Glassy State and Secondary Structures of Chiral Macromolecules: Polyisocyanates and Polyketones

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ABSTRACT: The temperature dependence of the optical activity in the amorphous and therefore nonbirefringent solid state is used here to study the conformational properties of polyisocyanates and isotactic polyketones. Optically active polyisocyanates, which are not entirely amorphous in the solid state, were rendered amorphous by blending, while the glass transition temperature of the inherently amorphous polyketones was varied from 145 to 1 °C by terpolymerization of alternating styrenic/CO units with alternating 1-alkene/CO units. In both polymer systems, the optical activity changed significantly at temperatures only above T_g. This result, which was controlled for the contribution of degradation and epimerization of stereocenters in the polyketones, requires that the chiral optical properties of these polymers arise from long-range conformational properties of the chain that are impeded from changing with temperature only in the glassy state. This is consistent with the known character of the polyisocyanates but acts to reveal the previously uncertain basis of the optical activity in the isotactic polyketones studied here.

Introduction

Optical activity and molecular shape maintain an intimate relationship so that temperature in its ability to cause changes in molecular shape can have a large influence on optical activity. Although normally these conformational changes are reversible, since equilibrium is maintained, by incorporating optically active molecules or macromolecules in a glassy matrix, one can subvert that equilibrium since at temperatures below the glass transition temperature, T_g, the optical activity may not be able to respond to changes in temperature.

Thus, if one spun-coat a sample at a temperature far below T_g and raised the temperature, the conformational states would be frustrated in their ability to respond to the increase in thermal energy and, as for the glass around it, would fall out of equilibrium. On traversing the glass transition just as the system can now attain equilibrium so could the conformational states controlling the optical activity, and therefore one would expect a sharp change in this optical characteristic. In this way one could chiral optically detect the movement from the glass to the melt state. Such an experimental result however would only be expected if the chiral optical characteristics were conformationally dependent. If the optical activity did not depend on a temperature-dependent shape-dependent property, then the movement from the glass to the melt state would have little effect.

In the work described below we have tested this idea by exploring the optical activity properties of a polyisocyanate forming an amorphous blend with a copolymer of styrene and *p*-hydroxylstyrene[1] and in a series of polyketones synthetically adapted to vary the glass transition temperature T_g over a wide range. In the polyisocyanate there is a well-described helical conformation in which the temperature dependence is understood to arise from changes in the ratio of left- and right-handed helical states.[2] These changes require the movement of a helical reversal,[3] causing a large change in the local shape characteristics of the polymer. This arises from the large angular change in the chain backbone around the helical reversal in combination with the high persistence length of the polyisocyanates.[2,3] This detailed understanding of the temperature-dependent chiral optical properties of the polyisocyanates therefore acts as a control on the idea presented above, which would demand that a polyisocyanate with blocks of left- and right-handed helical conformations show a large change in its optical activity properties only on traversing the glass transition from lower temperature.

In the polyketones, a class of polymer in which chain directionality based solely on configuration[4] causes the isotactic state to take a chiral symmetry,[5] the chiral optical properties and their temperature dependence in the dissolved state are not of certain origin. In one possible view, the optical activity can arise predominately from the configurational characteristics of the stereocenters in this polymer while another possibility points to a helical conformation of the backbone as the source of the optical activity.[6,7] In the polyketones the chiral stereocenters in the isotactic chain would cast the left- and right-handed helical conformations into a diastereomeric relationship in contrast to, for example, isotactic polypropylene, where there are local symmetry axes along the chain backbone arising from the absence of chain end effects that cause the stereocenters to lose their chiral characteristics.[2,4,8] Only if the conformational argument is correct, subject to the discussion made above, should the transition between the glass and melt states have a large effect on the optical activity in the polyketones.

The work described below was directed to exploring the interplay between the chiral optical properties of macromolecules and the glassy state and as well to

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answering this question of the source of the optical activity in the polyketones. As a prerequisite to this effort, we studied first a polyisocyanate with unequally populated blocks of left- and right-handed helical conformations along the backbone to test the concept.[9] There is, however, a general problem in the study of the optical activities of any molecular property in the solid state due to the possibility of form birefringence, which interferes with observations of the intrinsic molecular based chiral optical properties. In the polyisocyanates this manifests itself in the solid state since these polymers exhibit ordering transitions as seen by differential scanning calorimetry (DSC). This was overcome, as noted above and described below, by blending the optically active polyisocyanate with an amorphous polymer.[1]

In the polyketone work reported here, although the solid state is entirely amorphous and free of form birefringence, the T_g's of the optically active copolymers of substituted styrenes and carbon monoxide were quite high, leading to decomposition in this temperature range. This problem was overcome by incorporating 1-alkenes in the polyketones as described below.[10]

In the polyisocyanates, consistent with their known conformational properties and with the general idea proposed here, the optical activity was found to be invariant below T_g and exhibited a strong reduction on crossing to the melt state.[9] This result was also encountered in various of the polyketones, where the T_g was low enough to preclude decomposition or epimerization, as discussed below. This forces therefore the conclusion that the source of the optical activity in both classes of polymers is the same, that is, based in the conformational characteristics of the backbone.[11] This is certainly helical in the polyisocyanates and presumably helical in the polyketones as well.

Experimental Section

Materials. *tert*-Butylstyrene was donated by Deltech Corporation (Troy, OH). All other vinyl monomers were purchased from Aldrich (Milwaukee, WI) and were used as received. CP grade CO was purchased from Matheson Gas Products, Inc. (Secaucus, NJ). The bisoxazoline palladium catalyst was synthesized according to published techniques.[7,12]

Quartz disks, ultraviolet grade fused silica, were obtained from ESCO Products, Inc. (Oak Ridge, NJ). The quartz disks were edge-etched, and this marking was used to align the disks in the same orientation during each CD measurement relative to the light beam to eliminate any anisotropic effect. Blank quartz spectra were saved and used later to subtract for film analysis. The spectrum of a blank quartz was run at both 0 and 90° rotation, and no difference was noted. All data were nevertheless collected with the disks in an identical orientation.

Except where noted below, all solvents, including methanol, toluene, chloroform (HPLC grade), ether, butyronitrile, and pentafluorophenol, were purchased from Aldrich in the highest purity grade and used as received. CD_2Cl_2 was used as received from Cambridge Isotope Laboratories (Woburn, MA). Dichloromethane and acetonitrile were distilled under a nitrogen atmosphere from a drying agent immediately prior to use: CH_2Cl_2 from P_2O_5 and CH_3CN from CaH_2.

