propionate, [2,2′-thiobis(4-*tert*-octyl)phenolato](*n*-butylamine)nickel(II) and bis[2,2′-thiobis-(4-*tert*-octyl)phenolato]nickel(II) used in concentrations of up to 0.32 wt %. Only three of the additives examined, including those listed in Table I, caused the respective calculated ketone absorption values (I_a') to fall below 80% of the absorption (I_a^0) calculated for the additive-free ketone solutions (1.2×10^{-6} einstein l.$^{-1}$ sec^{-1}). For the more strongly absorbing additives, I_a' values ranged down to 5×10^{-6} einstein l.$^{-1}$ sec^{-1} (for diphenylamine, Table I) and 1.4×10^{-7} einstein l.$^{-1}$ sec^{-1} (for the two Ni(II) chelates) at the maximum concentrations employed. The correction for the significant absorption by the latter Ni(II) chelates could have obscured a small quenching effect by these compounds ($\tau k_q < 10\ M^{-1}$).

Compounds which were found to be effective in reducing the yields of photolysis products are listed in Table I. The observed quantum yield values in the presence of these additives gave Stern–Volmer plots which were initially linear; the initial slopes of these plots gave the τk_q values (lifetime of the excited state and quenching rate constant, respectively) shown in Table I. Experimental values for *cis*-1,3-pentadiene and dissolved oxygen quenching are included for comparison.

Irradiations of decahydronaphthalene solutions of 2-methyl-4-pentanone in the presence of the same additives as used with the heptanone gave very similar results with regard to additive quenching effectiveness. Quantum yields for isobutane and acetone (or propylene) production in the absence of quenching were found to be 0.010 ± 0.001 and 0.10 ± 0.01, respectively; the carbon monoxide quantum yield was always <0.0008.

The 1,3-pentadiene quenching data in Table I lead to a lifetime of $\sim 1 \times 10^{-8}$ sec for the excited state (probably the triplet) of 2,6-dimethyl-4-heptanone, if diffusion control is assumed.[10] This lifetime is in good agreement with the value ($\sim 1.5 \times 10^{-8}$ sec) calculated from the data of Bibart, *et al.*,[11] for the intramolecular abstraction of primary hydrogens from 2-pentanone, at low degrees of photolysis. The τk_q values (Table I) for the quenching of 2-methyl-4-pentanone formation by other additives are all quite similar, and quenching probably occurs at or close to the theoretical rate for diffusion-controlled processes in all cases. Hydrogen bonding between some additives and the ketone might allow collisional quenching at rates slightly greater than those anticipated from the bulk viscosity. Turro and Engel[12] have proposed that biacetyl quenching proceeds *via* a reversible hydrogen abstraction from phenols and by an electron or charge-transfer mechanism for aromatic amines. These mechanisms might also influence the collisional quenching of some of the compounds listed in Table I. The apparent τk_q values for isobutane production will, of course, reflect both the quenching effectiveness and the radical-scavenging efficiency of the additives. For example, the zinc diisobutyl dithiophosphate data indicate that the additive is not a quencher of the excited ketone states, but functions solely as an efficient i-$C_4H_9\cdot$ trap.[13]

The nickel(II) chelates studied do not appear to quench the Norrish type I process (to give mainly i-$C_4H_9\cdot$) or type II process (to give mainly 2-methyl-4-pentanone). This result is in disagreement with the conclusions of Chien and Conner[5] who showed that the photooxidations of isopropylbenzene solutions sensitized by 3-pentanone are retarded by a [2,2′-thiobis(4-*tert*-octyl)phenolato]nickel(II) complex. This retardation was attributed to a Förster type of long-range energy-transfer process. We have confirmed that certain nickel thiophenolate complexes do inhibit the initiation of ketone-sensitized photooxidations.[14] However, we conclude that this inhibition is probably attributable to the nickel chelates efficiently quenching singlet oxygen[15] which is involved in some ketone-sensitized photooxidations,[16] rather than attributable to the quenching of the excited ketone.

Collisional quenching in a solid polymer may be possible to some extent, since Heskins and Guillet[17] have shown that a 1,3-diene can quench the photodecomposition of ethylene–carbon monoxide copolymers, both in the liquid and solid phases. However, quenching was relatively inefficient in the latter case. The possibility of long-range energy transfer between ketonic impurities and uv stabilizers in solid polyolefins is not precluded by our data, but obviously requires further investigation.

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(10) Solution viscosity in decahydronaphthalene at 30° was 1.9 cP. Then $k_q = 4 \times 10^9\ M^{-1}$ sec^{-1}, calculated from the modified Debye equation.

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Crystalline Poly(DL-β-isopropyl-β-propiolactone)

The crystalline structure of the naturally occuring polyester, poly(D-β-hydroxy butyrate) (PHB) has been reported to be a compact right-handed helix with a twofold screw axis along the chain.[1] The same optically active polymer[2] and its

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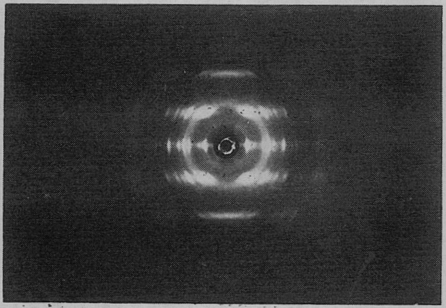

Figure 1. X-Ray fiber photograph of crystalline poly(DL-β-isopropyl-β-propiolactone).

racemate[3] can successfully be synthesized through the ring-opening polymerization of D(+)- and DL-β-methyl-β-propiolactone, respectively. The lower crystallinity of the reported synthetic polymer compared with that of naturally occurring PHB can be ascribed, at least in part, to some disorder in the polymer tacticity, because a highly crystalline and high molecular weight ($[\eta]$ = 8.20 dl/g, $CHCl_3$, 30°) polymer (**1**) having a crystalline structure identical with that of PHB was obtained[4] with $[Me_2AlOCPhNPh]_2$ catalyst by careful controlling of the polymerization conditions followed by repeated fractionation of the polymer.

