

155. The Enantioselective Copolymerisation of Allylbenzene, 1-Allyl-4-(trifluoromethyl)benzene, and 1-Allyl-4-methoxybenzene with Carbon Monoxide

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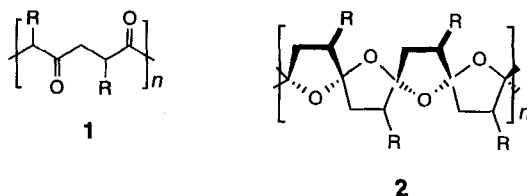
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The olefins mentioned in the title were copolymerized with CO in the presence of palladium catalysts modified with dicyclohexyl $\{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethyl\}$ phosphine. Productivities up to 95 g/(g Pd · h) were achieved. The obtained copolymers were recovered in the pure, regio- und stereoregular polyketone structure **3**. The isotactic poly[2-benzyl-1-oxopropane-1,3-diyl] (**3a**) and its analogues **3b**, **c** were found to isomerize to the corresponding spirocyclic poly[3-(arylmethyl)tetrahydrofuran-2,2,5,5-tetrayl-2-oxy-2-methylene]s **4** in a suspension in CHCl₃, thus indicating that the spiroketal structure is thermodynamically the most stable for these copolymers. However, the atactic material did not undergo any structural transformation. These results show that regularity at the centers of chirality in the main chain is a prerequisite for the conversion of the polyketone to the spiroketal structure.

1. Introduction. – The synthesis of alternating copolymers between carbon monoxide and alk-1-enes is easily achieved in the presence of a variety of N- or P-modified Pd^{II} complexes [1–3]. It is noteworthy that the polymer is formed not only in the well-known polyketone structure **1**, but also as a polyspiroketal **2**, as shown by research groups at the *Shell* company [4] [5]. The novel, unexpected structure received due consideration [6] only after reports about the synthesis of a copolymer between propene and CO appeared which showed that this copolymer had exclusively the poly[spiro-2,5-(tetrahydro-3-methylfuran)] (= poly(tetrahydro-3-methylfuran-2,2,5,5-tetrayl-2-oxy-2-methylene)) structure [7]. Since then, we have identified very active catalytic systems, namely Pd^{II} precursors modified by the ferrocenyl ligand dicyclohexyl $\{(R)-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethyl\}$ phosphine (Josiphos) which are able to copolymerize not only propene, but also higher olefins such as but-1-ene, 4-methylpent-1-ene, and allylbenzene with CO [8] [9]. Extension of the scope of the reaction confirmed the expected stabilization of the spiroketal structure by increasing the substitution at the olefin C=C bond [2]. In fact, the copolymer containing but-1-ene was recovered in percentages of spiroketal structure which varied according to the reaction conditions, while, in the case of 4-methylpent-1-ene as the olefin, the crude material was formed exclusively in the cyclic form [8].

The copolymerization of allylbenzene surprisingly produced the product in the pure polyketone structure [8]. Following our report [10] [11] on the possibility of controlling the regio- and stereochemistry of the copolymerization process, *Jiang* and *Sen* showed that in the presence of [Pd{1,2-bis[(*R,R*)-2,5-dimethylphospholano]benzene}], allylbenzene and CO gave a mixture of the polyketone and the spiroketal structures [12]. More-



over, it was reported that the above mixture could be converted to the pure polyketone in the presence of $(\text{CF}_3)_2\text{CHOH}$ and CHCl_3 and that, in the latter solvent, the pure polyketone converted to the pure spiroketal structure. However, neither a detailed characterization of the obtained copolymer, nor reliable data relative to the activity of the employed catalytic systems were given [12].

To better understand the olefin features necessary to achieve transformation between the two polymeric structures and to study their relative stability, we synthesized and studied the nature of copolymers between CO and 1-allyl-4-(trifluoromethyl)benzene or 1-allyl-4-methoxybenzene in addition to the mentioned copolymer containing allylbenzene as the olefin comonomer [8].

2. Results and Discussion. – Initially, we prepared poly(2-benzyl-1-oxopropane-1,3-diyl) in the presence of propane-1,3-diylbis(diethylphosphine) (Dppe). The catalytic activity (32 g/(g Pd · h)) was satisfactory, while the chain length (M_n 6000) was rather low. The obtained copolymer was linear alternating and completely regioregular, with *ca.* 75% content in *l*-diads (Fig. 1, b). In keeping with our previous reports [8–11] that chiral ligands allow for a higher degree of stereoregularity than achiral ones, the stereoselectivity increased to *ca.* 99% content in *l*-diads (Fig. 2, a) in the presence of dicyclohexyl{(*R*)-1-[(*S*)-2-(diphenylphosphino)ferrocenyl]ethyl}phosphine (Josiphos). Moreover, the productivity increased to 78 g/(g Ph · h) (Table). Upon epimerization of the centres of chirality along the main chain of the copolymer obtained in the presence of Josiphos, the single sharp ^{13}C carbonyl signal (Fig. 1, a) was transformed into a broad band spanning from *ca.* 212 to 210 ppm (Fig. 1, c). As the carbonyl signals of the copolymers obtained in the presence of either the chiral or the achiral ligand show up within this range and based on comparison with copolymers between propene and CO, these materials are indeed regioregular [11]. Furthermore, the high tacticity of the copolymer obtained in the presence of Josiphos is indicated by sharp signals, detectable not only in the carbonyl region (Fig. 1, a), but also in the complete ^1H - and ^{13}C -NMR spectra (Fig. 2). The extent of stereoselectivity was evaluated [13] [14] on the basis of the ‘enantiomorphic-site-control’ model by taking into account that 13 signals appear in the carbonyl region of the copolymer obtained in the presence of Dppe. Therefore, the system can discriminate at least to the level of the pentads (16 possible stereosequences overall).

