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Polyketones as alternating copolymers of carbon monoxide

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Abstract. Characteristic features of the catalytic synthesis of alternating copolymers of carbon monoxide with various olefins, dienes, styrene and its derivatives are considered. The diversity of catalyst systems used for the copolymerisation of carbon monoxide is demonstrated and their influence on the structure and the molecular mass of the resulting copolymers is analysed. The data on the structure and physicochemical and mechanical properties of this new generation of functional copolymers are generalised and described systematically for the first time. The bibliography includes 296 references.

I. Introduction

Alternating copolymers of carbon monoxide with acyclic and cyclic alkenes, dienes, styrene and its derivatives represent a new generation of functional low- and high-molecular-weight compounds.

$$n\,RCH{=}CH_2 + n\,CO \longrightarrow -(CH(R)-CH_2-C(=O))_n-$$

Systematic data on the synthesis, structure, and properties of these unusual copolymers have been appearing in the literature since the mid-1980s. Some of them (for example, copolymers of alkenes with carbon monoxide) have already found practical application.

The considerable interest of researchers in the problem of alternating copolymerisation of carbon monoxide with various monomers is indicated by the annual increase in the number of relevant publications. About 60% of these papers are devoted to the synthesis of alternating copolymers of carbon monoxide with alkenes, dienes, styrene and its derivatives. The European patent authority has now granted more than 300 patents for catalyst systems and methods for the preparation of alternating copolymers from carbon monoxide and alkene or diene monomers and for compositions of these copolymers with other polymers. A number of reviews have been devoted to the copolymerisation of carbon monoxide with olefins.[1–8]

The ready availability and low cost of carbon monoxide are important factors in the preparation of carbon monoxide copolymers.[9] The possibility of controlling the structure of copolymers by changing the order of connection of the CO groups to other monomer units allows one to prepare polymers with a set of new properties (high adhesion, high stability against photo- and biodestruction and so on).[2, 10, 11]

The purpose of this review is to analyse the key results obtained during the last decade in the field of catalytic alternating copolymerisation of carbon monoxide not only with olefins but also with dienes and functionalised olefins. Taking carbon monoxide copolymerisation with ethylene (the best studied pair of comonomers) as an example, the stepwise mechanism of copolymerisation is considered. The data on the structure and physicochemical and mechanical properties of a new generation of polyketones are described systematically for the first time.

II. Copolymers of carbon monoxide with olefins, dienes and other monomers

1. Carbon monoxide – ethylene

The alternating copolymers of carbon monoxide with ethylene were first synthesised under the action of $Ni(CN)_2$ in 1941.[12] Subsequently, $Pd(CN)_2$ [13] and its hydride form [14] have been used as the catalysts. The resulting ethylene – carbon monoxide copolymers have high molecular masses and melting points. The yield and the intrinsic viscosity ($[\eta]$) of the copolymers are markedly influenced by the nature of the solvent used as the reaction medium. In particular, the yield and the intrinsic viscosity increase in the sequence of solvents water < acetonitrile < *m*-cresol < chloroform < methyl ethyl ketone < ethyl acetate.

The data on the preparation of ethylene copolymers with carbon monoxide published in the patent literature before 1980 indicated that the synthesis had to be carried out at high temperature (100 – 200 °C) and that the product yields were low (see, for example, patents [12–14]). The activity of the catalysts (various Ni and Pd complexes) described in these publications was very low.

The possibility of copolymerisation of these monomers at room temperature was first reported in 1982.[15] As the catalyst, the researchers used the complex $[Pd(MeCN)(PPh_3)_3](BF_4)_2$. Copolymerisation was carried out in chloroform at a pressure of an equimolar monomer mixture of 5 MPa. The average copolymerisation rate did not exceed 10 $g\,g_{Pd}^{-1}\,h^{-1}$. Later, it has been shown [16–18] that the rate of alternating copolymerisation of

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carbon monoxide and ethylene can reach 1000 g g_{Pd}^{-1} h^{-1} when the process is carried out in acetic acid in the presence of monodentate organophosphorus ligands. Ethylene copolymerisation with carbon monoxide in an acid medium has been considered.[19]

