Diastereo- and Enantioselectivity in the Co-oligomerization of Propene and Carbon Monoxide to Dimethyl-4-oxoheptanedioates

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Abstract: The selectivity of the copolymerization reaction of propene with carbon monoxide, using cationic palladium complexes modified with various diphosphine ligands as the catalyst precursor, changes toward the formation of low molecular weight compounds in the presence of excess 1,4-benzoquinone. The isomeric composition of the products arising from two propene units and three carbon monoxide molecules, namely of the possible dimethyl 4-oxodimethylheptanedioates, has been analyzed for catalytic systems containing chiral and achiral ligands. The different isomeric and diastereomeric products have been identified and characterized by NMR. The enantiomeric excesses were determined for the products obtained with the chiral ligands, the best enantioselectivity being around 98% ee. In spite of the enantiomer pairs not having been identified with respect to their absolute configuration, this analysis allows us to define the factors responsible for enantioface discrimination during the co-oligomerization. Preferential *l*-topicity of the two enantiofaces is observed for the products arising from two olefin insertions with the same regioselectivity (isotactic enchainment). A change in the regioselectivity of the insertion process of the olefin always induces a preferential alternation of the enantioface inserted. The catalytic systems investigated show a parallelism relating the feature of regio- and stereoselectivity toward co-oligomerization and copolymerization. The dimethyl dimethyl-4-oxoheptanedioates are regarded as model compounds for the polymerization reaction. The results suggest that the enantioface discrimination during both the regioregular co-oligomerization and copolymerization is related both to the presence of the chiral ligand and to the chiral center of the last inserted olefin unit.

Introduction

Among the most successful recent developments in the field of the carbonylation reaction of olefinic substrates,[1] the alternating copolymerization of ethene and carbon monoxide deserves particular attention[2,3] because of its commercial significance.[4,5] The identification of catalytic systems of the type $[PdL_2X_2]$ (where L_2 is a chelate diphosphine ligand and X is an anion that is more or less easily displaced in a second coordination sphere) with high activity[6,7] also allowed the preparation of copolymer with α-olefins.[8] For propene in particular, it has been possible to obtain regioregular copolymers[9] showing high isotacticity.[10] The identification of the prevailing stereochemistry of the macromolecules was possible, since, in the presence of optically active ligands, copolymers with high optical activity were obtained.[9,10] On the basis of the enantiomorphic site control of the process,[11] it is reasonable to assume that high isotacticity is associated with an effective enantioface selection during the copolymerization.[10] In fact, the overall enantioselectivity of the process seems very high.[12] As usual in the polymer field, NMR analysis of regioregular copolymers[10] or even of regioirregular copolymers[13] was used to evaluate the stereoregularity in these materials. The absence of model compounds, however, makes the interpretation of the spectra rather difficult. Furthermore, there is still a need for a detailed understanding of the factors involved in regio- and stereoselectivity control in this alternating olefin−carbon monoxide copolymerization. In order to reach this scope monitoring stepwise the insertions of monomers could be an important clue. An analogous strategy has been already successfully applied in the metallocene-mediated polymerizations.[14]

We have already reported on the possibility of changing the chemoselectivity of the bis-carbonylation of styrene from polymeric to low molecular weight materials using the aforementioned catalytic systems.[15−17] With $[Pd(H_2O)_2\{(S)\text{-MeO-Biphep}\}](CF_3SO_3)_2$ as the catalyst precursor, an increase in the concentration of 1,4-benzoquinone causes a shift of the chemoselectivity of the reaction toward the formation of substituted dimethyl succinates with enantioselectivity up to 93% ee.[18] We

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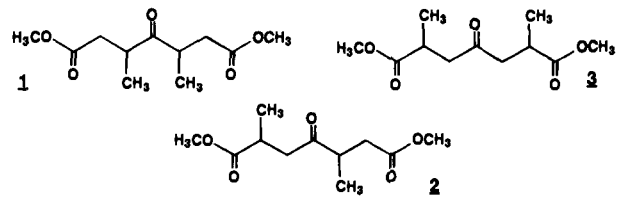
Chart 1



refer here to the possibility of obtaining all isomeric dimethyl dimethyl-4-oxoheptanedioates from propene and carbon monoxide with relatively good chemoselectivity and with enantioselectivity up to 98%, to their identification and NMR characterization, and to the investigation of their composition depending on the ligand (chiral and achiral) used.

Results

Formation, Identification, and Characterization of the Isomeric Dimethyl Dimethyl-4-oxoheptanedioates. Previous attempts to copolymerize propene with carbon monoxide in solvents containing methanol using cationic palladium systems modified by optically pure (6,6′-dimethylbiphenyl-2,2′-diyl)-bis(diphenylphosphine) (Biphemp) and (6,6′-dimethoxybiphenyl-2,2′-diyl)bis(diphenylphosphine) (MeO-Biphep), in the presence of small amounts of 1,4-benzoquinone, gave regioirregular optically active copolymers having molecular weights of about 1000.[19] A large portion of the chains contained carbomethoxy terminations in these materials. An increase in the concentration of 1,4-benzoquinone causes a shift of the chemoselectivity of the reaction toward low molecular weight materials.[18] The effect of the oxidant in reducing the polymerization degree might arise from coordinative interactions, as already observed in other Pd(II)-catalyzed reactions.[20] On the other hand, the hydroquinone formed as a consequence of the reaction of palladium–hydride to palladium–carbomethoxy intermediate[6] could participate to the formation of ester terminations by a fast attack at the acyl intermediates[16,17] followed by transesterification with methanol. We attempted the co-oligomerization of propene and carbon monoxide to give the possible dimethyl dimethyl-4-oxoheptanedioates **1**, **2**, and **3** (Chart 1) by using the optimum stoichiometric ratio between propene and 1,4-benzoquinone of 2. Under these conditions the selectivity of these products approaches 35%.

Gas-chromatographic analysis coupled to mass spectroscopy allowed us to identify the region of the dimeric products **1**, **2**, and **3**, in which six different signals can be recognized. Enantioselective gas-chromatographic analysis shows 10 different signals in the same region (Figure 1). All signals but one are base-line separated; separation for this signal is less effective but still acceptable. This indicates possible identification of all isomers arising from two propene units. Mixtures enriched in the various single products were separated by column chromatography and fully characterized by ^{1}H- and ^{13}C-NMR and by two-dimensional experiments.

The identification of enantiomeric pairs is based on the comparison of the GC analysis of mixtures obtained using either enantiomer of the MeO-Biphep ligand as well as with the achiral ligand 1,3-propanediylbis(diphenylphosphine) (Dppp) (Figure 1).