Evaluation of the ^1H , ^1H -coupling constant of the diastereotopic methylene protons of the main chain in the ^1H -NMR spectrum of poly(2-benzyl-1-oxopropane-1,3-diyl) (3a) revealed a geminal coupling ($^2J = 18.3$ Hz) and two different vicinal couplings ($^3J = 9.3$ and 4.0 Hz). Similar values were measured for the copolymer between propene and CO [11]. For both copolymers, the measured data were interpreted as an indication of conformational homogeneity of the chain in solution. In particular, in the case of

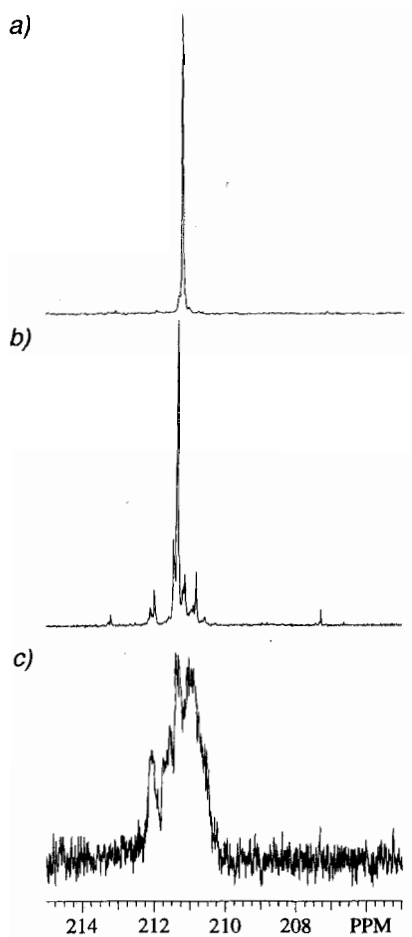
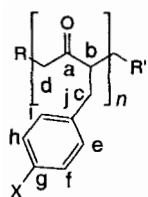


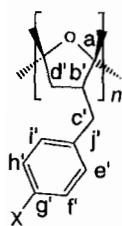
Fig. 1. Carbonyl region in the ^{13}C -NMR (500 MHz, CDCl_3) spectrum of the copolymer obtained from allylbenzene and CO in the presence of a) Josiphos b) Depp and c) Josiphos, after thermal epimerization. The signals at ca. 207 and at ca. 211 ppm correspond to the carbonyl signal of a conjugated terminal unsaturation and to the carbonyl group of a branched saturated end group, respectively.

3a, the circular dichroism measured in the region of the carbonyl $n\text{-}\pi^*$ transition, gave a value of the rotatory strength $\Delta\epsilon$ as high as $+2.34 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$ (at 280.6 nm in CHCl_3).



R, R' = end groups

- 3a** X=H
b X=MeO
c X=CF₃



R, R' = end groups

- 4a** X=H
b X=MeOH
c X=CF₃

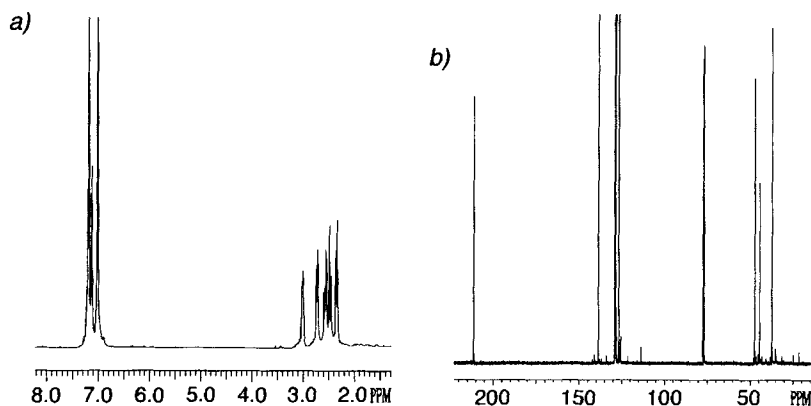


Fig. 2. a) ^1H - (500 MHz, CDCl_3) and b) ^{13}C -NMR (125 MHz, CDCl_3) spectrum of the crude copolymer (structure **3a**) obtained from allylbenzene and CO

Table. Productivity, Molecular Weight, and Melting and Glass-Transition Temperatures of the Allylbenzene, 1-Allyl-4-(trifluoromethyl)benzene, and 1-Allyl-4-methoxybenzene Copolymers with CO Obtained in the Presence of Dicyclohexyl{(E)-1-[(S)-2-(diphenylphosphino)ferrocenyl]ethyl}phosphine