The use of bidentate organophosphorus ligands and acids with $pK_a \leqslant 2$ as components of Pd catalysts has initiated new vigorous research in this field.[20] A detailed study[21,22] of the kinetics of carbon monoxide copolymerisation with ethylene in the presence of $Pd(OAc)_2$–diphosphine–acid systems has shown that the reaction rate depends on the natures of the phosphine and the acid, the presence of an oxidant (for example, 1,4-benzoquinone), and also the amounts of these components with respect to palladium acetate.† These results have been supported by studies of Chinese researchers.[25]

As a rule, ethylene copolymerisation with carbon monoxide under the action of $Pd(OAc)_2$ and other Pd complexes is carried out in a rather polar medium (methanol is the best choice).[26,27] For increasing the catalytic activity of the Pd catalyst, the solvent must contain trace amounts (in some cases, several percent) of methanol or water.[27–29] The long induction period and low copolymerisation rate are due to the disregard of this requirement.[28]

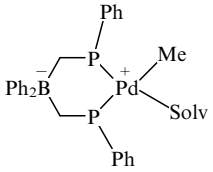
Copolymerisation of ethylene with carbon monoxide in the presence of the palladium complexes $[(L)Pd(MeCN)_2](BF_4)_2$, $[(L)Pd(H_2O)(TsO)](TsO)$ [L = $Ph_2P(CH_2)_3PPh_2$ (**1**)] and *trans*-$[(PCy_3)_2Pd(H)(H_2O)](BF_4)$ (Cy is cyclohexyl)[27–30] proceeds at a somewhat lower rate than that in the presence of the $Pd(OAc)_2$–diphosphine–acid system.

Usually, CF_3COOH or TsOH are employed as the acids in the $Pd(OAc)_2$–$Ph_2P(CH_2)_3PPh_2$–acid catalyst system (the copper salts of these acids can also be used).[16,31,32] Data on the activating effect of perchloric[33] and phosphoric[34] acids and nickel, copper, iron, zirconium or vanadium sulfates or perchlorates have been reported. It was shown[31,35] that the rate of ethylene copolymerisation with carbon monoxide depends on the type of the acid and decreases in the sequence CF_3SO_3H > *p*-$MeC_6H_4SO_3H$ > CF_3COOH > PhCOOH ≈ HBF_4 > CCl_3COOH > $C_6H_3Cl_2$.COOH > HCl. However, to establish a quantitative correlation between the copolymerisation rate and the acid pK_a, systematic studies are required.