The identification of **1**, **2**, and **3** is based on the determination of the NMR parameters of mixtures of known composition,

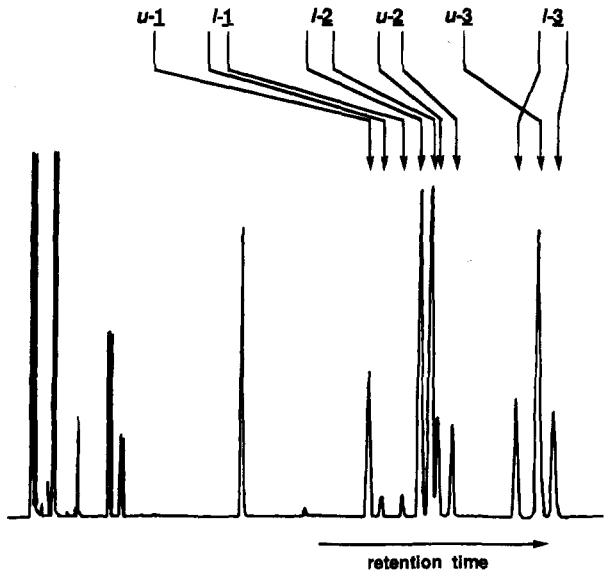


Figure 1. Enantioselective gas chromatography of the dimeric carbonylation products of propene (reaction mixture obtained with the Dppp ligand).

taking particular advantage of the sensitivity of the ^{13}C-NMR parameters of the middle ketocarbonyl group to the substitution of the connected carbon atoms.[9,13,21] The structural assignment to the individual *l*- and *u*-diastereomers[22] for dimethyl 2,5-dimethyl-4-oxoheptanedioate **2** is based on the assumption that the catalytic systems which produce isotactic poly[1-oxo-2-methyltrimethylene][10,23] would also give a larger amount of the *l*-diastereomer. The absolute configuration of the single enantiomers is at the moment unknown. However, even a complete identification of all enantiomers would not allow a full understanding of the system due to the fact that to form the 10 different products 16 different reaction pathways are possible (Scheme 1). The 16 pathways arise from the possible combinations of two olefin units, two enantiofaces, two regioselectivities, and the two directions of growth. In fact, we cannot define which ester end group corresponds to initiation or termination (cf. arrows in Scheme 1).

Regio-, Diastereo-, and Enantioselectivity in the Co-oligomerization and Copolymerization. Table 1 presents the isomeric composition of **1**, **2**, and **3** as well as their diastereomeric and enantiomeric ratios obtained in the dimeric biscarbonylation of propene with various catalytic systems. The modifying diphosphines ligands, which are represented in Chart 2, were of interest also for the copolymerization reaction of propene with carbon monoxide. The corresponding results have been already published.[24,25] The feature of regio- and stereoselectivity of the catalytic systems investigated toward co-oligomerization will be compared in the following for each ligand with that of the copolymerization in order to point out their similarities.

With the achiral Dppp, ligand formation of the head-to-tail dimer **2** takes place with a selectivity of ~50% and a diastereoselectivity that favors the *l*-diastereomer, the diaster-

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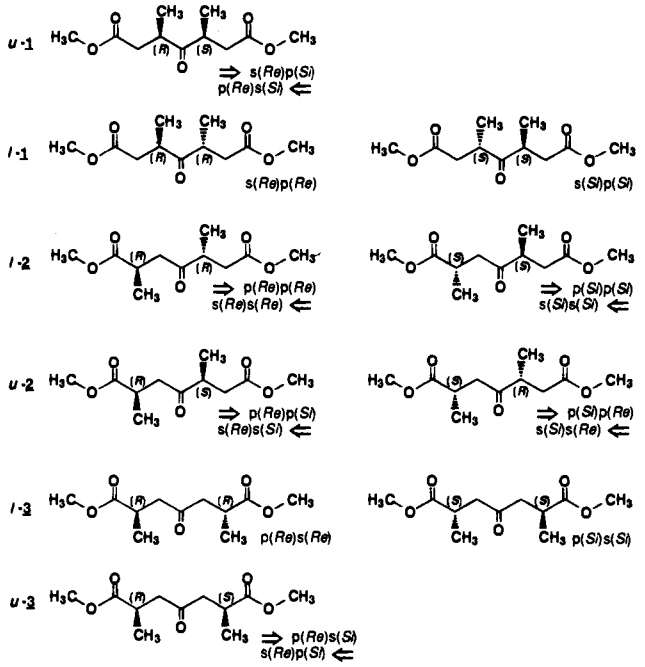
Scheme 1. Structure of the Dimethyl Dimethyl-4-oxoheptanedioates Arising from Propene and Carbon Monoxide and Regio- and Stereochemical Pathways (shown by the arrows) for Their Formation (p = primary, s = secondary insertion).



eomeric ratio (dr) being 22/78. In contrast, the *u*-dimer is preferentially formed for the products **1** and **3** arising from change in regioselectivity of the second insertion (dr = 80/20 and 57/43, respectively). The diastereoselectivity is more pronounced for isomer **1** than for isomer **3**. The same ligand gives catalytic systems able to copolymerize propene with ~60% of the regioregular head-to-tail enchainment.[9] Some stereochemical control seems to exist toward the isotactic copolymer (~50% of the *ll*-triad),[13] but due to the broadness of the bands, the stereoregularity is difficult to evaluate.[9,23] When using the other achiral ligand examined in this study, namely 1,3-propanediylbis[bis(*o*-methoxyphenyl)phosphine] (MeO-Dppp) that shows essentially no regiocontrol (~50% of the head-to-tail enchainment) in the copolymerization of propene,[23] the selectivity for the head-to-tail dimer **2** is only ~35%. The diastereoselectivity in the formation of **2** is much lower (dr = 38/62) than in the previous case. The tail-to-tail dimer **3** is the dimer formed in larger concentration (>58%). The diastereoselectivity in the formation of the head-to-head dimer **1** is remarkably high (dr = 89/11).

When chiral ligands are used for the copolymerization reaction, an enantiomorphic site control of the process is expected.[9,11] With 1,3-dimethyl-1,3-propanediylbis(diphenylphosphine) (Bdpp) some improvement in stereo- and regiocontrol with respect to Dppp is observed.[9,21] The better control in regioselectivity by the Bdpp with respect to Dppp ligand in the co-oligomerization causes a higher selectivity (~65%) toward dimer **2**. However, there is no improvement in the diastereoselectivity; moreover, the enantioselectivity is for all chiral dimers quite low.

