Table I

Catalyst System[a]	Ti:(−)-$C_{10}H_{19}OH$:Al Molar Ratio	Crude Polymer Ir Anal.[b] % Cis	% Trans	% 3,4	$[\alpha]_{546}^{20}$ (deg)[c]	Polymer (g)	Time (Days)
$Al(C_2H_5)_3$-(−)-$Ti(OC_{10}H_{19})_4$	1:4:7	73	17	10	−6.5	1.16	12
$Al(CH_2C_6H_5)_3$-(−)-$Ti(OC_{10}H_{19})_4$	1:4:7	nd	nd	nd	~−5	0.03	24
$Ti(CH_2C_6H_5)_4$-(−)-$C_{10}H_{19}OH$	1:1	53	35	12	~0	0.11	10
$Ti(CH_2C_6H_5)_4$-$Al(CH_2C_6H_5)_3$-(−)-$C_{10}H_{19}OH$	1:1:1	66	23	11	+3.0	0.11	5
Bimetallic compound-(−)$C_{10}H_{19}OH$	1:1.06:1.5	66	22	12	+4.5	0.33	3
Bimetallic compound-$Al(CH_2C_6H_5)_3$-(−)-$C_{10}H_{19}OH$	1:4.2:7.9	69	20	11	−3.7	0.73	7

[a] The polymerizations were run at 0° in toluene (25 ml) solution by using 0.6×10^{-3} mol of Ti and 6 g of *trans*-1,3-pentadiene. [b] Determined as described in literature.[7] [c] Determined in *n*-hexane solution.

benzyltitanium derivatives.[2] The table shows the results so obtained compared with the results of a typical polymerization carried out using Natta's catalyst.

The most important facts are as follows. (1) The combination of tetrabenzyltitanium with (−)-menthol gives rise only to traces of polymer having a negligible optical activity (if any). (2) Very low polymer yields are also obtained using catalyst systems consisting of (−)-titanium tetramenthoxide and tribenzylaluminum. (3) A catalyst was formed by reacting a bimetallic compound containing Ti-C-Al bonds, prepared according to Zucchini from tetrabenzyltitanium and tribenzylaluminum,[2] with one (−)-menthol molecule. This catalyst yielded an optically active polymer having a mainly cis-1,4 isotactic structure, similar to that obtained in the presence of Natta's catalyst, *but surprisingly the sign of rotation is (+) instead of (−)*. A lower yield is obtained if a mixture of tetrabenzyltitanium, tribenzylaluminum, and (−)-menthol is used as the catalyst system. (4) The sign of rotation of the polymer can be *reversed* by addition to the above catalyst of $Al(CH_2C_6H_5)_3$ previously allowed to react with the correct amount of (−)-menthol to achieve the same Ti-Al-menthol molar ratio as in the Natta's catalyst system.[3]

These findings probably mean that at least two types of catalyst complexes of different structure exist in the catalyst. Their relative amount depends on the stoichiometry of the whole catalyst system. Both types of catalyst complexes show the same stereospecific behavior, but opposite signs of asymmetric induction. In addition the bimetallic compound seems to be a catalyst precursor.

The reason that the (−)-titanium tetramenthoxide-triethylaluminum mixture is an active catalyst system, while the (−)-titanium tetramenthoxide-tribenzylaluminum is not, probably lies in the fact that in the former case the formation of a bimetallic compound through elimination of ethane is easier than in the latter case, which involves toluene elimination. In the latter case, the bimetallic compound must therefore be formed by reacting tetrabenzyltitanium with tribenzylaluminum, as described by Zucchini and Giannini.[2]

Experimental Section

trans-1,3-Pentadiene was prepared by thermal decomposition of the sulfone[4] and purified by distillation over sodium hydride. Benzyltitanium derivatives, tribenzylaluminum, and titanium menthoxide were prepared according to the literature.[2,5,6] The (−)-menthol was a Fluka product, $[\alpha]_{546}^{20}$ −45°. The solvent was dried by distillation over $LiAlH_4$.[1] The polymerization was run under nitrogen atmosphere.