The rate of ethylene–carbon monoxide copolymerisation in the presence of the $Pd(OAc)_2$–diphosphine–acid catalyst system depends also on the nature of the diphosphine. Patent data on the synthesis of ethylene–carbon monoxide copolymers indicate that $Pd(OAc)_2$–CF_3COOH–$(2\text{-}MeOC_6H_4)_2P(CH_2)_3P(C_6H_4OMe\text{-}2)$ (**2**) is the most active catalyst system.[36] In this case, copolymerisation rate can reach 33 000 g g_{Pd}^{-1} h^{-1} (with an overall pressure of 9 MPa). When the copolymerisation is performed at a low pressure and temperature, its rate and the yield of the copolymer decrease. For ethylene copolymerisation with CO in methanol in the presence of CF_3COOH used as the acid component, the reaction rate increases in the following sequence of diphosphines: bis(diphenylphosphino)methane (**3**) < 1,6-bis(diphenylphosphino)hexane (**4**) < 1,5-bis(diphenylphosphino)pentane < 1,4-bis(dibutylphosphino)butane (**5**) < 1,4-bis(butylphenylphosphino)butane (**6**) < 1,2-bis(diphenylphosphino)ethane (dppe) (**7**) < 2,3-bis(diphenylphosphino)butane (*meso*, *rac*) (**8**) < 2,4-bis(diphenylphosphino)pentane (*meso*, *rac*) (**9**) < 1,3-bis(di-n-butylphosphino)propane (dbpp) (**10**) < 1,4-bis(diphenylphosphino)butane (**11**) < 1,3-bis(diphenylphosphino)propane (**1**) < 1,3-bis[di(2-methoxyphenyl)phosphino]propane (**2**).[21,31,34,37–39] Comparison of the activities of various diphosphines with the activity of 1,3-bis(diphenylphosphino)propane used most often has shown that the introduction of alkyl substituents into the 2-position of propane barely influences the catalyst activity, whereas the introduction of alkyl groups into the 1,3-positions changes the activity of the palladium catalyst. This attests to the influence of the electronic and steric factors on the catalyst activity. It has been shown[40–43] that for copolymerisation of carbon monoxide with ethylene in the presence of the $[Pd(Me).(MeCN)(P\text{-}P)](PF_6)$ complexes (P-P are ligands **1** and **9** or **7** and **8**) in an aprotic solvent (CH_2Cl_2), the molecular mass of the copolymer increases in the sequences **1** > *meso*-**9** > *rac*-**9** and *meso*-**8** > *rac*-**8** > **7**. The presence of traces of water in the reaction medium results in the formation of μ-hydroxo complexes $[Pd(\mu\text{-}OH)(P\text{-}P)_2](PF_6)_2$ and in a higher yield of the copolymer, which increases in the sequence *rac*-**9** < *meso*-**9** < **1**. In the case of bischelate complexes, $[Pd(P\text{-}P)_2]^{2+}$, a different activity series is observed, namely, $[Pd(rac\text{-}\mathbf{9})_2]^{2+} < [Pd(\mathbf{1})_2]^{2+} < [Pd(meso\text{-}\mathbf{9})_2]^{2+}$. When bischelate palladium complexes are used and carbon monoxide–ethylene copolymerisation is carried out in methanol, the yield of the copolymer increases in the sequence **1** ≪ *rac*-**9** < *meso*-**9**.

Despite the fact that no quantitative data on the relationship between the copolymerisation rate and structural (or other) characteristics of diphosphines are currently available, presumably, the essential factors that determine the catalytic activity of palladium diphosphine complexes include the ligand conformation, the length of the methylene chain (*n*) between the P atoms and the rigidity of the complex. The P–Pd–P angle increases with an increase in *n* from 74° (for *n* = 1) to 175° (for *n* = 5). The palladium diphosphine complexes considered above have a planar square structure of the coordination unit with *cis*-arrangement of the phosphorus atoms for *n* = 1–4. As the methylene chain grows longer ($n \geqslant 5$), the formation of a dimer with *trans*-arrangement of the ligands becomes more favourable. The increase in the structural rigidity of the Pd complex resulting in a higher catalyst activity (by about an order of magnitude) in the copolymerisation of carbon monoxide with ethylene was shown for the 1,2,3,4-tetrakis(diphenylphosphino)cyclobutane complex of Pd(II).[44]

Worthy of note is the publication[45] concerning the possibility of alternating copolymerisation of carbon monoxide with ethylene induced by a zwitter-ionic palladium complex,



whose activity proved to be comparable with the activity of Pd complexes with 1,3-bis(diphenylphosphino)propane.

Some recent publications describe the use of palladium complexes with P-N and N-N bidentate ligands as catalysts of carbon monoxide copolymerisation with ethylene and the use of some aryl- and fluorine-containing arylboranes or their salts (Na, K or Li)[46–51] and alumoxanes,[52–55] instead of acids (CF_3COOH, *p*-$MeC_6H_5SO_3H$, *etc.*). Thus with the $Pd(OAc)_2$–$Ph_2P(CH_2)_3PPh_2$–$(Bu^t_2Al)_2O$ catalyst system, copolymerisation of ethylene with carbon monoxide in toluene proceeds at a rate of up to 2900 g g_{Pd}^{-1} h^{-1}.