The atropisomeric ligands Biphemp and MeO-Biphep[24] cause copolymerization of propene with low regioregularity as does the Binap ligand.[13] Therefore, it is difficult to evaluate the stereoregularity, but it also seems to be relatively low, e.g. ~70% for MeO-Biphep.[24] Both atropisomeric ligands cause formation of the head-to-tail dimer **2** in about 50% concentration with a level of diastereoselectivity (dr = 25/75 and 21/79, respectively), comparable to that observed for the achiral Dppp ligand. The enantioselectivity in the formation of the *l*-dimer (er = 83/17 and 91/9, respectively) is considerably higher than for the *u*-dimer (er = 63/37 and 62/38). The diastereoselectivity in the formation of head-to-head dimer **1** (dr = 85/15 and 89/11, respectively) is again higher than that observed in the formation of dimer **3** (dr =61/39 and 65/35 respectively).

When (*R*)-(6,6′-dimethoxybiphenyl-2,2′-diyl)bis[(*S,S*)-2,5-dimethylphospholane] ((*all-S*)(R_a)-MePhos-MeO-Biphep) is used as the ligand for the propene copolymerization, poly(1-oxo-2-methyltrimethylene) is formed with complete regioregularity and almost no stereoregularity.[24] The regioregularity most probably arises from consecutive primary insertions of the olefin substrate.[10] With this ligand, prevailing formation of the head-to-tail dimers **2** takes place but the selectivity (~84%) is somewhat lower than expected. Some secondary insertion is observed in the dimer formation, particularly for the second inserted propene unit (~10% **3**). The diastereoselectivity in the formation of **2** of the *l*-dimer is also higher than expected (dr = 29/71). The enantioselectivity (er = 72/28) is, however, lower than in the previous cases. With (*R*)-(6,6′-dimethoxybiphenyl-2,2′-diyl)-bis(dicyclohexylphosphine) ((*R*)-MeO-Bichep) as the ligand, poly(1-oxo-2-methyltrimethylene) forms with complete regioregularity and high stereoregularity (>96% *l*-diads).[23,24] Accordingly the formation of head-to-tail dimer **2** prevails and takes place with high chemoselectivity (>91%). The diastereoselectivity toward the formation of the *l*-dimer is high (dr = 7/93); this dimer shows a very high enantiomeric purity (er = ~99/1). Less than 1% formation of head-to-head dimer **1** takes place. However, more than 5% tail-to-tail dimer **3** is formed. In this case, too, the *u*-diastereomer of **3** prevails (dr = 66/34), the enantiomeric purity being low (er = 64/36).

Despite the lack of C_2 symmetry, (*R*)-(6,6′-dimethylbiphenyl-2-(dicyclohexylphosphine)-2′-(diphenylphosphine) ((*R*)-Cy_2-Biphemp), when used as the ligand, gives carbon monoxide–propene copolymers with excellent regioselectivity (>98% head-to-tail enchainment) and a stereoselectivity of ~80% of *l*-diads.[24] Accordingly, a selectivity of 89% and a similar diastereoselectivity (80% *l*-dimer) are found in the formation of **2**. It is noteworthy that the prevailing enantiomer in the formation of *l*-**2** does not parallel the constant relationship between the absolute configuration of the ligand used and the prevailing enantiomer formed.

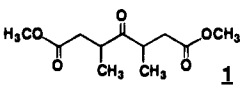
(*R*)-{1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethyl}dicyclohexylphosphine ((*R*)(S_p)-Josiphos) was recently found when used as the ligand to give an active catalyst for a very regioregular (>99% head-to-tail enchainment) and stereoregular (>96% *l*-diads) copolymerization of carbon monoxide with propene.[25] Correspondingly the selectivity in the formation of **2** is high (~94%); however, formation of the dimers is much less diastereoselective than in the previous case for the (*R*)-MeO-Bichep ligand. The dr in the formation of **2** is 17/83, the enantioselectivity for *l*-**2** being also lower (er = 86/14).

Moreover, as in the case of ((*R*)-Cy_2-Biphemp), the prevailing enantiomer in the formation of *u*-**2** is opposite to that expected on the basis of the results obtained with the C_2-symmetric ligands.

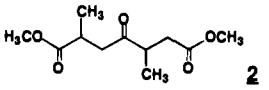
Discussion

The reported results show the possibility of controlling the formation of oligomeric dicarbonylation products of propene and of influencing the diastereoselectivity and the enantioselectivity of the process. The similarity with the results obtained in the corresponding copolymerization has been stressed.

Table 1. Influence of the Ligand on the Composition (%) of the Dimeric Bis-carbonylation Products of Propene[a]



1



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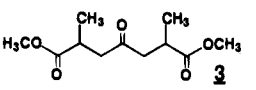
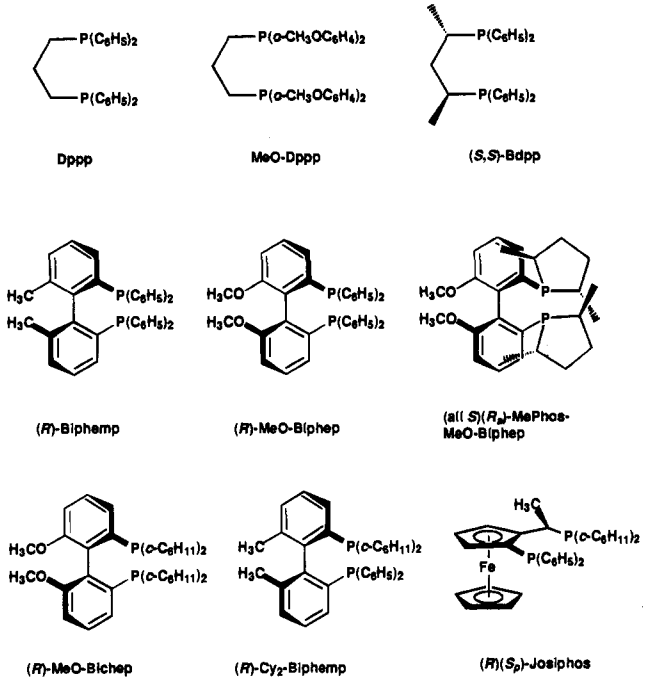