Substrate	Productivity [g/(g Pd · h)]	$M_n^a \cdot 10^3$	$M_w^a \cdot 10^3$	$M_p^a \cdot 10^3$	T_m^b	T_g^b
$\text{PhCH}_2\text{CH}=\text{CH}_2^c$	78.0	10.4	32.6	31.0	68.9	56.7
$p\text{-CF}_3\text{C}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2^d$	44.5	16.6	38.6	37.8	168.9	54.4
$p\text{-MeOC}_6\text{H}_4\text{CH}_2\text{CH}=\text{CH}_2^e$	95.0	11.2	44.7	43.5	168.0	55.0

^a) Measured by viscosimetry. ^b) Values obtained by DCS (differential scanning calorimetry) analysis. ^c) Allylbenzene. ^d) 1-Allyl-4-(trifluoromethyl)benzene. ^e) 1-Allyl-4-methoxybenzene. Reaction conditions as described in the *Exper. Part*.

Solid-state ^{13}C -MAS-NMR analysis of the crude copolymer showed that the product was exclusively formed in the polyketone structure **3a** (Fig. 3, a). When a sample of this crude copolymer was treated for 18 days with CHCl_3 (see *Exper. Part*), the pure polyketone **3a** fully converted to the spiroketal structure **4a** (Fig. 3, b). Fig. 4 shows the IR spectra measured on the two materials. However, when the crude copolymer was thermally epimerized first and then treated with CHCl_3 , the polyketone structure **3a** was retained. Retention of the polyketone structure also occurred when the epimerized poly(2-benzyl-1-oxopropane-1,3-diyl) was stirred in a MeOH solution containing *p*-toluenesulfonic acid, according to a procedure recently described in the patent literature [15] for the conversion of poly(1-oxopropane-1,3-diyl) to the corresponding spiroketal structure. In fact, we could not reproduce the reported results.

Overall, these findings indicate that *i*) the spiroketal structure seems to be the thermodynamically stable form of the isotactic material, and *ii*) regularity at the centers of chirality in the main chain is necessary to achieve transformation between the two structures, *i.e.*, the stereoregularity of the polymer influences the relative stability of the two structures.

Previous experiments [8] showed that, when a sample of the pure isotactic alternating polyketone obtained from but-1-ene and CO was precipitated with MeOH from a

solution of $(\text{CF}_3)_2\text{CHOH}$, the polyketone structure was largely retained. Thus, the question arose as to whether the electronic features of the olefin might rule the type of structure in which the crude copolymer is formed and/or is most stable. To gain insight into this problem, we synthesized copolymers between 1-allyl-4-(trifluoromethyl)benzene

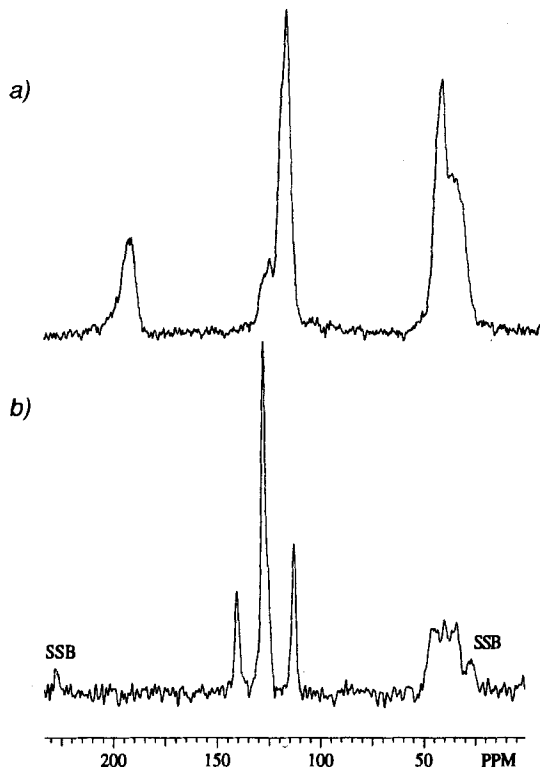


Fig. 3. Solid-state ^{13}C -MAS-NMR (100 MHz) spectrum of the alternating copolymer between allylbenzene and CO a) crude copolymer (structure **3a**); b) after treatment with CHCl_3 (structure **4a**). SSB: Spinning side band.