Instrumentation. a. Nuclear Magnetic Resonance Spectroscopy. ^1H and ^{13}C NMR were recorded on a Varian Gemini 300 MHz NMR spectrometer. All NMR were run in CD_2Cl_2 at 20 °C. Chemical shifts were referenced to residual ^1H and ^{13}C signals of the deuterated solvent. NMR data for polyketones are listed according to the scheme of ref 7.

b. Differential Scanning Calorimetry. A DuPont Instruments model 910 differential scanning calorimeter with Thermal Analyst 2000 software was used for determination of T_g. All DSC were run on 5−10 mg of polymer with helium purging. Samples were heated from room temperature to 180 °C at a rate of 10 °C/min, cooled back to room temperature at 20 °C/min, and then heated again—this time to 220 °C. For polymers with T_g below room temperature a DuPont cooling accessory was used, and heating cycles were initiated at −60 °C instead of room temperature.

c. Circular Dichroism Spectroscopy. CD and UV were both recorded with a Jasco J-710 spectrometer. Spectra were run from 400 to 185 nm for solid samples and from 350 to 250 nm for solutions. Run parameters included three accumulations, 0.2 resolution, 50 nm/min scan rate, 4 s response time, and 1.0 nm bandwidth. Preparations of samples for CD are presented below.

d. Gel Permeation Chromatography. Molecular weights were measured with a Waters GPC equipped with a model 510 solvent delivery system, a model 440 UV absorbance detector, and Millennium Quickset software. All samples were run with ∼1% solutions in $CHCl_3$ except where noted. GPC's were run using a filtered 40 μL sample volume and a collection time of 35 min against styrene calibration standards with a flow rate of 1.0 cm^3/min at 30 °C. Number-average molecular weight (M_n) and polydispersity index (PDI = M_w/M_n) were obtained for each sample. These molecular weights are not therefore absolutely known but only correspond to the same volume elution as for polystyrene standards.

Polyisocyanate Synthesis and Blending. Monomeric (*R*)-3,6-dimethylheptyl isocyanate and benzyl 4-isocyanatobutyrate were synthesized as reported elsewhere.[1,13] The polymerization was performed in toluene at −78 °C by initiation with a few drops of NaCN in DMF following the standard procedure.[1,2] For the copolymerization of isocyanates, two monomers were premixed in a desired composition before addition of the initiator. Blending of the polymers was also carried out in the same manner as described previously.[1] The blended polymer films were cast on quartz disks, allowed to dry in the air for 1 day, and further in a vacuum oven at 40 °C for 3 days prior to the CD measurements.

Polyketone Synthesis. Isotactic Poly(4-*tert*-butylstyrene-*alt*-CO). A flame-dried Schlenk flask was charged with 0.124 g (0.100 mM) of bis(oxazoline) catalyst and then back-filled three times with CO. To this flask was added 10 mL (55 mM) of 4-*tert*-butylstyrene without additional solvent. The solution turned yellow immediately upon addition of the monomer, and the catalyst appeared to completely dissolve. After 72 h, the solution was black and viscous. About 15 mL of CH_2Cl_2 was then added as a diluent, and the black solution was filtered through Celite filter aid. The recovered solution was clear yellow, and upon addition to a 20-fold excess of methanol, a white precipitate formed immediately. The product was collected by centrifugation and then dissolved in CH_2Cl_2, filtered through Celite a second time, and precipitated again. The final white product was collected by centrifugation and filtration, washed five times with methanol, and dried overnight *in a vacuum* at 40 °C. Yield = 2.32 g (22.6%), M_n = 18 200 D, PDI = 1.56. The ^1H NMR and ^{13}C NMR were consistent with the structure, as is the situation for all the polyketones described. The preparation of the isotactic poly(3(4)-methylstyrene-*alt*-CO) followed an identical procedure.

Isotactic Styrenic/α-Olefin Terpolymers. Isotactic Poly[(4-*tert*-butylstyrene-*alt*-CO)-*ran*-(1-hexene-*alt*-CO)]. In a typical isotactic terpolymerization, a flame-dried Schlenk flask was charged with 0.130 g (0.105 mM) of bis(oxazoline) catalyst and then back-filled three times with 1 atm of CO. To dissolve the catalyst, 0.5 mL of CH_2Cl_2 was added and stirring was begun. To this solution, 2.75 mL (22.0 mM) of 1-hexene and 6.05 mL (33.0 mM) of TBS were added simultaneously. After 72 h of stirring under 1 atm of CO, black deposits had formed on the wall of the flask and on the stir bar. The black solution was filtered through Celite, and the resultant yellow solution was precipitated in a 20-fold excess of methanol. The gray product was collected by centrifugation, redissolved in 10 mL of CH_2Cl_2, filtered through Celite a second time, and then precipitated in methanol. The white

Table 1. Terpolymer Reactions and Properties

feed ratio		TBS/Hex/CO				TBS/Dec/CO				MeSty/Dec/CO			
		terpolymer ratio				terpolymer ratio				terpolymer ratio			
styrenic	olefinic	TBS	hex	M_n (D)	T_g (°C)	TBS	Dec	M_n (D)	T_g (°C)	MeSty	Dec	M_n (D)	T_g (°C)
10	90	49.8	50.2	8 400	58			3 700	13			4 300	1
20	80	64.5	35.5	8 600	87	63.2	36.2	7 400	55	54.1	45.9	7 500	31
40	60	85.5	14.5		112	75.8	24.2	8 100	99	74.6	25.4	8 200	63
50	50	88.2	11.8	14 300	119								
60	40	92.0	8.0	16 300	131	84.5	15.4	15 400	116	85.5	14.5	14 900	83
80	20	97.7	2.3	17 600	138	95.0	5.0	22 700	133	92.9	7.1	18 700	96
90	10	99.3	0.7	20 500	143								
100	0	100	0	18 200	145	100	0	18 200	145	100	0	15 900	106

powder was collected by centrifugation and filtration through Whatman paper, washed five times with methanol, and then dried overnight in a vacuum at 40 °C. Integral comparison between the ^{1}H NMR methine peak of TBS and the ^{1}H NMR methyl peak of hexene was used to measure the ratio of TBS to hexene in the terpolymer. GPC data are shown in Table 1 along with data on experiments with variable feed ratio. Table 1 also shows similar data for TBS/Dec/CO and MeSty/Dec/CO terpolymers.

Solid State Optical Activity. Spin-Coating of Polymer Films. Polymer films were prepared by a spin-coating technique using a model PM101DT spin-coater with a model R485 bowl and a $^3/_8$ in. diameter chuck from Headway Research, Inc. (Garland, TX). In a typical coating, a solution of 0.100 M i-(TBS/CO) in toluene, which had been filtered through a 0.45 μm syringe filter, was prepared. A blank $^1/_2$ in. diameter × $^1/_{16}$ in. thick quartz disk was placed on the spin-coater chuck. Using a syringe, 50 μL of polymer solution was spread on the quartz surface. The spin-coater was then set to a speed of 6.0 (4250 rpm), an acceleration of 5.0, and a spin time of 20 s, and the spinning cycle was activated. Following the spin, the quartz disk—now with a film of polymer—was dried in a vacuum at 40 °C for 10 h.

An approximation of the film thickness was made by coating with a puddle of known concentration and volume onto a defined area and then allowing the solvent to evaporate thus forming a film of known thickness. By comparison of the CD signal of puddle-coated films from several concentrations with a spin-coated film, the spin-coating thickness was estimated at 0.3 μm, and the absolute value of the 286 nm molar ellipticity for the TBS/CO was estimated at 8500 cm^2/dmol. Because it is unlikely to have a very uniform surface with puddle coating, these value are rough approximations.

Circular Dichroism of Polymer Films. Prior to running CD spectra of polymer films coated on quartz disks, CD spectra were run on each blank quartz disk from 400 to 185 nm. Since the Jasco instrument was not equipped to hold a quartz disk in place, a holder was fabricated from $^1/_2$ in. thick polycarbonate. Blank quartz spectra were saved and used later to subtract for film analysis.