3

ligand	u (*R*,*S*)	$l\{(R^*,R^*)/(S^*,S^*)\}$	dr	$u\{(R^*,S^*)/(S^*,R^*)\}$	$l\{(R^*,R^*)/(S^*,S^*)\}$	dr	u (*R*,*S*)	$l\{(R^*,R^*)/(S^*,S^*)\}$	dr
Dppp	7.8	2.0	80/20	11.4	39.7	22/78	22.2	16.8	57/43
MeO-Dppp	5.5	0.7	89/11	13.6	21.8	38/62	35.8	22.6	61/39
(*S*,*S*)-Bdpp	7.3	2.2 {55/45}	77/23	13.9 {59/41}	50.7 {62/38}	22/78	15.8	10.1 {53/47}	61/39
(*R*)-Biphemp	5.3	0.9 {82/18}	85/15	13.1 {63/37}	39.2 {83/17}	25/75	25.3	16.2 {54/46}	61/39
(*R*)-MeO-Biphep	4.1	0.5 {86/14}	89/11	10.4 {62/38}	39.6 {91/9}	21/79	29.7	15.7 {60/40}	65/35
(*all-S*)(R_a)-MePhos-MeO-Biphep	4.6	1.6 {40/60}	74/26	24.0 {52/48}	60.1 {72/28}	29/71	5.2	4.6 {38/62}	53/47
(*R*)-MeO-Bichep	0.8	~0		6.5 {61/39}	85.3 {99/1}	7/93	4.9	2.5 {64/36}	66/34
(*R*)-Cy_2-Biphemp	2.1	0.4 {54/46}	84/16	17.8 {56/44}	70.8 {21/79}	20/80	5.1	3.8 {38/62}	57/43
(*R*)(S_p)-Josiphos	1.0	0.2 {52/48}	79/21	15.6 {37/63}	78.9 {86/14}	17/83	2.6	1.7 {59/41}	60/40

[a] Enantiomeric ratios are in brackets; the enantiomer with the shorter retention time is always considered first; dr = diastereomeric ratio (*u*/*l*).

Chart 2



According to model studies[26-31] and to the proposed mechanisms for carbalkoxylation of olefins,[32] the formation of the dimethyl-4-oxoheptanedioates should occur through olefin insertion[33-35] in intermediates of the type [$PdCOOCH_3$(L–L')(olefin)]$^+$ (**4**) and [$PdCOCR_2CR_2COOCH_3$(L–L')(olefin)]$^+$ (**5**) (Figure 2).

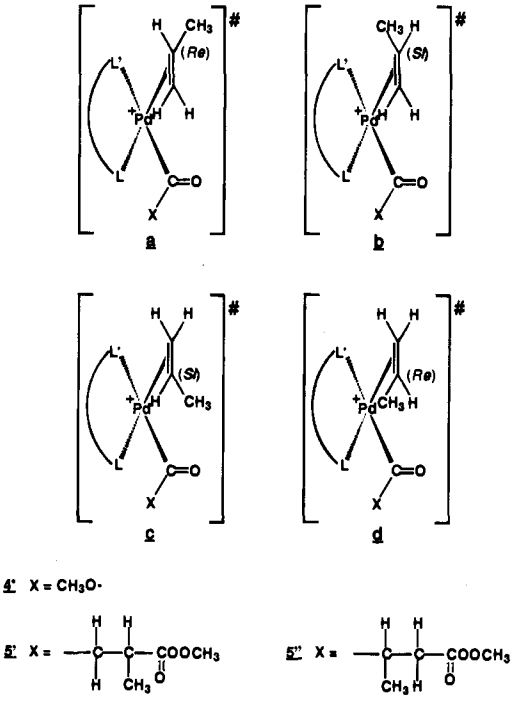


Figure 2. Possible transition states for propene insertion (a and b, secondary; c and d, primary) responsible for the formation of the dimethyl dimethyl-4-oxoheptanedioates.

If the regioselectivity features for olefin insertion were similar for both intermediates **4** and **5**, dimer **2** should form with selectivities greater or equal to 50% and dimers **1** and **3** should form at similar concentrations. However, **1** and **3** form in different amounts for all catalyst systems investigated; dimer **2** forms with only ~35% selectivity for the MeO-Dppp system.

A comparison of the relative concentration of dimers **1** and **3** suggests that the preferred overall regioselectivity for propene insertion is probably primary. Among the ligands that do not give a regioselective copolymerization, MeO-Dppp is the only one for which a preferred secondary regioselectivity of the second inserted propene unit takes place.

For the products **2** that arise from regioregular insertions (insertions with the same regioselectivity), there is a tendency to form the *l*-diastereomer, independent of whether the ligand is chiral or achiral. This tendency is hardly influenced by the

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Table 2. Extent of Enantioface Selection (*Re*/Si**) in the Formation of Dimethyl 2,5-Dimethyl-4-oxoheptanedioate **2** Using Various Chiral Ligands

chiral ligand	(*R*)-MeO-Bichep	(*R*)-Cy_2-Biphemp	(*all-S*)(R_a)-MePhos-MeO-Biphep	(*R*)(S_p)-Josiphos
first propene unit (*Re*/Si**)	15.2−25.7	0.3−0.4	1.9−2.0	3.5−4.6
second propene unit (*Re*Re*/Re*Si**)[a]	21−33	1.5−1.9	3.5−3.8	6.3−11.7
second propene unit (*Si*Re*/Si*Si**))[b]	3.0−4.7	0.1−0.2	~0.7	0.5−0.9

[a] After a first unit with the *Re** enantioface. [b] After a first unit with the *Si** enantioface.

enantioselectivity of the process for the ligands that are not very regiospecific in the copolymerization. For the Josiphos ligand the diastereoselectivity in the formation of dimer 2 is remarkably lower than the diastereoselectivity of the copolymerization process (>96% concentration of *l*-diads).

For products **1** and **3**, which arise from a change in regioselectivity of the second insertion, there is a tendency to form the *u*-dimer, i.e., there is a tendency to change the olefin enantioface together with the regioselectivity of the insertion. This tendency is much stronger after a first secondary (product **1**) than after a first primary insertion (product **3**).

Since we have so far not identified the single enantiomers of the different products, a precise evaluation of enantioface selection is impossible. For the ligands, for which the relative selectivity in the formation of dimer **2** is higher than or close to 90%, some considerations are, however, possible if the formation of the minor amounts of **1** and **3** is disregarded. In Table 2 the extent of enantioface discrimination is reported for the two olefin units. The discrimination was calculated on the basis of the enantiomeric and distereomeric composition. Since the single enantiomers were not yet identified, ranges are given in the table. These ranges are due to the two possibile relative assignments of descriptors to a diastereomer once an assignment is (arbitrarily) done for the other one.

The comparison of enantioface selection for the two propene units clearly shows that asymmetric induction is influenced not only by the presence of the chiral ligand but also by the already formed center of asymmetry (double stereodifferentiation[36]). The much higher enantiomeric purity for the *l*-**2** diastereomer, with respect to the *u*-**2** one normally observed, is also in keeping with this interpretation.