It has been shown[56] that dicationic Pd complexes containing N-heterocyclic carbene ligands with the formula [*cis*-$CH_2\{N(H)C{=}C(H)N(R)C\}_2Pd(NCMe)_2](BF_4)_2$ (R = Me, 2,4,6-$Me_3C_6H_2$)‡ are active catalysts for ethylene copolymerisation with carbon monoxide. The reaction occurs at a rate of up to 810 g g_{Pd}^{-1} h^{-1}. Recently, a new family of P-N and P-P ligands based on 2-methyl-2-(2-pyridyl)-1,3-bis(diphenylphosphino)propane[57] and C_2-, C_3- and C_4-bridging bisphospholyl[58] ligands have been synthesised; their Pd complexes were shown to be active catalysts of the alternating copolymerisation of carbon monoxide

† The replacement of palladium acetate by nickel, cobalt, copper or silver acetate decreases the copolymerisation rate by a factor of several tens.[20,23,24]

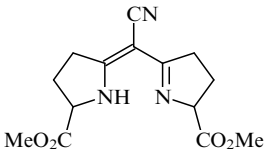
‡ These complexes proved to be inactive in carbon monoxide copolymerisation with propylene or styrene.

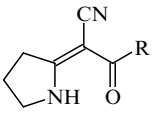
with ethylene. Palladium phosphineimine complexes [Pd(P-N)(Me)(MeCN)](BF$_4$) induce living copolymerisation and block copolymerisation of carbon monoxide with ethylene.[59]

The ruthenium(II) phosphine complexes, *cis*-[Ru(PPh$_2$CH$_2$CH$_2$PPh$_2$)$_2$](OTs)$_2$ and [Ru{PPh(CH$_2$CH$_2$CH$_2$.PPh$_2$)$_2$}$_2$](OTs)$_2$], exhibit a very low activity in the copolymerisation of carbon monoxide with ethylene. However, the addition of trifluoroacetic acid and 1,4-benzoquinone increases substantially the catalytic activity.[60] In this case, besides the high-molecular-mass copolymer, the reaction gives a low-molecular product soluble in methanol. A similar type of behaviour was found for 1,1′-palladium(II) bis(diphenylphosphino)ferrocene complexes, [Pd(H$_2$O)$_2${Fe(C$_5$R$_4$PPh$_2$)$_2$}](OTf)$_2$ (R = H, Me). The copolymerisation of carbon monoxide with ethylene in the presence of these complexes gives rise to oligoketone and methyl propionate (resulting from methoxycarbonylation of ethylene).[61] The following palladium complexes with diphosphine monoxide ligands have been synyhesised:[62] [(MeCN)(Me)Pd(κ^2-P,O-Ar$_2$P(CH$_2$)$_n$.P(O)Ar$_2$)]X (Ar = Ph, *p*-MeC$_6$H$_4$, n = 1–3, X = BF$_4$, SbF$_6$), [(η^3-C$_3$H$_5$)Pd{κ^2-P,O-Ar$_2$P(CH$_2$)$_n$P(O)Ar$_2$}]X (Ar = Ph: n = 2, 3, X = OTs, OTf; n = 1, X = SbF$_6$; Ar = *p*-MeC$_6$H$_4$: n = 1, X = SbF$_6$). Unfortunately, the catalytic activities of these complexes are lower than those of the catalyst systems described above.[20,36]

Due to the high cost of palladium, repeated attempts have been made at replacing it by cheaper nickel or copper. Nickel(II) phosphine complexes, [Ni{Ph$_2$PCH=C(Ph)O}(PEt$_3$)Ph], have been used[63] for copolymerisation of carbon monoxide with ethylene. A more recent study[62,64] reports the synthesis of nickel(II) complexes with N-O-bidentate ligands, [Ni(N-O).(*o*-MeC$_6$H$_4$)PPh$_3$] (N-O is 4-nitropyridine-2-carboxylate, pyrazine-2-carboxylate, 4-methoxypyridine-2-carboxylate) and with diphosphine monoxide ligands, [(η^3-CH$_2$C(Me)CH$_2$)Ni{κ^2-P,O-Ph$_2$PXP(O)Ph$_2$}]SbF$_6$ (X = *o*-C$_6$H$_4$, NH).