The CD spectra of spin-coated (or puddle-coated) films were run similarly to the blank quartz disks with the coated surface oriented toward the light source. The CD data on the graphs are all presented in millidegrees since the film thickness cannot be defined precisely. The CD intensities were recorded for the n−π* absorption maximum that occurred between 250 and 300 nm. In all cases the CD measurements were made at room temperature after quenching the film from the temperature of measurement. Under these conditions no further changes occurred in the spectra.

Heat Treatment of Films. A quartz disk spin-coated with i-TBS/CO was placed with the coated surface facing up in an oven dried custom-made 10 in. long × 17 mm o.d. × 1 mm wall thickness flat bottomed glass tube. The open end of the tube was then sealed with a septum that was wired tight. Using a syringe needle connected to a vacuum/Ar line, the tube was evacuated to <50 mTorr and then back-filled with Ar. This procedure was repeated a total of 10 times to ensure that no oxygen remained in the tube. After the final fill with Ar, the line was turned to vacuum for 5 s to create a slightly negative pressure in the tube, and the syringe needle was then removed. Using a propane torch, the tube was heated at its center until the glass softened and collapsed, forming two sealed halves—the lower of which contained the coated quartz. This sealed ampule was placed in an air-circulating oven at the specified temperature for 24 h. After the heating cycle, the ampule was removed and immediately quenched in a dry ice/acetone bath. The ampule was inspected for cracks that may have occurred during heating, and then the disk was removed by breaking the ampule at the upper end.

Circular Dichroism of Dissolved Films. After measuring the CD of heated films in the solid state, some films were dissolved and the CD of the reconstituted solution was measured. This was accomplished by placing the coated quartz in a test tube with 0.50 mL of butyronitrile. After allowing at least 30 min for dissolution with occasional shaking, the CD of the solution was run from 400 to 220 nm in a 0.1 cm quartz cell. A blank of butyronitrile in the same 0.1 cm cell was subtracted from the solution CDs for analysis.

Results and Discussion

Polyisocyanates. The optical activity of the poly(isocyanate)s has been shown to arise primarily from a helical structure with an excess of one helical sense.[2] In the situation where both helical senses are populated, the polymer maintains a low population of helical reversal states, which can move rapidly along the chain allowing dynamic interconversion of the unequally populated left- and right-handed helical states.[2,3] Since the population of reversals is temperature-dependent and since this population controls the cooperative characteristics of the chain and therefore the response to the chiral information distinguishing the helical senses, there is a large temperature dependence of the optical activity in solution.

To study the temperature dependence in the solid state of this polymer, as noted above, requires blending to form an entirely amorphous system. Successful formation of miscible blends consisting of an optically inactive polyisocyanate and a modified polystyrene was reported previously by utilizing hydrogen-bonding interactions.[1] Rather than using an optically inactive polyisocyanate for this blend, in the present work about 10−20 mol % of (*R*)-3,7-dimethylheptylisocyanate (R-CIC) was copolymerized with benzyl-4-isocyanatobutyrate (BICBE), the hydrogen bond acceptor monomer utilized to form PIES in the previous study.[1] This therefore yielded an optically active copolyisocyanate (Figure 1) with a hydrogen bond receptor necessary for blending.

The resulting copolyisocyanate was mixed with a 90/10 copolymer (PHS10) of styrene and *p*-hydroxystyrene to afford a miscible blend with a single glass transition temperature by DSC. For example, when the copolyisocyanate with an 80/20 molar composition of BICBE/(R)-CIC was blended with PHS10, a blend with 20% of the

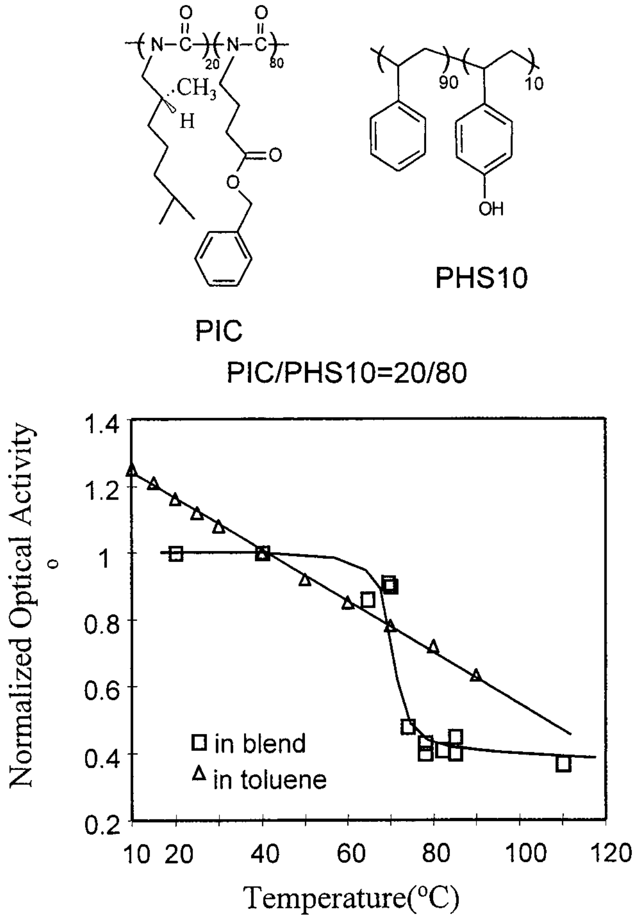


Figure 1. Optical activity of the copolyisocyanate (PIC) in the dilute solution in toluene and in the blend with PHS10 as a function of temperature. The ordinate is expressed in relative terms normalized to the optical activity at 40 °C.

copolyisocyanate and 80% of PHS10 showed a glass transition temperature near 70 °C.

The temperature dependence of the optical activity of the copolyisocyanate was studied both in dilute solution in toluene and in the blend with PHS10, and the results are presented in Figure 1 along with the structures of the copolyisocyanate and that of PHS10. In the blend it was determined that 20 h of heating at each temperature was adequate to reach a steady state of the optical activity. In toluene solution, there was a smooth and decreasing response of the polymer optical activity to temperature, which was instantaneous on a laboratory time scale.[2,3] However, the solid state optical activity of the blend showed no change below the glass transition temperature but dropped rapidly on reaching the region of the glass transition temperature.

Redissolving the polymer from the quartz disk demonstrated that no permanent change has occurred in the circular dichroism properties. The observation in the solid film indicates that movements of helical reversals can occur only when the matrix is relaxed above the glass transition temperature. The source of this observation must be the large volume swept out of the surrounding polymer matrix in order for the reversal to move along the chain.

Although the results exhibited in Figure 1 are consistent with the overall expectation of how the optical activity of the copolyisocyanate should respond to the matrix, it is not clear why the optical activity at temperatures above T_g does not continue to fall, and we have no explanation for this aspect of the result. As we shall see, a parallel response of optical activity to temperature above T_g is encountered also in the polyketones discussed below.

