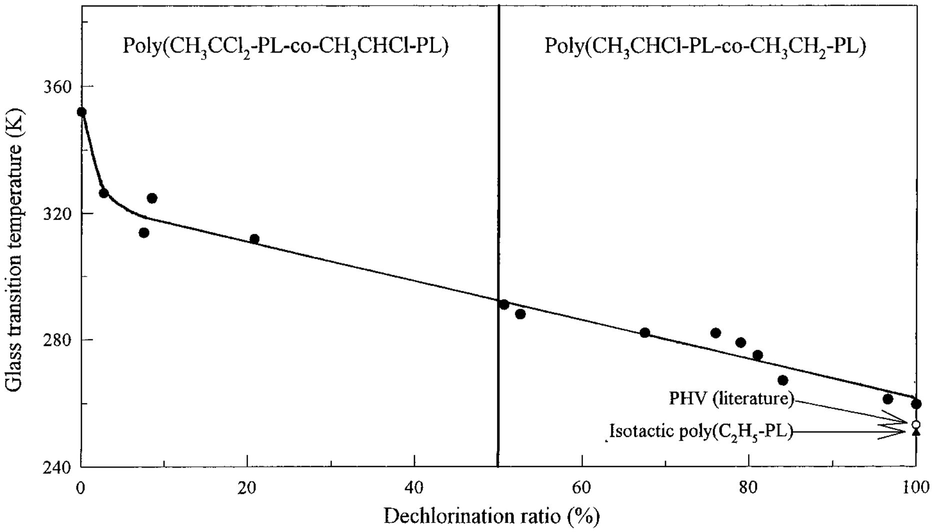


Figure 11. Evolution of the glass transition temperature (T_g) of atactic and isotactic poly(CH$_3$CCl$_2$-PL) with dechlorination ratio.

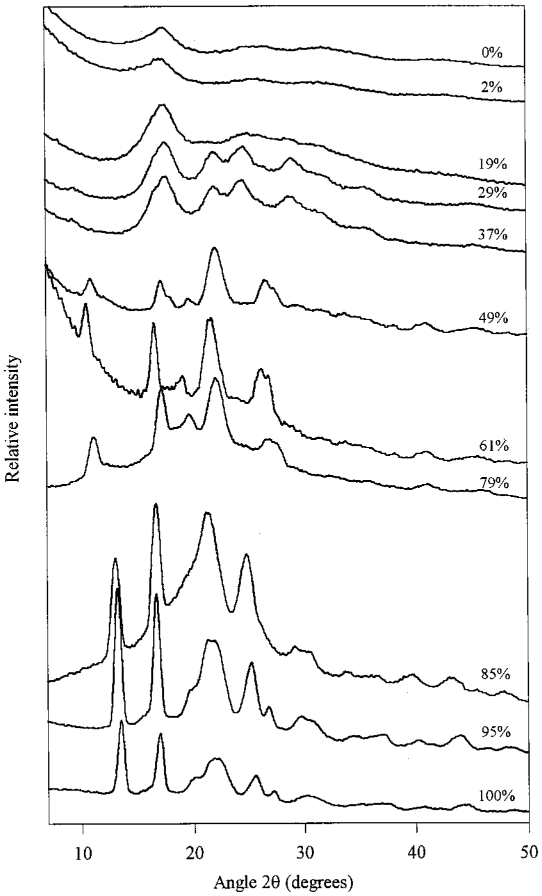


Figure 12. X-ray patterns of partially dechlorinated isotactic poly(CCl$_3$-PL).