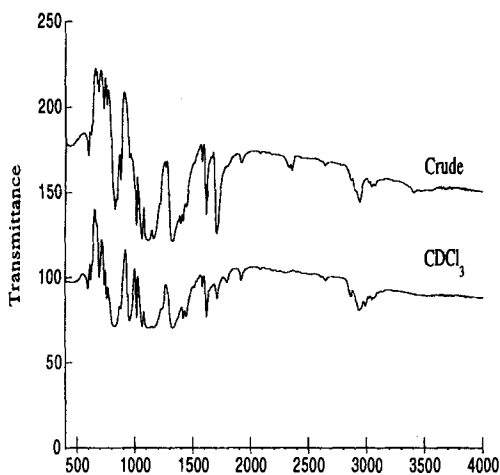


Fig. 4. IR Analysis (KBr) of the crude and CDCl_3 -treated copolymer between allylbenzene and CO (structures **3a** and **4a**, resp.). The carbonyl peak at $\text{ca. } 1700 \text{ cm}^{-1}$ shown by the crude material, disappears in the treated sample and, at the same time, a modification in the region between 1000 and 1400 cm^{-1} occurs, which is related to the presence of the spiroketal structure (see 2).

or 1-allyl-4-methoxybenzene with CO in the presence of the same catalytic system as employed for allylbenzene. The productivity was as high as 95 g/(g Pd · h) in the case of the 1-allyl-4-methoxybenzene substrate (Table), but the highest molecular weight was reached with 1-allyl-4-(trifluoromethyl)benzene as olefin (M_n 16600, Table). The stereo- and regioregularity of the former copolymer (mainly structure **3b**) is indicated by the sharp signals in the ^1H - and ^{13}C -NMR spectra (Fig. 5). As far as the latter copolymer is concerned, the crude product was poorly or non-soluble in most common organic solvents. On the contrary, when the material (structure **3c**) was converted to the spiroketal structure **4c**, it dissolved in THF (see Fig. 6 for ^{13}C -NMR). In both experiments, the crude material was isolated in the polyketone structure. In the case of poly[2-(4-methoxybenzyl)-1-oxopropane-1,3-diyl] (**3b**), we attempted to determine whether the signal at ca. 114 ppm in the ^{13}C -MAS-NMR spectrum (Fig. 7, a) corresponded to the aromatic C-atoms in *ortho*-position to the MeO-substituted position at the benzene ring (predicted shift: 113.9 ppm) [16], or whether a low concentration of spiroketal structure **4b** was also present. Thus, we carried out an NQS (*non-quaternary suppression*) experiment. Unfortunately, the results were unsatisfactory. Nonetheless, even if the spiroketal structure **4b** had been formed, its concentration would have been very low compared with that of the polyketone structure **3b**.

When samples of poly[2-(4-methoxybenzyl)-1-oxopropane-1,3-diyl] and poly{1-oxo-2-[4-(trifluoromethyl)benzyl]propane-1,3-diyl} were stirred in CHCl_3 as above, a complete conversion to the spiroketal structure **4** occurred, as shown for the former copolymer in Fig. 7, b.

The nature of the end groups was extensively analyzed for the poly[2-(4-methoxybenzyl)-1-oxopropane-1,3-diyl] (**3b**) as the analogous poly{1-oxo-2-[(trifluoromethyl)benzyl]propane-1,3-diyl} (**3c**) polymer presented the above-mentioned solubility problems, and poly[2-benzyl-1-oxopropane-1,3-diyl] (**3a**) was most soluble in CHCl_3 which, unfortunately, also promoted its conversion to the spiroketal structure. Among the possible end groups [6] [11], *i.e.*, methoxycarbonyl and saturated and unsaturated, we will describe only those that could be clearly assigned. In the ^1H -NMR spectrum of **3b** peaks which

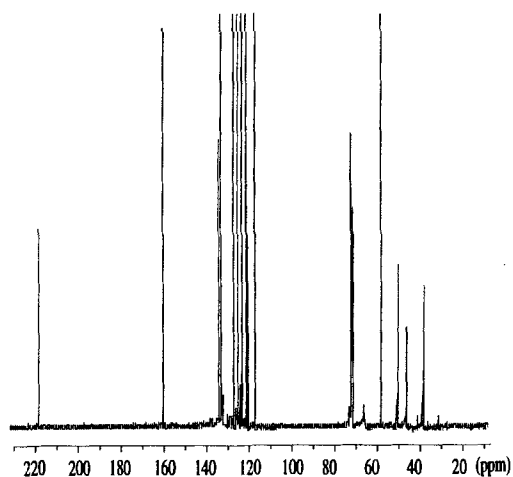
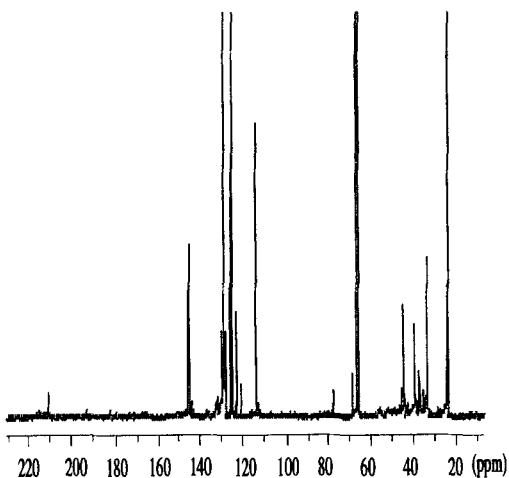
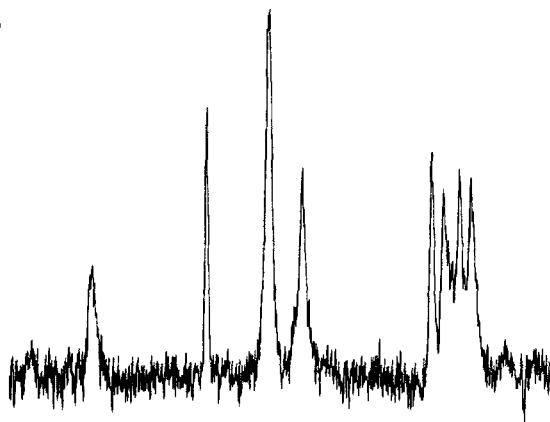