Polyketones: Optical Activity Properties and Conformation. Polyketones, such as those formed via the copolymerization of carbon monoxide and ethylenically unsaturated monomers, independent of their chiral properties, have been of considerable interest for four primary reasons.[5,12,14] First, the building blocks of most polyketones, i.e., carbon monoxide and common olefins, are readily available. Second, due to the carbonyl functionality in the polymer backbone, polyketones are photodegradable. This property suggests potential uses in resists and other coating operations. Third, the carbonyl backbone also suggests a possible mode for biodegradation.[14] Finally, it is possible to introduce many new functionalities into the polymer chain by post-polymerization reactions with the carbonyl group.[15]

Following on the realization of potential optical activity of an isotactic polyketone because of chain directionality,[4] reports of isotactic copolymerization followed not long after syndiotactic structures were first synthesized. Wong reported, in a 1990 patent, the use of a chiral bis(phosphine) Pd(II) catalyst for the copolymerization of propylene (P) and CO.[16] The P/CO products were stereoregular with small negative specific rotations that depended on the nature of the catalyst ligand.

Since Wong's patent, others have reported isotactic P/CO copolymers using phosphine catalysts with either a chiral center ligand or a biphenyl based ligand such as (6,6′-dimethylbiphenyl-2,2′-diyl)bis(dicyclohexylphosphine). These include Consiglio[17,18] and Sen.[6,19] The highest activity in a P/CO polymer, as well as the highest molecular weight, was found by Sen, who reported a molar rotation at ambient temperature at the D line of +49° (specific rotation = 34°) using an enantiomerically pure 1,2-bis(2,5-dimethylphospholano)benzene−Pd catalyst.[19]

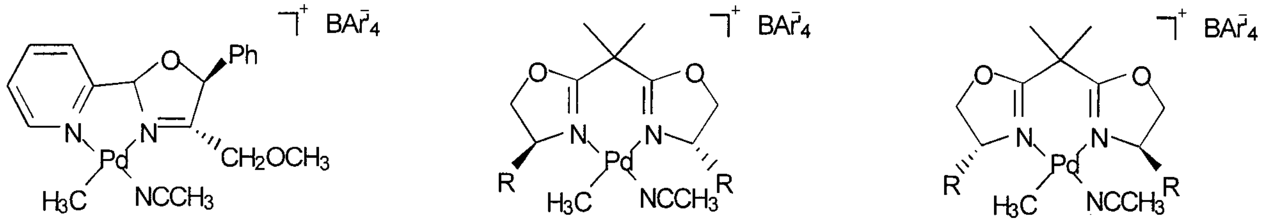
A polyketone with a higher chiral optical effect came from work using *tert*-butylstyrene (TBS) as the comonomer in place of propylene.[7,12,20] The higher optical activity as compared to the previously reported efforts are the result of both the styrenic monomer unit with its higher wavelength chromophore and the ligand used in the polymerization catalyst, the latter giving rise to a higher isotacticity. The ligands employed are shown in Scheme 1.

With catalyst **1** at atmospheric pressure and ambient temperature, a copolymer with moderate optical activities ($[\Phi]_D^{25} = -54°$) was shown to have some isotactic character, but the structure remained largely syndiotactic.

Catalysts **2** and **3**, in which R is either methyl or isopropyl, were synthesized in enantiomeric purity from readily available amino acids. The resulting TBS/CO copolymers were >98% isotactic and, in one example, exhibited a molar optical rotation of $[\Phi]_D^{25} = -536°$. DSC revealed the products to be amorphous with a T_g of 145 °C.

Recently, X-ray studies have yielded information on the conformational properties of the stereoregular polyketones.[21−25] In the crystalline state the structure of isotactic polyketones synthesized from styrene (ST) and carbon monoxide maintains a nearly planar zigzag conformation. DeRosa has calculated minimum energies for the isolated chain of isotactic ST/CO.[24]

Scheme 1. Chiral Catalysts Used for the Isotactic Copolymerization of TBS/CO. BAr′$_4$ Represents the Counterion, Tetrakis(bis-3,5-trifluoromethylphenyl)borate



Evidence of an ordered secondary structure, that is, a helix, in solutions of isotactic polyketones is mixed. The tool most used to search for secondary structure in solution has been observation of the molar rotation temperature dependence ($\Delta[\Phi]_D/\Delta T$). Pino[26] has shown that the temperature dependence in vinyl polymers increases in direct proportion with the isotactic content and connected this observation to helical structures in solution. Following Pino's approach, values of this temperature dependence in solution were determined for several isotactic polyketones and corresponding small molecule models.[6,7,19]

The data did not yield a clear picture. In some cases, the polymer temperature dependence is very similar to or even less than that of the model compound leading to the conclusion that the optical activity involves localized contributions of the chirotopic stereogenic centers while in other cases the polymer optical activity temperature dependence is significantly greater than that of the model leading to the opposite conclusion, that is, that a conformational property, presumably a helix, plays an important role. In the latter case, the observed temperature changes would be altering the ratio of left- and right-handed helical states or even the ratio of helix to random coil.

As a result of these conflicting findings, the contribution from secondary structure to the optical activity remains unknown, and therefore information on the conformational properties of the polyketones in the solid amorphous state, where these polymers find their use, also remain uncertain. This problem led to the approach described in this work in which variation of T_g is essential. This could reasonably be accomplished via variation in the side chains, which could be undertaken by incorporating aliphatic vinyl comonomers of various chain lengths. The only polyketone research known to specifically seek control of T_g with side chain length variation is the recent work of Rieger and co-workers[27] where it was reported that terpolymers of lower olefins with higher α-olefins and CO lower the T_g by manipulating the mole percent of higher olefin in the product. Terpolymers of propylene, octadecene, and CO were shown to have T_g's of 19 and −15 °C with 13 and 30 mol % of the octadecene moiety, respectively.

Polyketones: Synthetic Work To Vary T_g. Our first solid state optical activity studies as a function of temperature demonstrated that the high glass transition of the TBS/CO polyketone caused decomposition and oxygen sensitivity (see below). This necessitated synthesis of optically active amorphous polyketones with lower glass transition temperatures requiring the preparation of optically active polyketones with incorporation of 1-alkenes as termonomers with CO and the styrenic monomers.

Catalyst **2** with R = methyl was used for polymerization of the isotactic polyketones as reported in the literature.[7,12] Each of these terpolymers consisted of (1) a substituted styrenic monomer, (2) an aliphatic olefinic monomer, and (3) carbon monoxide. TBS and the isomers of 3- and 4-methylstyrene (MeSty) were the styrenes chosen for the terpolymerization. To maximize the ability to control T_g using olefins that had been shown to terpolymerize with the achiral catalyst, the isotactic terpolymerizations were conducted with 1-hexene and 1-decene. Thus, the terpolymer reaction systems to be discussed below include *tert*-butylstyrene-CO-*co*-1-hexene-CO (TBS/Hex/CO), *tert*-butylstyrene-CO-*co*-1-decene-CO (TBS/Dec/CO), and 3(4)-methylstyrene-CO-*co*-1-decene-CO (MeSty/Dec/CO).