Recently, a series of [(L)Ni(*o*-MeC$_6$H$_4$)(PPh$_3$)] nickel complexes with bidentate N-N- and N-O-chelate ligands (L),



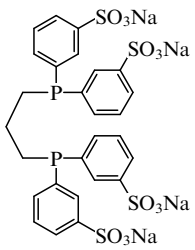


R = Me, OMe, Ph, CF$_3$, C$_3$F$_7$, C$_7$H$_{15}$.

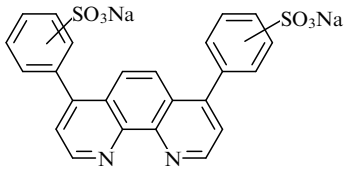
have been prepared. These complexes catalyse carbon monoxide–ethylene copolymerisation at a rate of up to 2300 g g_{Ni}^{-1} h^{-1}.[65] In 1998, it was reported that Ni(*o*-MeC$_6$H$_4$)(PPh$_3$)(Tp^{Ph}) [Tp^{Ph} is a tripodal tris(pyrazolyl)borate ligand] performs copolymerisation of carbon monoxide with ethylene giving rise to a high-molecular-weight product (T_m = 260 °C, M_w = 5770).[66] However, the rate of copolymerisation at 50 °C was low, 1.2 g g_{Ni}^{-1} h^{-1}.

The conduction of carbon monoxide–ethylene copolymerisation in methanol or in another polar solvent poses some difficulties associated with the process safety, environmental impact, the necessity of regenerating the solvent and so on. These aspects play a crucial role in the design of the industrial process. Therefore, in recent years, vigorous search for catalysts that would perform the copolymerisation in aqueous media has been carried out. This possibility was first mentioned in the 1990s.[67–69] Palladium complexes with sulfonated bidentate ligands have been used as the catalysts.

It was shown[68,69] that in the presence of a water-soluble diphosphine ligand, dppp-(SO$_3$Na)$_4$, and the palladium complex, Pd(TsO)$_2$(MeCN), copolymerisation of carbon monoxide with ethylene can be carried out in an aqueous medium at 90 °C to give copolymers with the molecular mass (6–8) × 10^3; the reaction rate reaches 4000 g g_{Pd}^{-1} h^{-1}.



dppp-(SO$_3$Na)$_4$

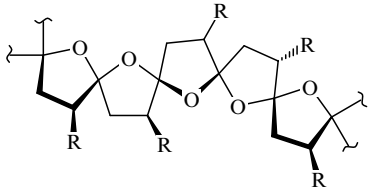


phen-(SO$_3$Na)$_2$

In the same years, data on conduction of the carbon monoxide–ethylene copolymerisation in the gas phase, appeared in the patent literature.[70–76] In this case, the Pd(OAc)$_2$–diphosphine–HBF$_4$ catalyst is applied onto a support (for example, the CO/C$_2$H$_4$ copolymer) impregnated with a nonpolymerising organic diluent. The gas phase should contain traces of methanol. The rate of this reaction is comparable with the rate of a similar process carried out in methanol.[35,77–79] Other polymers have also been used as catalyst supports, for example, porous polypropylene[79] or silica.[80] Although the first industrial process for the production of the alternating copolymer of carbon monoxide with ethylene was based on the reaction in solution,[81] subsequently, a pilot plant for gas-phase synthesis of polyketone has also been designed.[68] Copolymerisation of CO and C$_2$H$_4$ carried out in the gas phase would be noticeably more economic.

2. Carbon monoxide copolymers with propylene and higher olefins

When conducting copolymerisation of carbon monoxide with propylene and higher α-olefins (or with styrene or its derivatives), one should take into account a number of factors that influence the structure of the copolymer formed.[5] In addition to the major product with the 1,4-diketone structure [CHR–CH$_2$C(O)]$_n$, copolymerisation of carbon monoxide with α-olefins, styrene or its derivatives gives a copolymer with a spiroketal structure.[69,82]



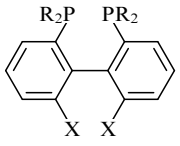
In the case of propylene, this copolymer is formed when the reaction is carried out at low temperature. In the copolymerisation of higher α-olefins (for example, hept-1-ene) with carbon monoxide, the spiroketal copolymer is formed at 50 °C.[83]