Fig. 5. ^{13}C -NMR (125 MHz, $(\text{CF}_3)_2\text{CDOD}$) Spectrum of 1-allyl-4-methoxybenzene CO copolymer (mainly structure **3b**). $(\text{CF}_3)_2\text{CDOD}$ signals between 127 and 120 ppm and between 72 and 70 ppm.

Fig. 6. ^{13}C -NMR (125 MHz, THF) Spectrum of poly{tetrahydro-4-[4-(trifluoromethyl)benzyl]furan-2,2,5,5-tetrayl-2-oxy-2-methylene} (**4c**). THF Signals as broad bands at ca. 70 and 25 ppm.



a)



b)

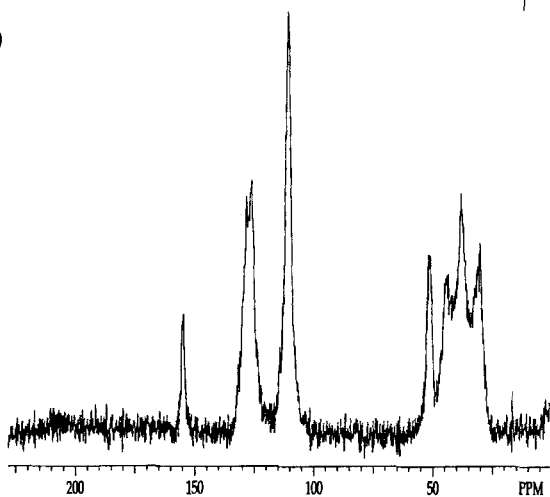


Fig. 7. Solid-state ^{13}C -MAS-NMR (100 MHz) spectrum of the alternating copolymer between 1-allyl-4-methoxybenzene and CO: a) crude copolymer (structure **3b**); b) after treatment with CHCl_3 (structure **4b**)

are marked (Fig. 8) with the same label were shown to correlate to each other by COSY-90 and COSY-long-range experiments. They arise from the end groups A (☆) and B (□), respectively.

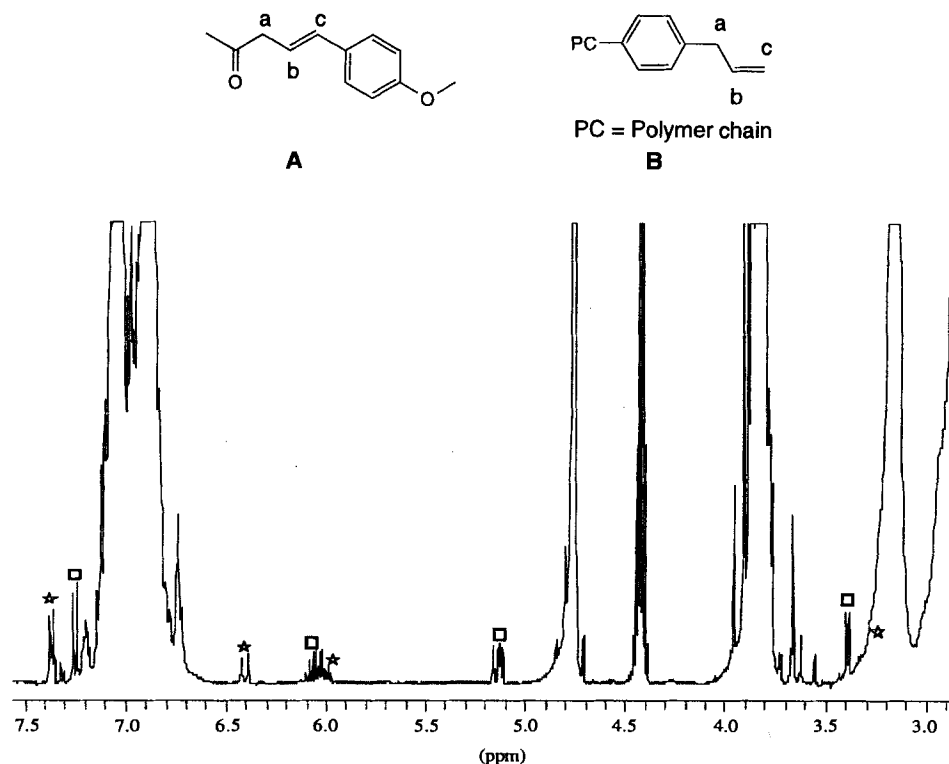


Fig. 8. Signals of the end groups A (☆) and B (□) in the $^1\text{H-NMR}$ (500 MHz, $(\text{CF}_3)_2\text{CDOD}$) spectrum of the copolymer between 1-allyl-4-methoxybenzene and CO (structure 3b)