Using the bis(oxazoline)−Pd(II) catalyst, terpolymers were synthesized with 100, 90, 80, 60, 50, 40, 20, and 10% of the styrenic monomer feed (TBS or MeSty) relative to the total monomer content excluding the dissolved CO content. The amount of each monomer in the feed and the respective product amounts are given in Table 1. It is clear that the catalyst favors styrenics over the aliphatic olefins since the amount of olefin in the feed needed to obtain a nearly 50:50 ratio in the product is close to 90%.

In all terpolymers, the infrared and ^{13}C NMR spectra of each product showed the definitive carbonyl peaks for polyketones. The IR carbonyls were all sharp peaks between 1708 and 1713 cm^{-1}, and the ^{13}C NMR all showed a resonance between 206.9 and 207.2 ppm. The C-2 methylene backbone ^{13}C NMR chemical shifts are all within the range shown to be indicative of isotactic stereochemistry.[7]

The amount of each monomer in the product was determined from the ^{1}H NMR spectrum. The integrals of the styrenic methine proton and the olefinic methyl protons were compared to calculate the relative molar ratios. From the ^{1}H NMR integration and the relative amounts of each unit, the average base unit molecular weight was calculated for each terpolymer. These data are given in Table 1 and were used—along with the polymer molecular weights determined by GPC—to calculate the average degree of polymerization (DP). The DP decreases with increasing aliphatic olefin proportion, but even at 50% olefin in the terpolymer, chain length was sufficient to allow formation of a true polymer rather than an oligomer.

The question of whether the products of the terpolymer polymerizations are homogeneous materials must be considered. Given the wide disparity in productivities, we would expect that a nonhomogeneous product would show a significant difference in molecular weights for the separate copolymers—or even homopolymer—products. However, the GPC curves for each of the terpolymerization products were shown to be singular, offering no evidence of anything but a homogeneous terpolymer.

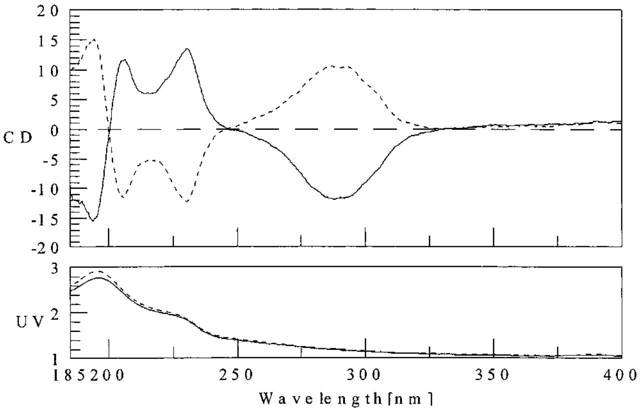


Figure 2. Film CD and UV spectra of isotactic-TBS/CO enantiomers synthesized from bisox–Pd(II) catalysts having enantiomeric ligands. Ordinate is expressed in millidegrees as measured in the CD spectrum. UV data expressd in absorbance units. See experimental section for approximate film thickness.

The distribution of dimer units in the terpolymers was determined by calculating the reactivity ratios.[10] The terpolymers were in this manner determined to be a random distribution.

The changes in glass transition temperature with changing terpolymer composition are tabulated in Table 1. The decrease in T_g with decreasing styrenic monomer content—and, hence, increasing aliphatic olefin content—is nearly linear. It should, therefore, be possible by selection of monomer feed ratios to obtain any glass transition temperature between the lowest and highest values reported. In practice, however, terpolymers with greater than 50% olefin in the product could prove very difficult to synthesize with the bisox–Pd(II) catalyst due to the very low reactivity of this particular monomer. However, without regard to tacticity other catalysts may not suffer this problem, allowing the possibility of high yield in combination with control of T_g.

By use of 1-decene instead of 1-hexene with *tert*-butylstyrene and also with methylstyrene, the lower practical limit of the glass transition has been decreased from 58 to 1 °C for products with just over 50% olefin content. However, the low yield of the products with T_g of 13 and 1 °C meant that the lowest T_g of a fully characterized terpolymer with sufficient product to conduct optical activity analyses was 31 °C.

Secondary Structure Elucidation through Solid State Circular Dichroism Measurements. The CD and ultraviolet (UV) spectra through the near-UV of the spin-coated films of the TBS/CO copolymers synthesized from each of two enantiomeric catalysts are shown in Figure 2. The curve with the initial positive Cotton effect—dashed line—is that of TBS/CO copolymerized from the R, R catalyst enantiomer while the mirror-image curve with the initial negative Cotton effect is that of TBS/CO from the S, S catalyst. This figure represents the first reported solid state chiral optical study of isotactic polyketones and is also the first CD observations below 250 nm. Solvent absorption obscured this region in the solution CD measurements.

Despite a relatively weak absorption in the n → π^* region between 250 and 300 nm, the circular dichroism (CD) intensity is substantial, and this intensity was one of the necessary components in allowing our study in the solid films. The CD effects for the enantiomeric polymers are equal and opposite. This, in combination with the similar shape of the CD absorption in the solid and in the accessible region in solution demonstrates that the films are isotropic and that the spin-coating technique itself does not introduce any anisotropy due to the high shear forces.

With the TBS/CO copolymer, solid state optical activity studies were carried out over a wide temperature range to just above the glass transition. Since the temperatures required were too high for in situ study in the spectropolarimeter, the elevated temperature studies were all done by heating the spin-coated film separately followed by quench removal from the heat source. In all cases in the discussion to follow, the polymer was heated to that temperature for the specified time period and then quenched to ambient temperature. All the CD measurements were carried out at room temperature.

At 160 °C for 8 h, the CD of TBS/CO ($T_g = 145$ °C) was unchanged from its original value despite the fact that this was 15 °C above the glass transition. However, at 35 °C above T_g, the CD did show a significant decrease in amplitude when heated for the same length of time. However, analysis of the TBS/CO by GPC of the polymer in solution that had been redissolved from this film showed a significant broadening of the molecular weight distribution. A yellowish discoloration of the polymer film after heating was also noted. These results demonstrate degradation of both molecular weight and structure, which are likely significantly contributing to the loss of optical activity.

Using an ampule to seal the polymer film in an oxygen-free argon atmosphere prior to heating (see Experimental Section), the optical activity thermal analysis was repeated with the same isotactic TBS/CO copolymer film as above. The result is shown in the CD plot in the upper portion of Figure 3 and is typical of the CD data for the other polymers reported below.

All heating experiments from this point forward were carried out for 24 h at the specified temperature, which was shown to be adequate to reach a constant value of the circular dichroism intensity for all cases. No attempt to measure the kinetic parameters of the change were carried out in the work reported here. At low temperatures where no change in the optical activity was observed in 24 h, an increase in exposure to 1 week had no effect on the optical activity.

The results in Figure 3 show little significant change in optical activity at temperatures below and including 170 °C in the argon atmosphere; however, at 180 °C, the polymer begins to lose optical activity rapidly until the product shows no optical activity whatsoever at 210 °C. The attempted exclusion of air, although causing an absence of yellow coloration, still allowed decomposition of the polymer as evaluated by dissolution and GPC analysis. These CD data are shown graphically as the triangles in the lower portion of Figure 3.