The activity of propylene in the reaction with carbon monoxide is about an order of magnitude lower than that of ethylene. The rates of copolymerisation of carbon monoxide with ethylene, propylene and but-1-ene under comparable conditions catalysed by the Pd(OAc)$_2$–CF$_3$COOH–Ph$_2$P(CH$_2$)$_3$PPh$_2$ system are 6000, 400 and 250 g g_{Pd}^{-1} h^{-1} (see Ref. 84). A similar dependence is observed with other catalyst systems, for example, heterogeneous and most of homogeneous Ziegler–Natta catalysts and the [(Ph$_2$P(CH$_2$)$_3$PPh$_2$)Pd(MeCN)$_2$](BF$_4$)$_2$ complex in a nitromethane–methanol medium.

The catalyst of choice for propylene–carbon monoxide copolymerisation is the [L$_2$PdX$_2$]$^{n+}$ complex (X is a weakly coordinating or non-coordinating anionic or neutral ligand, L is diphosphine) and an MeOH-containing solvent mixture is the best reaction medium.

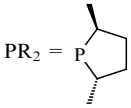
Until recently, the resulting copolymers of CO and propylene had low molecular masses. A detailed study[85] of carbon monoxide copolymerisation with propylene has revealed the reasons for the formation of low-molecular-weight polymers. The main reason is the lack of control of the contents of MeOH and H$_2$O in the reaction medium. Later, CO/MeCH=CH$_2$ copolymers with M_w = 43.2 × 10^4 have been obtained.[5,86,87] As in the case of

ethylene – carbon monoxide copolymerisation, the highest rate of carbon monoxide copolymerisation with olefins is observed in the presence of 1,ω-bis(diphenylphosphino)alkanes, $Ph_2P(CH_2)_nPPh_2$, with $n = 3$ and 4. The activity of the $Pd(OAc)_2$ – diphosphine – p-$MeC_6H_4SO_3H$ catalyst system in the copolymerisation of propylene and CO increases in the following series of diphosphines:[38] $Ph_2P(CH_2)_3PPh_2 < Bu_2P(CH_2)_3PBu_2 < Bu_2P(CH_2)_4PBu_2$. The copolymers of propylene and carbon monoxide obtained using bis(diphenylphosphino)alkanes are characterised by poor stereoregularity. It was shown[85] that by varying the nature of the diphosphine ligand, one can obtain fully iso- or atactic carbon monoxide – propylene copolymers. For example, *P*,*P*-(6,6′-dimethoxybiphenyl-2,2′-diyl)bis(2,5-dimethylphospholane) (**12**) has been used to prepare completely atactic copolymer, while using *P*,*P*-*o*-phenylenebis(2,5-dimethylphospholane) (Me-DUPHOS, **13**), a completely isotactic polymer was obtained. The use of enantiopure C_2-symmetrical diphosphine (**12**, **13**) and phosphine – phosphite (**14**) ligands gives copolymers with a higher stereoregularity.

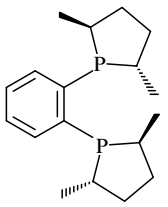


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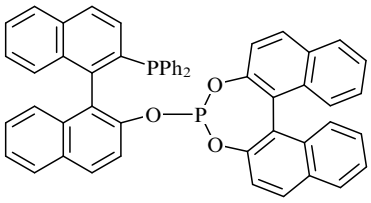
$PR_2 = PPh_2$: X = Me, OMe;
$PR_2 = PCy_2$: X = H, OMe;



, X = OMe.