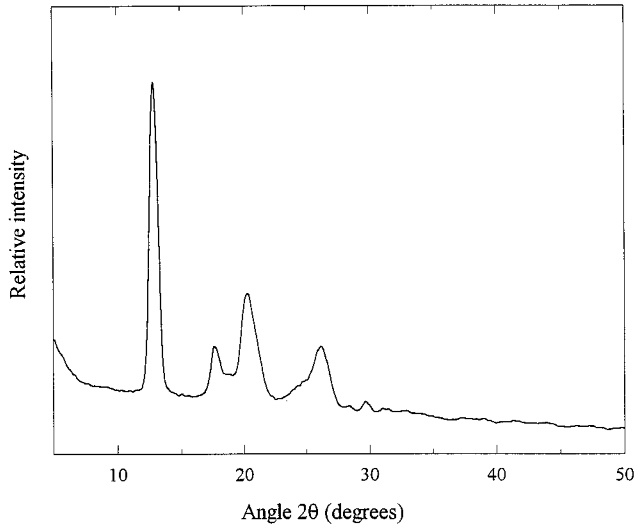


Figure 13. X-ray pattern of isotactic poly(C$_2$H$_5$-PL).

whereas the most intense peak is located at 22°. In addition, the disappearance of the peaks previously located at 25 and 29° is observed. Finally, for τ values of 85, 95, and 100%, main peaks are located at 13, 17, 21, and 25°. These four different crystal patterns are believed to be characteristic of each homopolymer, i.e., poly(CCl$_3$-PL) for $\tau = 0$ and 2%, poly(CHCl$_2$-PL) for $\tau =$ 19, 29, and 37%, poly(CH$_2$Cl-PL) for $\tau = 49$, 61, and 79%, and finally, poly(CH$_3$-PL) for $\tau = 85$, 95, and 100%. This result confirms that each homopolymer has its own crystalline structure and, therefore, a different T_m. It also confirms that the semicrystalline copolymers adopt a crystalline structure similar to that of the homopolymer poly(CCl$_3$-PL), poly(CHCl$_2$-PL), poly(CH$_2$Cl-PL), or poly(CH$_3$-PL) given in Figure 12, which resembles them the most. In other words, each of the crystalline structures can accept a small number of defects at the expense, however, of a decrease in melting temperature. The X-ray diffraction pattern of the isotactic poly(CH$_3$-PL) is similar to that of natural PHB given in the literature,[56,57] which exhibits chains in the 2_1 helical conformation packed in an orthorhombic unit cell, whose dimensions are $a = 0.576$, $b = 1.320$, and $c = 0.596$ nm.[58]

Figure 13 shows the X-ray diffraction pattern of isotactic poly(C$_2$H$_5$-PL) with characteristic peaks at 13, 17, 20, and 26°. This pattern is similar to that of poly(HB-*co*-HV) containing 95% of HV units.[56] It has been established that the crystalline chains of poly(C$_2$H$_5$-PL) adopt the 2_1 helical conformation with an orthorhombic unit cell, whose dimensions are $a = 0.932$, $b = 1.002$, and $c = 0.556$ nm.[59]

Conclusion

The main achievement of this work was to prepare highly isotactic poly(CH$_3$-PL) and poly(C$_2$H$_5$-PL) from the corresponding chlorinated polymers via a dechlorination procedure. It was observed that this reaction occurs with a full retention of the polymer configuration. In addition, it is shown, especially using NMR spectroscopy, to occur by a sequential mechanism where only one of the chlorine atoms of each CCl_3 (or CCl_2) groups is lost first, before the second one begins to be eliminated. This sequence leads, for example in the case of poly(CCl_3-PL), to the successive generation of poly($CHCl_2$-PL), then poly(CH_2Cl-PL), and finally, poly(CH_3-PL). Each of these polymers can be isolated and characterized since the reaction is relatively slow. This procedure also provides the opportunity to prepare intermediate polymers, in fact statistical copolymers, for example, those having a poly(CCl_3-PL-*co*-$CHCl_2$-PL) chain structure. The properties of each homopolymer, which have distinct melting points, enthalpies of fusion, and crystal structures, were determined. Even though only one polyenantiomer of PHB and PHV has been synthesized in this work, it would be easy to obtain homologues with the other configuration, simply by changing the nature of the catalysts used in the polymerization of the chlorinated polymer.

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