The difference in selectivity between the two olefin units for the formation of the dimethyl dimethyl-4-oxoheptanedioates could be influenced by the difference in nature of the chain involved (cf. Figure 2, group X in 4 and 5). However, we believe that the diastereoselectivity effects observed in the formation of the regioregular dimers **2** represent a reasonable model for the growth of the chain during copolymerization, at least for the regioregular copolymer. As a matter of fact, the terpolymers obtained in the enantioselective terpolymerization of ethene, propene (or 1-butene), and carbon monoxide (molar ratio of ethene/propene > 10) with the same ligands show a lower intensity, with respect to the copolymer, of the circular dichroism band associated with the carbonyl chromophore normalized to the α-olefin content.[24,25] Possible conformational differences of the olefin unit are not probable as indicated by the same ^{1}H-NMR-coupling pattern in the terpolymer and in the copolymer.[10] These results are consistent with enantioface selection being less effective when the growing chain contains no asymmetric carbon atom close to the inserting unit. The mutually reinforcing effect of the growing chain and of the enantiomorphic catalytic site in the control of the stereochemistry of the copolymerization clearly results.

Taking into account the intermediates **4** and **5** for the formation of the dimethyl dimethyl-4-oxoheptanedioates, the composition of the products should reflect the relative activation energy for propene insertion in the four possible transition states (two enantiofaces, and two orientations) arising from the intermediates **4** and **5** (Figure 2).

The results in the co-oligomerization and in the copolymerization[9,10] show the prevailing role of electronic factors in controlling regioselectivity (orientation). On the other hand, assuming that enantioface discrimination is mostly sterical in origin, the preferential formation of the *l*-**2** diastereomer and of the *u*-**1** and *u*-**3** diastereomers is easily rationalized. Let us first consider the formation of the regioregular dimer **2** and assume, for instance, that it is formed through two primary insertions and that for the first insertion **4'd** is preferred from a sterical point of view over **4'c** (cf. Figure 2). The preference should arise from the fact that due to the presence of the chiral ligand the methyl group esperiences different steric hindrance in the two transition states.[37] Subsequent insertion of the second propene unit with the same regioselectivity would be subject to a similar steric situation, and therefore, **5'd** would be preferred to **5'c**. Accordingly (Scheme 1, pathway p(*Re*)p(*Re*)) the *l*-diastereomer is preferentially formed. For the formation of dimer **3** after the primary first insertion (**4'd** preferred over **4'c**) the regioselectivity needs to be changed. For the second inserted unit a similar steric situation is found now in transition state **b** rather than in **a**. Since the opposite enantioface (**5'b** over **5'a**) is preferred, the *u*-**3** diastereomer (Scheme 1, pathway p(*Re*)s(*Si*)) will preferentially form. Similarly, if the first insertion is secondary (e.g., **4'b** preferred over **4'a**), change of regioselectivity would cause preference of **5''d** with respect to **5''c** leading to *u*-**1** (Scheme 1, pathway s(*Si*)p(*Re*)).

The reason why for the C_1-symmetric ligands the prevailing enantiomer in the formation of *l*-**2** and *u*-**2**, respectively, does not parallel the constant relationship between the absolute configuration of the ligand used and the enantiomer prevailing formed is not clear. It is possible that the number of intermediates and transition states (e.g., cf. Figure 2) doubles for these types of ligands.[34] Even though the above-mentioned results for the regio- and stereoselectivity of the copolymerization of propene obtained with the Biphemp (or MeO-Biphep), Bichep (or MeO-Bichep), and Cy_2-Biphemp ligands[24] seem to suggest a site selectivity as in the field of Ziegler−Natta catalysis,[38,39] at least at the level of the olefin insertion step, it is possible that this control is not completely effective.[34,35]

The reported results show the interplay of regioselectivity and enantioface discrimination to control the regularity in the co-oligomerization (and therefore, probably, in the copolymerization) process. Catalyst systems able to give regioregular atactic and isotactic copolymers of propene (and of other α-olefins) with carbon monoxide were identified.[24,25] The present results suggest that manipulation of the MeO-Dppp ligand may help to achieve the still unknown syndiotactic copolymerization of aliphatic α-olefins.

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Experimental Section

Starting Materials. 1,4-Benzoquinone, $PdCl_2$, silver tetrafluoroborate ($AgBF_4$) and silver trifluoromethanesulfonate ($AgSO_3CF_3$) are Fluka products. Dppp was purchased from Strem and Tetrakis(acetonitrile)-palladium(II) tetrafluoroborate from Aldrich. (*R*)-Biphemp, (*R*)-MeO-Biphep, (*R*)-MeO-Bichep, and (*all-S*)(R_a)-MePhos-MeO-Biphep[40-43] were generous gifts by Hoffmann-LaRoche. (S)(R_p)-Josiphos,[44] MeO-Dppp,[45] $PdCl_2(NCPh)_2$,[46] and [Pd(OTf)(Me_2CO)(Dppp)](OTf)[45] were prepared according to published methods. The precursors for the synthesis of (S)(R_p)-Josiphos were kindly given by Dr. F. Spindler (Ciba-Geigy).

General Procedures. Unless otherwise stated, all reactions and manipulations were carried out under purified nitrogen using either Schlenk techniques or a glovebox MBraun MB 150B-G-I. ^{1}H- and ^{13}C-NMR spectra were measured on a Bruker AMX 400 or a Bruker AMX 500 spectrometer with tetramethylsilane or 85% H_3PO_4 as the internal standard. 2D spectra (COSY and HC- and HCC-correlation) were effected in order to allow correct assignment. Gas chromatographic analyses were carried out on a on a Hewlett Packard 5890 II GC with flame ionization detector using Hewlett Packard HP1 (50 m) and Chrompack CP Sil 19 (10 m) capillary columns with acetophenone as the internal standard. The enantiomeric excess was determined by gas chromatography using heptakis(6-*O*-TBDMS-2,3-*O*-methyl)-β-cyclodextrin as the stationary phase. The chiral column was kindly given by Prof. Dr. W. A. König (University of Hamburg). Helium was used as the carrier gas. Absolute methanol over molecular sieves was purchased from Fluka. The other solvents were dried according to conventional methods prior to use.

Synthesis of [$PdCl_2${P—P}]. The preparation of [$PdCl_2${(*R*)-MeO-Biphep}]·H_2O is described in detail. The other compounds were prepared in a similar way. The recrystallization of the products was effected at air using nondried solvents due to the stability of the dichloro complexes.