The change in the GPC characteristics of the redissolved sample subject to various temperatures are shown in the middle plot of Figure 3. The degradation at high temperature resulted in both a shift in the elution volume and a broadening of the GPC peak. The degradation appears therefore to result in both loss of molecular weight and increase in polydispersity. This has been noted in the literature of polyketones[14] to be the result of radical chain scission, resulting in lower M_n species, followed by some radical cross-linking and recombination, resulting in higher M_n species.

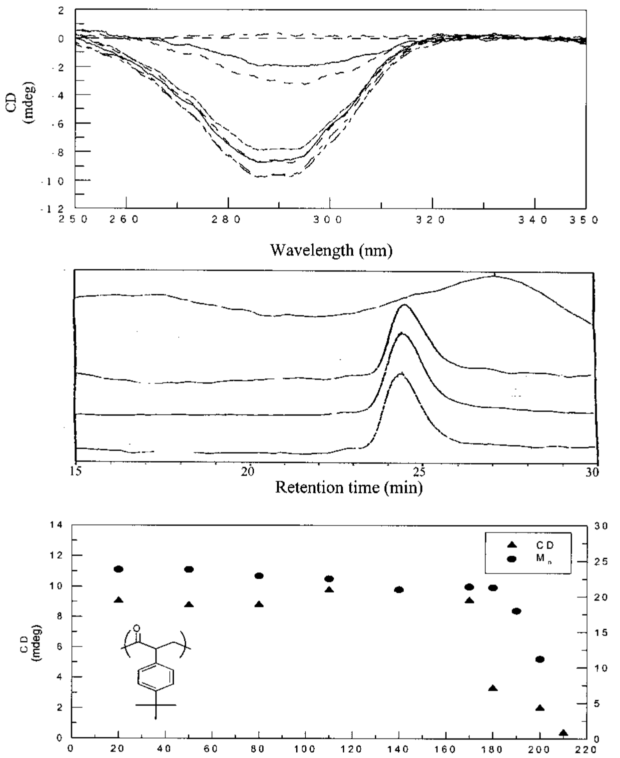


Figure 3. Thermal response of circular dichroism and molecular weight for TBS/CO (T_g = 145 °C) films heated to temperatures ranging from 50 to 210 °C for 24 h. Upper plot: no significant difference in CD was seen up to and including 170 °C. The top three curves indicting an inverse relationship between temperature and optical acitivity are for 180, 190, and 210 °C. Middle plot: GPC curves at temperatures of 50 (bottom curve), 100, 170, and 200 °C (top curve). Lower plot: circular dichroism and molecular weight as a function of temperature. All CD intensitites expressed in millidegrees. For approximate film thickness to estimate molar ellipticities see Experimental Section.

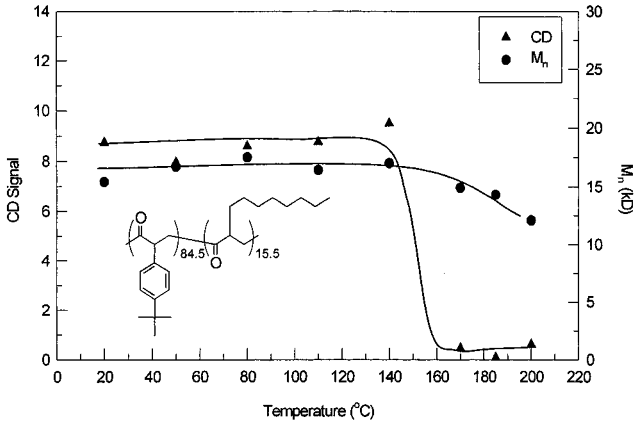


Figure 4. Optical activity and molecular weight as a function of temperature for films of TBS$_{84.5}$/Dec$_{15.5}$/CO (T_g = 116 °C). CD signal is expressed in millidegrees.

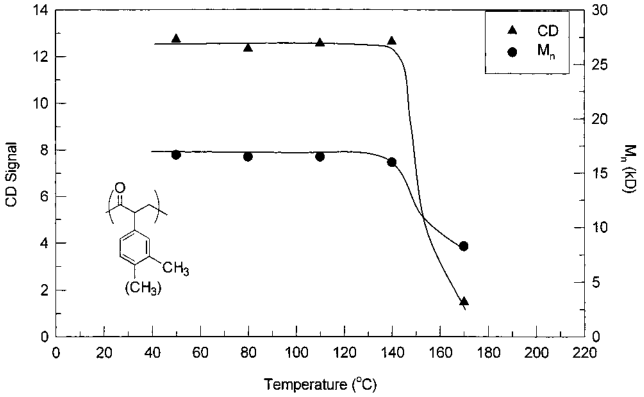


Figure 5. Optical activity and molecular weight as a function of temperature for films of MeSty/CO (T_g = 106 °C). CD signal is expressed in millidegrees.

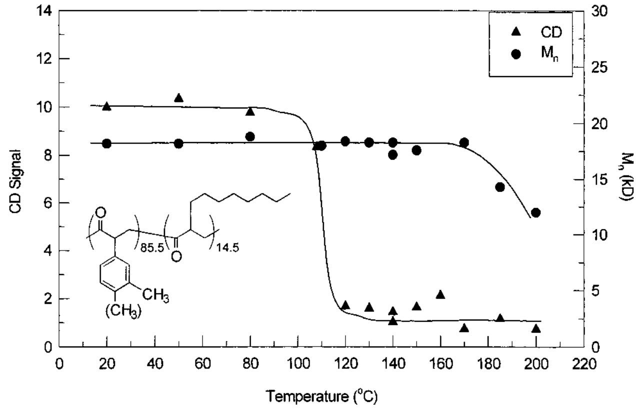


Figure 6. Optical activity and molecular weight as a function of temperature for films of MeSty$_{85.5}$/Dec$_{14.5}$/CO (T_g = 83 °C). CD signal is expressed in millidegrees.

The molecular weight results are shown in the lower plot of Figure 3 as the solid circles. Comparison of the CD and the M_n shows that optical activity decrease and degradation occurred at nearly the same temperature. This indicates that the optical activity was unchangeable except through the scission of bonds. This made necessary the syntheses of isotactic polyketones with lower glass transition temperatures for the purpose of attempting to gain sufficient separation of T_g and the temperature of degradation.

The results for experiments conducted on polyketones of variable T_g are shown in Figures 4–8, which are presented in the order of decreasing T_g. In all cases the conditions were as described for the results in Figure 3 above so that the circular dichroism intensity was measured as a function of temperature in the film followed by dissolution of the film and investigation of the GPC characteristics of the polymer subjected to the heating process. The variation in T_g as discussed earlier involved incorporation of 1-alkene units in the polyketone structure in Figures 4, 6, 7, and 8 while in Figure 5 the results for a fully aromatic system, the 3,4-dimethylstyrene, are exhibited. The incorporation of the unsymmetrical methyl substituents acts to lower the T_g significantly compared to *tert*-butylstyrene (Figure 3).