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Far-Infrared Spectra of Copoly(γ-benzyl D,L-glutamates) and Sequential Copolymers of γ-Benzyl D- and L-Glutamates

Conformation of copoly(D,L-α-amino acids) has been studied with regard to the effect on the backbone structure of D- and L-amino acid residues in a single polypeptide chain.[1] Wada[2] and Tsuboi *et al.*[3] synthesized copoly(γ-benzyl D,L-glutamates) with various D- and L-residue ratios (PBD,LG) by the *N*-carboxyanhydride method and studied their conformation by means of dielectric dispersion,[2] infrared spectroscopy, and X-ray diffraction.[3] They found that each chain of the meso copolymers of γ-benzyl D- and L-glutamates has a random-coil portion and an α-helix portion and that the latter consists of the L and D residues with the ratio of D:L = 5:1 or 1:5. Based on this finding, they also proposed a simplified polymerization mechanism to this copolymer. Recently Heitz and Spach[4] synthesized poly(γ-benzyl-D-glutamyl-γ-benzyl L-glutamate) and studied its conformation in solution and in solid state. They concluded that the sequential copolymer takes the α-helical conformation and suggested that the meso copolymer of γ-benzyl D- and L-glutamates may assume the α-helical conformation even if it has a random sequence of the D and L residues. This is inconsistent with the hypothesis of Wada[2] and Tsuboi *et al.*[3]

In order to investigate in more detail the conformation and the D- and L-residue sequence of PBD,LG we measured the infrared spectra in a region from 700 to 200 cm^{-1} of PBD,LG and compared them with those of the

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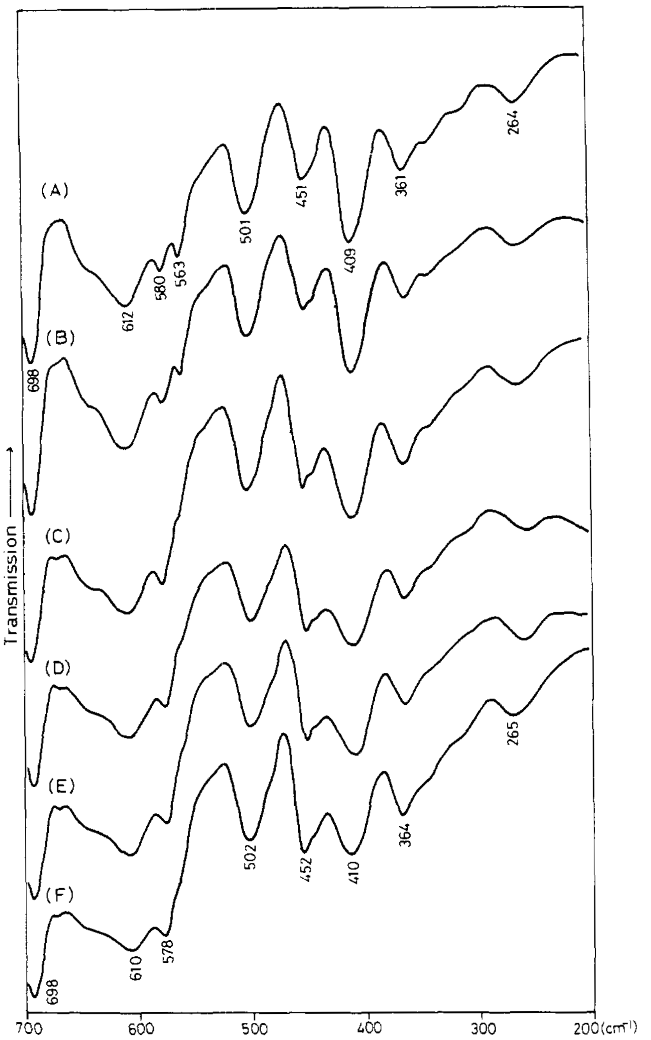

Figure 1. Infrared spectra in the region from 700 to 200 cm^{-1} of poly(γ-benzyl L-glutamate) and copoly(γ-benzyl D,L-glutamates). (Sample number is the same as that used in the ref 3.) (A) The L-residue fraction (f_L) = 100% (sample 911); (B) f_L = 93.5% (sample 912); (C) f_L = 70.8% (sample 914); (D) f_L = 59.7% (sample 916); (E) f_L = 54.6% (sample 918); (F) f_L = 50.0% (sample 943).