A solution of $PdCl_2(NCPh)_2$ (0.985 g, 2.57 mmol) in toluene (150 mL) was heated to 70 °C. To this red-brown solution was added (*R*)-6,6′-dimethoxybiphenyl-2,2′-diyl)bis(diphenylphosphine) [(*R*)-MeO-Biphep] (1.530 g, 2.63 mmol) in toluene (50 mL) dropwise. The solution became brighter, and a yellow precipitate formed. The suspension was held for another 2.5 h at this temperature and was then allowed to cool to room temperature. Addition of pentane (200 mL) caused completion of precipitation. The complex was filtered, washed with diethyl ether and dried under reduced pressure. Another crop of crystals could be obtained from the mother solution by cooling at 4 °C overnight. The product was recrystallized from a mixture of THF/hexane. Yield: 95% (1.821 g, 2.40 mmol). ^{1}H-NMR (200 MHz, $CDCl_3$, 25 °C): δ 3.50 (s, 6H, OCH_3), 6.43−6.47 (m, 2H), 6.53−6.62 (m, 2H), 6.84−6.94 (m, 2H), 7.20−7.39 (m, 12H, H_{arom}), 7.65−7.76 (m, 4H_{arom}), 7.89−7.99 (m, 4H_{arom}). ^{31}P-NMR (81.02 MHz, $CDCl_3$, 25 °C): δ 27.61. Anal. Calcd for $C_{38}H_{34}P_2O_3Cl_2Pd$ (777.96): C, 58.67; H, 4.41. Found: C, 58.56; H, 4.60.

[$PdCl_2${(*S,S*)-Bdpp}]. White, yield: 92%. ^{1}H-NMR (300 MHz, CD_2Cl_2, 25 °C): δ 1.05 (d, ^3J(H,H) = 7.0 Hz, 3H, CH_3), 1.10 (d, ^3J(H,H) = 7.0 Hz, 3H, CH_3), 2.04−2.21 (m, 2H), 2.61−2.71 (m, 2H), 7.28−7.36 (m, 4H, H_{arom}), 7.43−7.53 (m, 8H, H_{arom}), 7.73−7.80 (m, 4H, H_{arom}), 7.88−7.94 (m, 4H, H_{arom}). ^{31}P-NMR (121.5 MHz, CD_2Cl_2, 25 °C): δ 24.11. Anal. Calcd for $C_{29}H_{30}P_2Cl_2Pd$ (617.8): C, 56.38; H, 4.89. Found: C, 55.82; H, 4.99.

[$PdCl_2${MeO-Dppp}]. White, yield: 84% (recrystallized from CH_2Cl_2/Et_2O). ^{1}H-NMR (300 MHz, CD_2Cl_2, 25 °C): δ 1.89−2.06 (m, 2H), 2.44−2.49 (m, 4H), 3.74 (s, 12H, OCH_3), 6.98−7.07 (m, 10H, H_{arom}), 7.53−7.58 (m, 6H, H_{arom}). ^{31}P-NMR (121.5 MHz, CD_2Cl_2, 25 °C): δ 16.27. Anal. Calcd for $C_{31}H_{34}P_2O_4Cl_2Pd$ (709.9): C, 52.45; H, 4.83. Found: C, 51.79; H, 4.61.

[$PdCl_2${(*R*)-Biphemp}]. Yellow, yield: 96%. ^{1}H-NMR (200 MHz, $CDCl_3$, 25 °C): δ 1.61 (s, 6H, CH_3), 6.83−7.92 (m, 26H, H_{arom}). ^{31}P-NMR (81.02 MHz, $CDCl_3$, 25 °C): δ 29.13. Anal. Calcd for $C_{38}H_{32}P_2Cl_2Pd$ (727.9): C, 62.70; H, 4.43. Found: C, 63.07; H, 4.86.

[$PdCl_2${(*S*)-MeO-Bichep}]·H_2O. Bright yellow, yield: 92%. ^{1}H-NMR (200 MHz, $CDCl_3$, 25 °C): δ 0.7−2.1 (m, 42H, C_6H_{11}), 3.49 (m, 2H, C_6H_{11}), 3.74 (s, 6H, OCH_3), 7.1−7.5 (m, 6H, H_{arom}). ^{31}P-NMR (81.02 MHz, $CDCl_3$, 25 °C): δ 33.9 (broad). Anal. Calcd for $C_{38}H_{58}O_3P_2Cl_2Pd$ (802.15): C, 56.90; H, 7.29; Cl, 8.84. Found: C, 57.48; H, 7.22; Cl, 8.45.

[$PdCl_2${(*R*)(S_p)-Josiphos}]. Bright orange, yield: 85%. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ 1.1−2.4 (m, 21H, C_6H_{11}), 1.82 (dd, ^3J(H,H) = 7.2 Hz, ^3J(P,H) = 11.3 Hz, 3H, CH*Me*P), 3.21 (m, 1H, C*H*MeP), 3.31 (m, 1H, C_6H_{11}), 3.76 (s, 5H, C_5H_5), 4.18 (m, 1H, C_5H_3), 4.39 (m, 1H, C_5H_3), 4.61 (m, 1H, C_5H_3), 7.16−7.59 (m, 8H, H_{arom}), 8.25−8.32 (m, 2H, H_{arom}). ^{31}P-NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 21.33 (d, ^2J(P,P) = 4.2 Hz), 79.82 (d, ^2J(P,P) = 4.2 Hz). Anal. Calcd for $C_{36}H_{44}FeP_2Cl_2Pd$ (771.9): C, 56.02; H, 5.75. Found: C, 56.36; H, 6.11.

Synthesis of [$Pd(H_2O)_2${P-P}](OTf)$_2$. The preparation of [$Pd(H_2O)_2${(*R*)-MeO-Biphep}](OTf)$_2$ is described in detail. The other compounds were prepared in a similar way. In the case where BF_4^- acts as the counteranion, acetone was used as the solvent because of the lower solubility of these complexes in THF.

A solution of AgO_3SCF_3 (0.632 g, 2.46 mmol) in THF (25 mL) was added dropwise under exclusion of light to a solution of [$PdCl_2$-{(*R*)-MeO-Biphep}] (0.936 g, 1.23 mmol) in THF (125 mL). The reaction mixture was stirred for 2 h at room temperature. The precipitated AgCl was filtered off on Celite and washed twice with THF (15 mL). The filtrate was concentrated to a total volume of about 30 mL by evaporation under reduced pressure. Pentane was added to initiate crystallization which was completed after 24 h at 4 °C. The yellow precipitate was filtered off and dried under reduced pressure. The crude product was recrystallized from THF/hexane and acetone/pentane, respectively. Yield: 77% (0.971 g, 0.95 mmol).