Protons H–C(c) and H–C(b) of A show at 6.4 ppm a d ($J = 16$ Hz) and at 5.98 ppm a dt ($J = 16$ and 7 Hz). The d at 6.4 ppm correlates with a d at 7.35 ppm ($J = 9$ Hz). The latter d is part of an $AA'BB'$ system, typical of *para*-disubstituted aromatic rings. The COSY-90 experiments show the other half of the dd at 6.95 ppm, under the main aromatic signal. The dt at 5.98 ppm (H–C(b)) correlates to a signal at ca. 3.2 ppm that, unfortunately, overlaps with a large signal of the main chain. According to the chemical-shift predictions, the latter signal corresponds to the CH_2 (a) group (see A).

Part of the expected aromatic $AA'BB'$ system of B can be identified as a d at 7.22 ppm ($J = 8.5$ Hz). The COSY-90 experiments show the other half of the dd at 6.95 ppm, under the main aromatic signal. The signal at 7.22 ppm correlates to a d at ca. 3.35 ppm ($J = 7$ Hz; CH_2 (a)), which, in turn, correlates to two m , one centered at ca. 6.03 ppm ($J = 7$ and 10 Hz; H–C(b)) and the other at ca. 5.1 ppm (CH_2 (c)). Fig. 9 shows in detail the patterns arising from H–C(b) of B ($v =$ four strongly overlapped t) and to the t of H–C(b) of A ($t = t$).

Unsaturation such as in the end group B can be generated either by an aromatic electrophilic substitution at the *ipso*-position (*ipso* attack [17]), or by activation of the C–H aromatic bond by $[\text{Pd}(\text{OAc})_2]$ [18]. The presence of the end group A is supported by a comparison with the end groups identified for the analogous copolymer between allylbenzene and CO. However, in both cases, it remains unclear as to whether the olefin

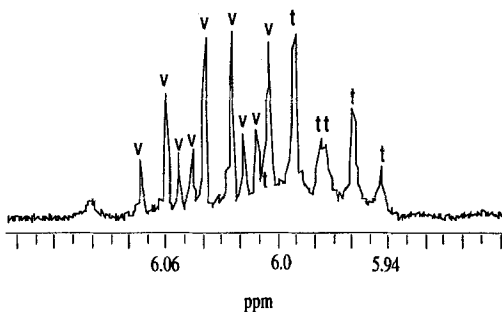


Fig. 9. $^1\text{H-NMR}$ (500 MHz, $(\text{CF}_3)_2\text{CDOD}$) Region of the unsaturated allyl end groups **A** and **B**. Peak labelling: $t = t$ arising from $\text{H-C}(b)$ of **A**; $v = m$ arising from $\text{H-C}(b)$ of **B**.

unit is at the end of the polymer chain, (*i. e.*, it is an end group) or whether the olefin *ipso*-position is bonded to a C-atom along the main chain.

3. Conclusions. – It was not by chance that we chose the title allylbenzenes analogues to carry out our investigations. It has been reported recently that, instead of the target polyketone, a '[1₆]ketonand' a cyclic polyketal, a '[1₆]starand', was obtained as product of the oxidation of the benzylic methylene groups of [1₆]orthocyclophane [19–21]. *Ab-initio* calculations [21] suggest an 'ionic' character of the polyketal C–O bond. If these assumptions are true, then it should be possible to influence the stability of the C–O (ionic) bond and, eventually, destabilize the spiroketal ('starand') to give the polyketone ('ketonand') structure. For this purpose, we chose aromatic substituents causing opposite electronic effects. The poly[2-benzyl-1-oxopropane-1,3-diyl] copolymer was isolated in the polyketone structure **3a**, in agreement with the destabilization of the ionic C–O bond *via* the benzyl group, an electron-withdrawing substituent. When 1-allyl-4-(trifluoromethyl)benzene with the strongly electron-withdrawing CF_3 group ($\sigma = +0.53$) was copolymerized with CO, the crude product was again recovered in the polyketone structure (see **3c**). If 1-allyl-4-methoxybenzene ($\sigma = -0.28$, EDG) was employed, the crude product had mainly the polyketone structure **3b**. This result, might be explained by the MeO group being too weak an electron donor to allow the generation of the crude product in the sole spiroketal structure **4b**. The reported results show that the title copolymers can be efficiently copolymerized with CO in the presence of Pd^{II} catalysts modified by diphosphine ligands. Transformation from the polyketone to the spiroketal structure can be achieved if the copolymers are stereoregular, under which conditions the latter structure is the thermodynamically stable form of these materials.