The results show that the copolyketone in Figure 5 does not fit into the T_g pattern of results established for the terpolymers in that the loss of optical activity in the film occurs in concert with decomposition of the polymer as evidenced by loss of molecular weight. Thus, while the steep decrease in optical activity occurs for the fully aromatic polyketone in Figure 5 in the range 140–160 °C, the same range for the loss of optical activity encountered in the polyketone in Figure 4; the latter shows no evidence for decomposition until nearly 200 °C, far above the loss of molecular weight seen in Figure 5. In fact, the GPC evidence of decomposition in Figure 5 occurs at a far lower temperature than that seen for the *p*-*tert*-butylstyrene-based copolyketone exhibited in Figure 3. The similarity of the structures of the polyketones in Figures 3 and 5 makes this

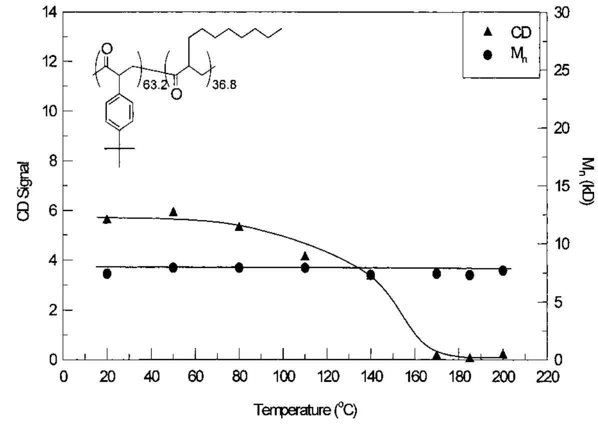


Figure 7. Optical activity and molecular weight as a function of temperature for films of TBS$_{63.2}$/Dec$_{36.8}$/CO (T_g = 55 °C). CD signal is expressed in millidegrees.

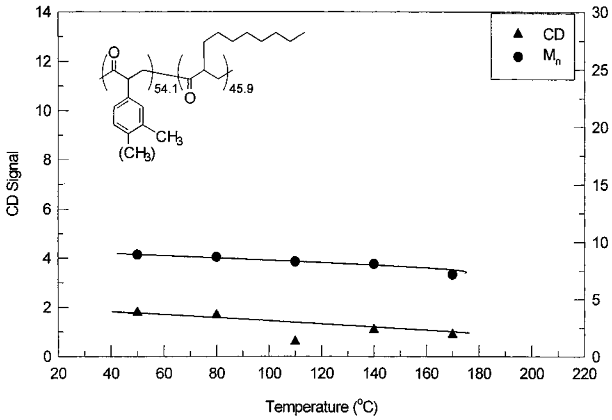


Figure 8. Optical activity and molecular weight as a function of temperature for films of MeSty$_{54.1}$/Dec$_{45.9}$/CO (T_g = 31 °C). CD signal is expressed in millidegrees.

difference difficult to understand unless it is somehow related to the only factor that distinguishes these polymers, that is, T_g (see further discussion below). For Figures 4–9 the ordinate gives the millidegrees measured on the circular dichroism instrument.

The pattern of results in Figures 4, 6, and 7 is also distinguished from that of the very low T_g polyketone exhibited in Figure 8. Here the molecular weight and optical activity are both low. The difficult polymerizable characteristics of the aliphatic olefins is responsible for the low molecular weight, which might contribute to the low optical activity because of the high concentration of chain ends, although certainly the reduced proportion of the aromatic chromophore must also act to reduce the chiral optical power. The low optical activity acts to obscure the temperature-dependent changes although there is an indication in the data of a gradual loss of optical activity without evidence for loss of molecular weight consistent with the clearer behavior of the other terpolymers (see below).

The two terpolymers presented in Figures 4 and 6 present a clearer picture. Here we observe a steep decline in the optical activities at somewhat above 140 °C in Figure 4 and somewhat above 100 °C in Figure 6, which parallel the changes in T_g, which occur at 116 and 83 °C in the compared terpolymers. The terpolymer presented in Figure 7 shows the same general pattern with a far more gradual dependence of optical activity on temperature. In all cases the GPC evidence of decomposition occurs far above the point where the optical activity changes are occurring with the interesting additional observation that the polyketone aliphatic content appears to correlate directly with the resistance to molecular weight change on heating. Higher aliphatic content causes a higher decomposition temperature.

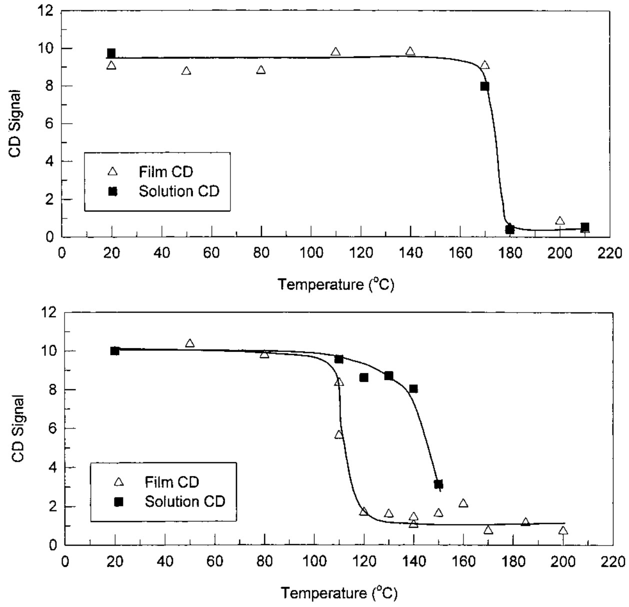


Figure 9. Optical activity of films and the solutions recovered from films as a function of the heating temperature of the films under Ar for TBS/CO, T_g = 145 °C (upper plot), and MeSty$_{85.5}$/Dec$_{14.5}$/CO, T_g = 83 °C (lower plot). CD signal is expressed in millidegrees.

Before drawing any conclusions from the results presented in Figures 4 and 6, an additional kind of experiment was conducted that focused on the possibility that epimerization of the stereocenters on heating could be contributing to these results. Such a change could not be detected by the GPC but would contribute to the changes in optical activity. To test for this possibility, a series of films prepared from two of the polyketones of high and low T_g were subjecting to heating at various temperatures, and the CD spectra in the solid state were run as before (Figures 3 and 6). The films subjected to exposure at each temperature considered were then dissolved in butyronitrile, and the solution CD's were measured. A baseline control was established by conducting the experiment for films that had been heated at a temperature that caused no change in the CD in the solid film. In these cases the polymers extracted from the film state into butyronitrile (redissolved) exhibited CD spectra without change in the molar ellipticity from the original, as synthesized, state.

At temperatures for which the CD in the solid film was diminished, if the CD of the redissolved polyketone did not recover to the as-synthesized state, this must be interpreted as arising from either degradation of the polymer, which would have been seen in the GPC measurements discussed above, or a configurational change in the structure caused by the heating. The only reasonable configurational change is epimerization of the stereocenters that is, loss of stereoregularity (isotacticity). Such isomerization must lead to lowered optical activity.

The results of this series of experiments are shown graphically in Figure 9 for the copolymer with a T_g of 145 °C (upper plot) and for the terpolymer with a T_g of

83 °C (lower plot). In the upper plot, the CD of the redissolved polymer after heating in the solid film parallels the CD of the solid film. This result is not surprising since it was shown previously by GPC measurements for this polyketone (Figure 3) that the solid state CD change was accompanied by a nearly parallel degradation to different chain lengths. It is reasonable that the energetic conditions necessary for degradation may also be adequate for epimerization, which may contribute further to the loss of optical activity (see below).