Sometimes only an oily product could be obtained after crystallization overnight. In these cases, the solvents were removed *in vacuo* and the residue was redissolved in THF (30 mL) and poured into cooled (0 °C) pentane (100 mL) while the mixture was rapidly stirred. The resulting powder was immediately filtered off and dried. The recrystallization was carried out as described above. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ 3.51 (s, 6H, OCH_3), 4.05 (s, 4H, H_2O), 6.58−6.60 (m, 2H), 6.79−6.86 (m, 2H) 7.02−7.09 (m, 2H), 7.37−7.88 (m, 20H, H_{arom}). ^{31}P-NMR (121.02 MHz, $CDCl_3$, 25 °C): δ 33.4. Anal. Calcd for $C_{40}H_{36}P_2O_{10}F_6S_2Pd$ (1023.4): C, 46.95; H, 3.55. Found: C, 46.74; H, 3.63.

[$Pd(H_2O)_2${(*S,S*)-Bdpp}](OTf)$_2$. Yellow, yield: 84%. ^{1}H-NMR (200 MHz, $CDCl_3$, 25 °C): δ 1.30 (d, ^3J(H,H) = 7.2 Hz, 3H, CH_3), 1.38 (d, ^3J(H,H) = 7.2 Hz, 3H, CH_3), 2.21−2.49 (m, 2H), 2.83−3.01 (m, 2H), 4.74 (s, broad, 4H, H_2O), 7.37−7.76 (m, 20H, H_{arom}). ^{31}P-NMR (81.02 MHz, $CDCl_3$, 25 °C): δ 30.56. Anal. Calcd for $C_{31}H_{34}O_8F_6P_2S_2Pd$ (881.1): C, 42.26; H, 3.89. Found: C, 42.06; H, 4.19.

[$Pd(H_2O)_2${MeO-Dppp}](OTf)$_2$. Yellow, yield: 72%. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ 2.32−2.48 (m, 2H), 2.87−2.91 (m, 4H), 3.28 (s, broad, 4H, H_2O), 3.75 (s, 12H, OCH_3), 6.85−6.90 (m, 4H, H_{arom}), 6.97−7.02 (m, 4H, H_{arom}), 7.21−7.28 (m, 4H, H_{arom}), 7.48−7.53 (m, 4H, H_{arom}). ^{31}P-NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 18.69. Anal. Calcd for $C_{33}H_{38}O_{12}F_6P_2S_2Pd$ (973.1): C, 40.73; H, 3.94. Found: C, 42.25; H, 3.68.

[$Pd(H_2O)_2${(*R*)-Biphemp}](BF_4)$_2$. Yellow, yield: 72%. ^{1}H-NMR (200 MHz, $CDCl_3$, 25 °C): δ 1.63 (s, 6H, CH_3), 3.01 (s, broad, 4H, H_2O), 6.98−7.92 (m, 26H, H_{arom}). ^{31}P-NMR (81.02 MHz, $CDCl_3$, 25 °C): δ 34.57. Anal. Calcd for $C_{38}H_{36}B_2O_2F_8P_2Pd$ (866.7): C, 52.66; H, 4.19. Found: C, 52.21; H, 4.10.

[$Pd(H_2O)$(THF){(*S*)-MeO-Bichep}](OTf)$_2$. Yellow, yield: 72%. ^{1}H-NMR (200 MHz, $CDCl_3$, 25 °C): δ 0.7−2.3 (m, 42H, C_6H_{11}), 1.85 (m, 4H, THF), 2.90 (m, 2H, C_6H_{11}), 3.74 (m, 4H, THF), 3.77 (s, 6H,

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OCH_3), 4.95 (s_{broad}, 2H, H_2O), 7.28 (m, 2H, H_{arom}), 7.50 (m, 2H, H_{arom}), 7.65 (m, 2H, H_{arom}). ^{31}P-NMR (81.02 MHz, $CDCl_3$, 25 °C): δ 41.2 (broad). Anal. Calcd for $C_{44}H_{66}P_2O_{10}F_6S_2Pd$ (1101.5): C, 47.98; H, 6.04; P, 5.62; F, 10.35. Found: C, 47.67; H, 6.01; P, 5.58; F, 10.48.

[Pd(H_2O)$_2$\{(*R*)(*S$_p$*)-Josiphos\}](OTf)$_2$. Violet, yield: 79%. ^{1}H-NMR (300 MHz, $CDCl_3$, 25 °C): δ 0.9−2.1 (m, 25H, C_6H_{11}, CH*Me*P), 2.6 (s_{broad}, 4H, H_2O), 3.48 (m, 1H, C*H*MeP), 3.84 (s, 5H, C_5H_5), 4.52 (m, 1H, C_5H_3), 4.61 (m, 1H, C_5H_3), 4.79 (m, 1H, C_5H_3), 7.38−7.73 (m, 8H, H_{arom}), 8.11−8.22 (m, 2H, H_{arom}). ^{31}P-NMR (121.5 MHz, $CDCl_3$, 25 °C): δ 28.15, 87.72. Anal. Calcd for $C_{38}H_{48}O_8F_6S_2P_2FePd$ (1035.1): C, 44.09; H, 4.67. Found: C, 42.22; H, 4.50.

Carbonylation of Propene. A 250 mL stainless steel autoclave was charged under an atmosphere of N_2 with benzoquinone (9.45 g, 87.5 mmol). After evacuation, a solution of the catalyst precursor (0.175 mmol) in methanol (100 mL) was transferred as well as propene (7.5 g, 175mmol). The autoclave was pressurized with 250 bar of CO and heated to 50 °C. After 20 h, the autoclave was cooled to room temperature and the residual gas released. Immediate quantitative gas-chromatographic analysis was carried out on a Hewlett Packard HP1 (50 m) column using acetophenone as the internal standard. After removal of the methanol from the reaction mixture under reduced pressure, about 150 mL of toluene was added, causing most of the hydroquinone to precipitate. The filtrate was evaporated and the residue fractionally distilled by Kugelrohr. Each fraction was purified by column chromatography over silica (70−230 mesh) using hexane−ether (3:1) as the eluent. The products were characterized by NMR and GC−MS. The enantiomeric excess was determined by gas chromatography using heptakis(6-*O*-TBDMS-2,3-*O*-methyl)-β-cyclodextrin as the stationary phase.

In the case of (*all-S*)(R_a)-MePhos-MeO-Biphep the catalytic precursor was formed *in situ*. [Pd(CH_3CN)$_4$](BF_4)$_2$ (77.7 mg, 0.175 mmol) and (*all-S*)(R_a)-MePhos-MeO-Biphep (79.7 mg, 0.18 mmol) were suspended in MeOH and stirred until a clear solution was obtained (~0.5 h). The successive manipulations were effected as described above.