Experimental Part

1. *General.* $\text{Ni}(\text{ClO}_4)_2$ and 1,3-naphthoquinone were purchased from *Fluka*. $[\text{Pd}(\text{AcO})_2]$ was purchased from *Aldrich*. *Dppe*, $[\text{Pd}(\text{Dppe})(\text{AcO})_2]$, and *Josiphos* were prepared according to [22] [23]. Solvents were dried according to usual procedures under N_2 . Manipulation of the air-sensitive products was carried out under N_2 or Ar using *Schlenk* techniques. Circular dichroism spectra: *Jasco 600*; in CHCl_3 ; λ in nm ($\Delta\epsilon$ in $\text{l mol}^{-1}\text{cm}^{-1}$). Light scattering, gel permeation chromatography (GPC) and viscosimetry measurements. *Knauer* HPLC system equipped with a *KMX-6 Chromatix* (laser-light source at 633 nm), a *Knauer-DRI* refractometer, and a *Viskotek* differential viscosimeter, model 502. Differential-scanning calorimetry (DSC) measurements: *Mettler-DSC-30* instrument. IR Spectra *Mattson Instruments 6020 Galaxy*, series *FTIR*; as KBr pellets; in cm^{-1} . NMR Spectra: *Bruker-AMX-400* (solid state MAS (magic-angle spinning)) and a *Bruker-500* spectrometer; in $(\text{CF}_3)_2\text{CDOD}$ or in CDCl_3 with Me_4Si as the internal standard; (δ in ppm, J in Hz).

2. *Copolymerization Experiments*. 2.1. A mixture of $[\text{Pd}(\text{AcO})_2]$ (0.1 mmol), $[\text{Ni}(\text{ClO}_4)_2]$ (0.3 mmol), and Josiphos (0.11 mmol), in a mixture of *t*-BuOH (14 ml), toluene (2 ml), and MeOH (1.3 ml) was stirred for at least 15 min at r.t. under N_2 , prior to introduction into a 125-ml stainless-steel autoclave. 1,4-Naphthoquinone (1.5 mmol) had been introduced into the autoclave prior to evacuation under high vacuum and purging with N_2 . Allylbenzene (178 mmol) was introduced into the autoclave under N_2 flow. The reaction vessel was charged with CO (40 bar), heated at 40° , and stirred for 25 h. After cooling to r.t., the pressure was released, and MeOH was added to the obtained powder. The suspension was stirred and left at 4° overnight. The copolymer was filtered, washed with MeOH, and dried under high vacuum: 20.8 g of poly(2-benzyl-1-oxopropane-1,3-diyl) (**3a**), productivity 78 g/(g Pd · h). Viscosimetry analysis: M_w 32600, M_n 10400, M_p 31000. DSC: T_m 68.9°, T_g 56.7°. CD (CHCl_3 , $c = 1.57$ mg/ml): 280.6 ($\Delta\epsilon = +2.34$). $[\alpha]_D^{25} = +122.3$ (CHCl_3 , $c = 1.57$ mg/ml). $^1\text{H-NMR}$ (500 MHz, CDCl_3): 7.2 (*m*, 3 H, Ph); 7.0 (*m*, 2 H, Ph); 3.05 (CH_2 (b)); 2.72, 2.34 (2 H, PhCH_2 (c)); 2.57, 2.47 (2 H, PhCH_2 (c)). $^{13}\text{C-NMR}$ (500 MHz, CDCl_3): 211.2 (C(a)O); 138.5 (C(g), Ph); 128.9, 128.5 (4 C, Ph); 126.5 (C(j), Ph); 47.3 (CH(b)CO); 44.4 (CH_2 (d)CO); 37.2 (PhCH_2 (c)). $^{13}\text{C-MAS-NMR}$ (Rot. 8 K): 209.5 (br., C(a)O); 142–120 (Ph); 46–25 (CH(b)CO; CH_2 (d)CO, PhCH_2 (c)). Anal. calc. for $(\text{C}_{16}\text{H}_{16}\text{O})_n$ (146.181): C 82.2, H 6.9; found: C 82.2, H 6.9.

After thermal treatment of **3a**, poly(3-benzyltetrahydrofuran-2,2,5,5-tetra-2-oxo-2-methylene) (**4a**) was obtained. $^{13}\text{C-MAS-NMR}$ (Rot. 8 K): 140.8 (br., Ph, C(i')); 138–124 (Ph); 116.6. (C(a')); 49–38 (CH(b')CO; CH_2 (d')CO, PhCH_2 (c')).

2.2. Analogously to 2.1, with $[\text{Pd}(\text{Dppe})(\text{AcO})_2]$ (0.06 mmol), $\text{Ni}(\text{ClO}_4)_2$ (0.15 mmol), *t*-BuOH (7 ml), toluene (1 ml), MeOH (0.7 ml), 1,4-naphthoquinone (0.75 mmol), allylbenzene (89 mmol), and CO (40 bar; 40° for 48 h): 9.3 g of copolymer, productivity 32 g/(g Pd · h). Viscosimetry analysis: M_w 21100, M_p 18500, M_n 6000.