There has been interest[5] in the related polyesters with respect to their polymer conformations. Further advances in this field require solution of a synthetic problem in order to realize the highly stereoregulated ring-opening polymerization of substituted β-propiolactones. Now we would like to report the stereospecific polymerization of the isopropyl derivative, DL-β-isopropyl-β-propiolactone (**2**).

Monomer **2** obtained by reacting isobutyraldehyde with ketene was purified by distillation after being dried over calcium hydride for 7 days: bp 49–50° (2 mm), yield ~60% based on isobutyraldehyde.

The behavior toward polymerization catalysts was very similar for both monomers **1** and **2**. Thus, the polymerization of **2** with $BF_3 \cdot OR_2$, a typical cationic catalyst, gave oily products and that with *n*-BuLi, a typical anionic one, gave no polymer. Highly crystalline high molecular weight polymers were obtained with $AlEt_3$–H_2O (1:1), $AlEt_3$–H_2O–epichlorohydrin (1:1:1), and $[Me_2AlOCMeNPh]_2$ catalysts after prolonged polymerization time, whereas only low molecular weight amorphous polymers were obtained with $AlEt_3$ or $ZnEt_2$–H_2O (1:0.8) catalyst.

A typical example of the stereospecific polymerization of **2** is described. A solution which was prepared by adding 6.5 μl (0.36 mmol) of water with vigorous stirring to 2 ml of a toluene solution of 0.05 ml (0.36 mmol) of $AlEt_3$ at $-78°$ was heated slowly to 60° in order to complete the reaction. Epichlorohydrin (33 mg, 0.36 mmol) was added to the solution at $-78°$ and allowed to react at room temperature for about 10 min. To the catalyst solution thus prepared, 1.97 g (17.3 mmol) of **2** was added at $-78°$. The ampoule containing the polymerization system was sealed and allowed to polymerize for 30 days at 60°. All operations mentioned above were carried out under dry argon atmosphere. The polymerization was terminated by adding a petroleum ether–water (20/1 v/v) mixture, and the precipitated polymer was dissolved in benzene. The clear solution obtained by centrifugation was lyophilized to give the raw polymer. The yield was 0.63 g (31.5%). The raw polymer was fractionated by extracting with boiling ether: the insoluble fraction (0.32 g, 16.0%) was crystalline and the soluble one (0.31 g, 15.5%) was amorphous. The melting point (87–89°) of the crystalline fraction ($[\eta]$ = 1.38 dl/g) is far lower than that (167–169°) of isotactic poly(DL-β-methyl-β-propiolactone).

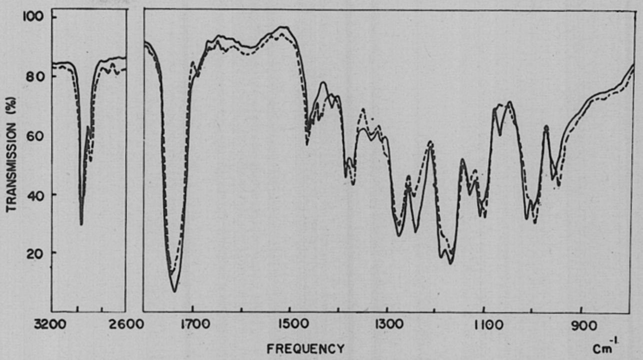

Figure 2. Polarized absorption spectrum of crystalline poly(DL-β-isopropyl-β-propiolactone): (——) electric vector perpendicular to elongation, (- - - - - -) electric vector parallel to elongation.

These two fractions proved to be poly(β-isopropyl-β-propiolactone) by elemental analysis and proton nmr spectra. Proton nmr spectra recorded for carbon tetrachloride solution of the crystalline and amorphous polymers (internal standard, TMS) have a common characteristic feature in having a quartet assigned to the main-chain methine proton at 4.98 ppm, a doublet to the methylene protons at 2.35 ppm, a multiplet to the side-chain methine proton at 1.75 ppm, and a doublet to the methyl protons at 0.72 ppm, in an intensity ratio of 1:2:1:6.

The crystalline polymer is so highly crystalline as to give 28 independent reflections in the X-ray diagram of the oriented sample (Figure 1). The unit cell (orthorhombic, $Z = 8$, $a = 10.63$, $b = 18.13$, c (fiber axis) = 6.49 Å, d_{calcd} = 1.21, d_{obsd} = 1.10) is compared with that of the corresponding methyl derivative (orthorhombic, $Z = 4$, $a = 5.71$, $b = 13.06$, c (fiber axis) = 5.89 Å, d_{calcd} = 1.29). The polarized ir spectrum of the oriented film of the crystalline polymer is shown in Figure 2.

The high crystallinity of the crystalline polymer indicates that the main-chain configuration is regular isotactic or syndiotactic. Polymerization variables such as the temperature, the nature of catalyst, and the solvent required for preparing the crystalline polymers are almost identical for monomers **1** and **2**. Therefore, it is reasonable to assign an identical main-chain configuration for both crystalline polymers. The isotactic configuration is assigned to the polymer of **2** similarly to that of **1**.

More detailed studies on the crystal structure of this crystalline polymer are carrying out by Professor Tadokoro's group of our department.

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