The results for the lower T_g polymer shown in the lower plot of Figure 9, on the contrary, demonstrate clearly that decrease in the solid state optical activity was the result of secondary structural changes. As with the upper plot, the solution CD recovers, as it must, in those cases where the solid CD showed no change. This is where the film was subjected to temperatures below and in the region of the T_g. Unlike the higher T_g polymer, however, there exists a range with this material between 110 and 140 °C for which the solution CD signal obtained from the redissolved film is fully recovered despite the loss of optical activity in the solid. Therefore, not only is there no degradation of the polymer as had been demonstrated by the GPC results in Figure 6 but as well, the primary isotactic structure had to be maintained at all heating temperatures below about 140 °C from the data in Figure 9 (lower plot). This requires that the optical activity decrease in the heated film had to be the result of temperature dependent *reversible* changes. When redissolved, the secondary structure, since there is no change in the primary structure, reverts to its lowest energy state at the temperature at which the CD spectrum is taken.

There is, however, a single data point in the lower plot of Figure 9 at 150 °C, demonstrating that change in the primary structure can occur without degradation. Here, the recovered polyketone from the heated film does not show the same CD recovery as its lower temperature counterparts. The temperature of this particular experiment is however still below the temperature of the degradation onset of 170 °C, the latter determined by the GPC work on the redissolved polymer (Figure 6). This suggests epimerization, which was confirmed by the following experiment. NMR studies of the terpolymer of Figure 9 (lower plot) were carried out after heating to 120 and 150 °C. Both the ^{1}H and ^{13}C NMR of the polymer at 120 °C were *unchanged* from the as synthesized material, which for the TBS/CO copolymers were >98% isotactic. These results were shown by C-13 NMR to be comparable to those of Brookhart and Wagner.[7,12]

At 150 °C, however, several changes in the NMR spectra were observed. In the ^{13}C NMR, broadening of both the C-1 methine and the C-2 methylene backbone carbon peaks were noted while in the proton NMR an additional peak related to the syndiotactic structure[7] appears.

For the terpolymers with lower T_g's of 55 and 31 °C (Figures 7 and 8), the change in CD intensity with temperature, $T\Delta$CD, is not as sharp as for the terpolymers with higher T_g's. In the polyketone with a T_g of 55 °C, a gradual downward slope was observed starting just above the T_g. It may be possible that this gradual decline may be similar to the gradual slope of the solution CD change with temperature. Since the T_g here is not far above ambient, the secondary structural characteristics restricted from changing in the glassy state with changing temperature are not far out of equilibrium on reaching the melt state. Thus, on reaching the melt state the optical activity does not change as steeply as observed in the higher T_g polyketones. In the latter polyketones the secondary structural characteristics on reaching the melt state after heating from ambient temperature are very far out of equilibrium and therefore must undergo a far larger change on reaching the ergodic melt state with a resulting far larger change in optical activity as observed.

Through the experiments discussed above, we demonstrate, as hypothesized, that chiral optical studies in concert with glass-forming properties can reveal information about the conformational properties of optically active polymers. This approach informs us that the optical activity properties of the polyketones involve important contributions from secondary structure. Although we have no direct evidence for the nature of the conformational changes allowed to occur in the solid film above T_g, the involvement of a helix seems probable. DeRosa[24] has shown that the lowest energy state for crystalline isotactic ST/CO is **s**(2/1). Molecular models suggest that the helix would also be a stable structure for copolymers with *tert*-butyl and methylstyrene substituents—with their amorphous nature arising from disruption of the unit cell and not the helix. The nature of the helix disruption could then be either interconversion of right- and left-handed helices as seen in the polyisocyanates[2,3] and in earlier studies on vinyl polymers[26] or simply a loss of helix structure resulting in a molecularly disordered conformation at high temperature. These changes would then be restricted in the glassy state or more specifically until the motions of the polymer on the appropriate length scale were consistent with the necessary chain motions of the chiral polymer.

The molecular weight data obtained from the GPC experiments of the redissolved heated films of Figures 3−8 also present evidence on the mode of polymer degradation and its relationship to both T_g and polymer structure. Looking first at just the two copolymers, TBS/CO and MeSty/CO in Figures 3 and 5, respectively, the onset of degradation was seen at about 35 °C above the T_g for both materials. It seems unreasonable that the energy necessary for onset of chain scission should be correlated to the T_g. More likely is that the bond breaking prerequisite to chain scission is occurring at the same and lower temperatures within the glass for the two aromatic copolymers. But the glass may act to restrict the translational motion of the radicals formed in the chain cleaving steps, therefore favoring radical recombination. Only on reaching into the melt state would the bond breaking lead to lowered molecular weight.

This type of cage effect is known and has been reported for E/CO polyketones by Guillet,[28−30] and further evidence is found in the work of Forbes,[31] who reported a relatively short radical life for a TBS/CO polyketone during photolysis. The bond breaking within the glass could however be contributing to epimerization since the cleaved bond could easily lose configurational integrity even within the constrained motion imposed by the glass. By comparison with the two aromatic copolymers, the four terpolymers of Figures 4 and 6−8, containing aliphatic units, have much greater stability relative to their respective glass transitions. This is reasonably related to the fact that the aliphatic units in forming secondary not resonance stabilized radicals, in contrast to the benzylic radicals formed by the fully aromatic copolymers, should act to retard chain scission.

In carrying out this work, we demonstrate that the transition between the glass and melt states of a polymer may be studied via optical activity changes. It is interesting that early in the nineteenth century Biot used the birefringent properties of glasses formed from sugar molecules to support the hypothesis that the basis of optical activity could be molecular, therefore forming a foundation under the ideas of molecular chirality to be developed later.[32] Here we use optical activity to explore the relationships between chiral macromolecules and the amorphous state, allowing insight into the nature of the basis of optical activity in the polymers. In another area, to be reported elsewhere,[33] we turn this interplay between optical activity and the glassy state from a method to reveal information about the conformational properties of macromolecules to a method instead to reveal information about the nature of the glassy state itself.

Summary

The work described above demonstrates that chiral optical properties of macromolecules may be studied in the amorphous solid state and that the restrictions to motion in the glass can be used to reveal conformational characteristics of these macromolecules. In this way we can see how the movement of the well-studied helical reversals in the polyisocyanates are affected by the transition between the melt and glass states. When this approach is turned to isotactic polyketones, it discriminates between differing ideas as to the source of their chiral optical properties and points firmly to a conformational source as the most important contribution to the optical activity properties. While in the polyisocyanates, blending is necessary to form the prerequisite nonbirefringent characteristics necessary for these studies; in the polyketones it is found necessary to vary the T_g over a wide range to separate the effect of the glass melt transition from degradation of the polymer. This is accomplished by incorporation of aliphatic units derived from terminal alkenes. In this effort we discover a cage effect in the polyketones below T_g, which although allowing epimerization of the stereocenters acts to block chain scission from leading to lowered molecular weight. Such chain scission leading to degradation of the polymer above T_g is additionally shown to be retarded by an increased proportion of aliphatic over aromatic units in the polyketones.

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