2.3. Analogously to 2.1, with $[\text{Pd}(\text{AcO})_2]$ (0.02 mmol), $\text{Ni}(\text{ClO}_4)_2$ (0.06 mmol), Josiphos (0.02 mmol), *t*-BuOH (2.8 ml), toluene (0.45 ml), MeOH (0.3 ml), 1,4-naphthoquinone (0.32 mmol), 1-allyl-4-(trifluoromethyl)benzene (37 mmol), and CO (40 bar; 40° for 45 h): 4.45 g of copolymer, productivity 44.5 g/(g Pd · h). Viscosimetry analysis: M_n 16.600, M_w 38.600, M_p 37.800. DSC: T_m 168.49°, T_g 54.4°. Anal. calc. for $(\text{C}_{11}\text{H}_9\text{F}_3\text{O})_n$ (214.183): C 61.7, H 4.2, F 26.6; found: C 61.6, H 4.1, F 26.3.

Peak labelling for the $^{13}\text{C-NMR}$ spectrum shown in Fig. 6 and according to structure **4c**. $^{13}\text{C-NMR}$ (125 MHz, THF): 210.8 (COH); 145.9, C(j) (Ph); 130.9–128.8 (C(e), C(i'), C(g') (Ph)); 125.8 (C(f), C(h') (Ph)); 114.4 (C(a'')); 46.1 (CH(b')CO); 41.0 (CH_2 (d')CO); 35.2 (PhCH_2 (c')).

2.4. Analogously to 2.1, with $[\text{Pd}(\text{AcO})_2]$ (0.04 mmol), $\text{Ni}(\text{ClO}_4)_2$ (0.11 mmol), Josiphos (0.04 mmol), *t*-BuOH (4.9 ml), toluene (0.78 ml), MeOH (0.5 ml), 1,4-naphthoquinone (0.55 mmol), 1-allyl-4-methoxybenzene (65 mmol), and CO (40 bar); for 26 h: 9.6 g of copolymer, productivity 95 g/(g Pd · h). Viscosimetry analysis: M_n 11.200, M_w 44.700, M_p 43.500. DSC: T_m 168.0°, T_g 55°. Anal. calc. for $(\text{C}_{11}\text{H}_{12}\text{O}_2)_n$ (176.207): C 78.0, H 6.9; found: C 78.1, H 6.9.

Peak labelling for the $^{13}\text{C-NMR}$ spectrum shown in Fig. 5 and according to structure **3b**. $^{13}\text{C-NMR}$ (125 MHz, $(\text{CF}_3)_2\text{CDOD}$) 217.4 (C(a)O); 159.6 (C(g), Ph); 133.5 (C(j), Ph); 132.3 (C(j), C(e), Ph); 116.5 (C(f), C(h), Ph); 57.4 (MeO); 50.2 (CH(b)CO); 44.7 (CH_2 (d)CO); 38.1 (PhCH_2 (c)).

3. *Treatment with Chloroform*. In a typical procedure, a soln. of polymer (1 g) in CHCl_3 (ca. 15 ml) was stirred at r.t. for 18 days. The solvent was removed and the obtained product dried under high vacuum.

4. *Thermal Epimerization*. Preliminary experiments carried out on a sample of isotactic poly(2-ethyl-1-oxopropane-1,3-diyl) showed that a complete epimerization of the chirality centers had occurred after the copolymer was thermally treated for ca. 10 h. Therefore, in a typical procedure, a sample of the raw copolymer (ca. 2 g), was heated in an oil bath at 200° under N_2 for 10 h. The glassy product was cooled to r.t. and dried under high vacuum. The obtained material was analyzed by $^{13}\text{C-NMR}$.

5. *Synthesis of 1-Allyl-4-(trifluoromethyl)benzene*. To a soln. of allyl bromide (0.137 mol) in Et_2O (ca. 140 ml), [4-(trifluoromethyl)phenyl]magnesium bromide, (prepared from Mg turnings (0.178 mol) and 4-(trifluoromethyl)phenyl bromide (0.178 mol) in Et_2O (ca. 150 ml)) was added dropwise under vigorous stirring at r.t. The reaction was self-sustained by a gentle reflux of Et_2O . After the addition was completed, the mixture was further stirred for 48 h at r.t. The reaction was quenched by careful addition of ice cubes. The org. phase was extracted with brine and Et_2O , the org. layer dried (MgSO_4) and evaporated, and the thick brown oil distilled under normal pressure. A colorless liquid was obtained which, by GC, showed traces of the starting 4-(trifluoromethyl)phenyl bromide and of its dimer. A second distillation using a Vigreux column yielded pure product at 172 – 174° . Yield 60%. $^1\text{H-NMR}$ (200 MHz, CDCl_3): 7.54, 7.29 (*dd*, $J = 8$, 4 arom. H); 5.95 (*m*, $\text{CH}_2 = \text{CHCH}_2$); 5.1 (*m*, $\text{CH}_2 = \text{CHCH}_2$); 3.45 (*d*, $J = 6.7$, $\text{CH}_2 = \text{CHCH}_2$). $^{19}\text{F-NMR}$ (188 MHz, CDCl_3): -62.6 (s). $^{13}\text{C-NMR}$ (200 MHz, CDCl_3): 144.2 ($\text{CH}_2 = \text{CHCH}_2$); 136.3 (arom. C); 128.9 (4 arom. C); 125.5 (CF_3); 125.5 (arom. C); 116.6 ($\text{CH}_2 = \text{CHCH}_2$); 39.9 ($\text{CH}_2 = \text{CHCH}_2$).

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