sequential copolymers, poly(γ-benzyl-D-glutamyl-γ-benzyl L-glutamate) (PB(DL)G), poly(γ-benzyl-D-glutamyl-γ-benzyl-L-glutamyl-γ-benzyl L-glutamate) (PB(DLL)G), and poly(γ-benzyl-D-glutamyl-γ-benzyl-L-glutamyl-γ-benzyl-L-glutamyl-γ-benzyl L-glutamate) (PB(DLLL)G). Poly(γ-benzyl L-glutamate) (PBLG) and PBD,LG are the same as those used in the previous studies.[2,3] The sequential copolymers were synthesized by following the procedure reported by Heitz and Spach.[4] The polymerization products were fractionated by gel permeation chromatography using Merckogel OR-20000. Dimethylformamide was used as the eluent. The average molecular weight of the sample in each fraction was estimated from the elution volumes of standard samples with known molecular weight. The detailed procedure will be reported elsewhere.[5] The molecular weight of each sample used in this study is as follows: PB(DL)G, (4.0 ± 1.0) × 10^4; PB(DLL)G, (2.0 ± 0.5) × 10^4; PB(DLLL)G, (4.0 ± 1.0) × 10^4. Even a trace of the β form was not found in each sample by the measurement of the infrared spectra in the amide I region. Figure 1 shows the infrared spectra of PBLG and PBD,LG, and Figure 2 those of PB(DLLL)G, PB(DLL)G, and PB(DL)G. Films cast from chloroform solutions of these samples were measured. The intensities of infrared bands were estimated from their peak heights.

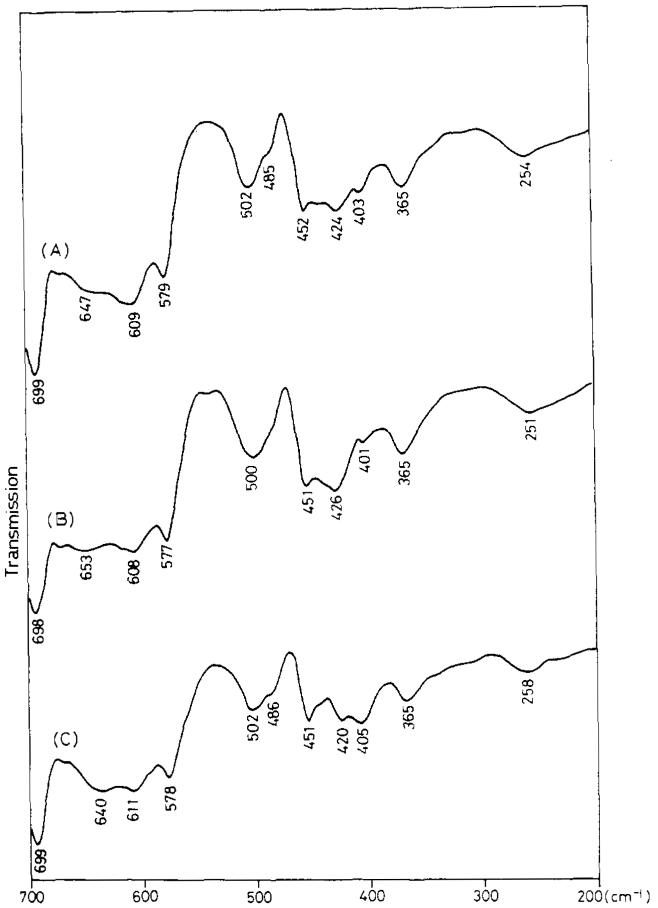

Figure 2. Infrared spectra in the region from 700 to 200 cm^{-1} of the sequential copolymers of γ-benzyl D- and L-glutamates: (A) PB(DLLL)G; (B) PB(DLL)G; (C) PB(DL)G.