Characterization of the Dimethyl Dimethyl-4-oxoheptanedioates. ***u*-Dimethyl 3,5-Dimethyl-4-oxoheptanedioate (*u*-1).** ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.16 (d, ^3J(H,H) =7.2 Hz, 6H, CH_3), 2.31 (dd, ^2J(H,H) = 16.7 Hz, ^3J(H,H) = 6.5 Hz, 2H, CH_2), 2.81 (dd, ^2J(H,H) = 16.7 Hz, ^3J(H,H) = 7.5 Hz, 2H, CH_2), 3.22 (m, 2H, CH), 3.66 (s, 6H, OCH_3). ^{13}C-NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 16.6 (2 × CH_3), 37.1 (2 × CH), 41.1 (2 × CH_2), 51.6 (2 × OCH_3), 172.6 (COOR), 214.7 (CO).

***l*-Dimethyl 3,5-Dimethyl-4-oxoheptanedioate (*l*-1).** ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.21 (d, ^3J(H,H) = 7.2 Hz, 6H, CH_3), 2.30 (dd, ^2J(H,H) = 16.9 Hz, $^3J_{H,H}$ = nd, 2H, CH_2), 2.82 (dd, ^2J(H,H) = 16.9 Hz, ^3J(H,H) = 9.2 Hz, 2H, CH_2), nd (m, 2H, CH), 3.64 (s, 6H, OCH_3). ^{13}C-NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 17.1 (2 × CH_3), 36.4 (2 × CH), 40.3 (2 × CH_2), 51.7 (2 × OCH_3), 172.7 (COOR), 214.3 (CO).

***l*-Dimethyl 2,5-Dimethyl-4-oxoheptanedioate (*l*-2).** ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C) of first unit $CH_3OOCCH(CH_3)CH_2CO-$: δ 1.20 (d, ^3J(H,H) = 7.0 Hz, 3H, CH_3), 2.56 (dd, ^2J(H,H) = 17.7 Hz, ^3J(H,H) = 4.8 Hz, 1H, CH_2), 2.99 (m, 1H, CH); 3.07 (dd, ^2J(H,H) = 17.7 Hz, ^3J(H,H) = 8.6 Hz, 1H, CH_2), 3.67 (s, 3H, OCH_3). ^{1}H-NMR of second unit $-COCH(CH_3)CH_2COOH_3$: δ 1.16 (d, ^3J(H,H) = 7.2 Hz, 3H, CH_3), 2.30 (dd, ^2J(H,H) = 16.9 Hz, ^3J(H,H) = 4.9 Hz, 1H, CH_2), 2.79 (dd, ^2J(H,H) = 16.9 Hz, ^3J(H,H) = 9.3 Hz, 1H, CH_2), 2.99 (m, 1H, CH); 3.65 (s, 6H, OCH_3). ^{13}C-NMR (125.7 MHz, $CDCl_3$, 25 °C) of first unit. $CH_3OOCCH(CH_3)CH_2CO-$: δ 17.1 (CH_3), 34.4 (CH), 44.6 (CH_2), 51.8 (OCH_3), 176.3 (COOR), 210.9 (CO). ^{13}C-NMR of second unit $-COCH(CH_3)CH_2COOH_3$: δ 16.6 (CH_3), 36.8 (CH_2), 42.0 (CH), 51.7 (OCH_3), 172.8 (COOR).

***u*-Dimethyl 2,5-Dimethyl-4-oxoheptanedioate (*u*-2).** ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C) of first unit $CH_3OOCCH(CH_3)CH_2CO-$: δ 1.19 (d, ^3J(H,H) = 7.0 Hz, 3H, CH_3), 2.64 (dd, ^2J(H,H) = 19.9 Hz, ^3J(H,H) = 8.4 Hz, 1H, CH_2), 3.00 (m, 1H, CH), 3.02 (dd, $^2J_{H,H}$ = nd, ^3J(H,H) = nd, 1H, CH_2), 3.68 (s, 3H, OCH_3). ^{1}H-NMR of second unit $COCH(CH_3)CH_2COOH_3$: δ 1.15 (d, ^3J(H,H) = 7.2 Hz, 3H, CH_3), 2.32 (dd, $^2J_{H,H}$ = 16.8 Hz, ^3J(H,H) = 6.5 Hz, 1H, CH_2), 2.77 (dd, ^2J(H,H) = 16.8 Hz, $^3J_{H,H}$ = 8.2 Hz, 1H, CH_2), 3.00 (m, 1H, CH), 3.66 (s, 6H, OCH_3). ^{13}C-NMR (125.7 MHz, $CDCl_3$, 25 °C) of first unit $CH_3OOCCH(CH_3)CH_2CO-$: δ 17.0 (CH_3), 34.6 (CH), 44.2 (CH_2), 51.8 (OCH_3), 176.1 (COOR), 210.6 (CO). ^{13}C-NMR of second unit $-COCH(CH_3)CH_2COOH_3$: 16.4 (CH_3), 36.6 (CH_2), 42.1 (CH), 51.7 (OCH_3), 172.5 (COOR).

***u*-Dimethyl 2,6-Dimethyl-4-oxoheptanedioate (*u*-3).** ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.18 (d, ^3J(H,H) = 7.0 Hz, 6H, CH_3), 2.47 (dd, ^2J(H,H) = 16.9 Hz, ^3J(H,H) = 5.2 Hz, 2H, CH_2), 2.90 (dd, ^2J(H,H) = 16.9 Hz, ^3J(H,H) = 7.7 Hz, 2H, CH_2), 2.95 (m, 2H, CH); 3.67 (s, 6H, OCH_3). ^{13}C-NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 17.0 (2 × CH_3), 34.61 (2 × CH), 45.90 (2 × CH_2), 51.9 (2 × OCH_3), 176.0 (COOR), 206.6 (CO).

***l*-Dimethyl 2,6-Dimethyl-4-oxoheptanedioate (*l*-3).** ^{1}H-NMR (500 MHz, $CDCl_3$, 25 °C): δ 1.17 (d, ^3J(H,H) = 7.1 Hz, 6H, CH_3), 2.48 (dd, ^2J(H,H) = 17.1 Hz, ^3J(H,H) = 4.9 Hz, 2H, CH_2), 2.89 (dd, ^2J(H,H) = 17.1 Hz, ^3J(H,H) = 8.6 Hz, 2H, CH_2), 3.03 (m, 2H, CH); 3.67 (s, 6H, OCH_3). ^{13}C-NMR (125.7 MHz, $CDCl_3$, 25 °C): δ 17.1 (2 × CH_3), 34.58 (2 × CH), 45.92 (2 × CH_2), 51.8 (2 × OCH_3), 176.2 (COOR), 206.9 (CO).

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