As already reported,[6] the measurement of the infrared spectra in the region from 700 to 200 cm^{-1} is very useful for the elucidation of the local conformation of composite amino acid residues of polypeptides. Figures 1 and 2 show clearly the difference between the structure of PBD,LG and that of the sequential copolymers. Figure 1 tells that the infrared spectra in the region from 550 to 200 cm^{-1} of PBD,LG (Figures 1B-F) are almost identical with that of PBLG (Figure 1A) except that the relative intensity of the 409-cm^{-1} band *vs.* the 451-cm^{-1} band decreases as the D-residue fraction increases. The former band has been assigned to the α-helical conformation by Miyazawa.[7] The latter can also be found for PBLG with the β form and γ-benzyl L-glutamate.[7] Therefore, it is independent of the backbone conformation and then ascribed to the side chains of γ-benzylglutamyl residues. From the relative intensity of these peaks, we can obtain the fraction of the D and L residues with the α-helical conformation for PBD,LG by assuming that the fraction is 100% for PBLG. The result is shown in Figure 3. This is almost identical with the plot of the content of the (regular + perturbed) helix *vs.* the D-residue fraction obtained for PBD,LG by Tsuboi *et al.*[3] (Figure 7 of the ref 3). Therefore, the regular and perturbed helices have the same local conforma-

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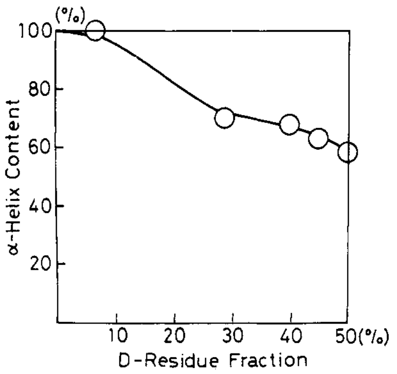

Figure 3. The content of the D and L residues with the α-helical conformation plotted against the D-residue fraction in copoly(γ-benzyl D,L-glutamates).

tion since both of them show the infrared band near 409 cm^{-1}. The spectra of PB(DLLL)G, PB(DLL)G, and PB(DL)G (Figure 2) are different from those of PBLG and PBD,LG (Figure 1). Especially the 409-cm^{-1} band characteristic of the α-helical conformation of PBLG and PBD,LG cannot be observed for the sequential copolymers. They show two distinct bands in the region from 426 to 401 cm^{-1}. All the sequential copolymers examined show a 610-cm^{-1} band assignable to the amide V vibration of the α helix.[8] Therefore, the sequential copolymers are considered to assume an α-helix-like local conformation. If the helix sense of PB(DLLL)G and PB(DLL)G is right handed, the bands near 425 cm^{-1} observed for these polymers are considered to correspond to the 409-cm^{-1} band of PBLG and assigned to the L residues with a right-handed α-helix-like local conformation. (A preliminary CD experiment[9] on PB(DLLL)G showed that this assumes a right-handed α-helix-like conformation in hexafluoroisopropyl alcohol solution.) The weak bands near 402 cm^{-1} observed for PB(DLLL)G and PB(DLL)G may be ascribed to the D residues with a right-handed α-helix-like local conformation. The 420- and 405-cm^{-1} bands observed for PB(DL)G cannot be assigned definitely since the helix sense cannot be determined only from the CD pattern of this polymer. (The CD spectrum of this polymer in hexafluoroisopropyl alcohol is different from that of the α helix.[9])

The observation mentioned above indicates the following points. (i) PBD,LG does not have any ordered structure other than the α-helical one (regular + perturbed). In the spectra of PBD,LG no new band appears besides those of PBLG. (ii) The α-helical portion of PBD,LG consists of the right-handed α-helical conformation of the L-residue-rich sequence and the left-handed α-helical one of the D-residue-rich sequence. (iii) The amount of the L residues incorporated into the left-handed α helix and the D residues with the right-handed one is small because the infrared bands assignable to these structures (These bands were observed at 580, 478 and 420 cm^{-1} for copoly(D,L-alanines).[10,11]) do not exist in the spectra of PBD,LG. (iv) PBD,LG does not have any ordered sequences of the D and L residues similar to those of PB(DLLL)G, PB(DLL)G, and PB(DL)G. The former does not show the 420- and 405-cm^{-1} peaks which appear for PB(DL)G, and so on. These results are consistent with the conformational model proposed to PBD,LG by Wada[2] and Tsuboi *et al.*[3] Thus, the polymerization mechanism proposed by them is still good at least for the polymerization in dioxane with sodium methoxide initiation.

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