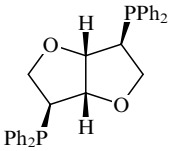


13 (Me-DUPHOS)



14 (BINAPHOS)

It is possible to prepare both dextro- and levorotatory stereoisomers.[88] The use of higher α-olefins (but-1-ene, hept-1-ene and oct-1-ene) in the copolymerisation with carbon monoxide in the presence of a Pd complex with diphosphine ligand **15** results in the formation of optically active copolymers.[89, 90]



15 (DDPPI)

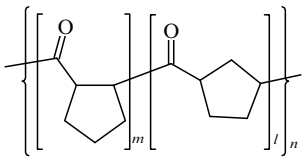
The alternating copolymerisation of α-olefins or styrene and its derivatives, dienes and some other monomers with carbon monoxide catalysed by chiral palladium complexes is a promising method for the preparation of optically active copolymers, mainly for two reasons: (i) the chirality of the backbone can be provided by using prochiral monomers; (ii) the presence of ketone groups in the backbone enables easy functionalisation of these polymers.

Olefins with internal double bonds can also be introduced in the copolymerisation with carbon monoxide. Thus it was shown[28] that in the presence of the $[Pd(Me\text{-}DUPHOS)(MeCN)_2](BF_4)_2$ catalyst, *cis*-but-2-ene copolymerises with CO to give an isotactic optically active oligomer with $M_n = 600$. The activity of *cis*-but-2-ene in this reaction is an order of magnitude lower than that of but-1-ene, which reacts with CO to give copolymer with $M_n = 4.0 \times 10^4$ and with both 1,4-ketone and the spiroketal structures in the backbone. The authors suggested that *cis*-but-2-ene isomerises into but-1-ene during copolymerisation. *trans*-But-2-ene does not copolymerise with carbon monoxide.

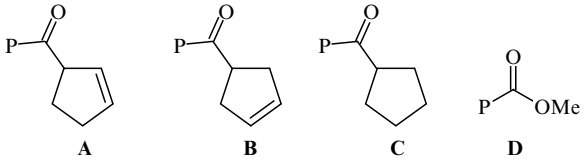
The synthesis of $C_2H_4/CO/MeCH=CH_2$ terpolymers with different contents of the CO/C_2H_4 and CO/C_3H_6 blocks in the polymer chain has been carried out in a hydrocarbon medium and the properties of the resulting copolymers have been studied.[85] Similar copolymers have been obtained in an aqueous medium[67] using water-soluble palladium complexes with dppp-$(SO_3Na)_4$ and phen-$(SO_3Na)_2$ as the catalysts. It is noteworthy that the rate of copolymerisation of propylene, ethylene and carbon monoxide in water was 4 – 22 g g_{Pd}^{-1} h^{-1}. These values are very low compared to those attained for the process carried out in methanol.[3] It was found that the rate of carbon monoxide copolymerisation with propylene in water is about 10 times as low as the rate of $CO/CH_2=CH_2$ copolymerisation under similar conditions. This is the main reason for the formation of a low-molecular-weight oily co-oligomer in the case of propylene. Co- and ter-polymerisation of ethylene, propylene and carbon monoxide in water catalysed by the $(NaO_3SC_6H_4CH_2)_2C(CH_2PPh_2)_2Pd(CF_3COO)_2 - TsOH - C_6H_4O_2$ system or by water-soluble palladium complexes with the $P(C_6H_4SO_3Na\text{-}m)_3$ and $(C_6H_4SO_3Na\text{-}m)_2P(CH_2)_3.P(C_6H_4SO_3Na\text{-}m)_2$ ligands have been reported.[91, 92] In the latter case, the product yield was $(2.6 - 7.2) \times 10^3$ g g_{Pd}^{-1} h^{-1}. Analysis of the structure of the resulting copolymers (at the terminal groups) by NMR shows that they have a diketone structure. When copolymerisation is carried out in methanol, the resulting copolymers have three types of terminal groups, namely, ketone, ketoester and ester groups.[92] Only low-molecular-weight terpolymers have been obtained in the aqueous medium.[92, 93] The possibility of copolymerisation in an aqueous emulsion in the presence of water-insoluble Pd complexes has been reported.[94]

3. Carbon monoxide – cyclic olefins

Copolymerisation of cyclopentene and carbon monoxide proceeds as 1,2- and 1,3-insertion of cyclopentene in the polymer chain.



Study of the influence of the natures of the solvent and the ligand, the temperature and carbon monoxide pressure on the rate of carbon monoxide – cyclopentene copolymerisation and on the molecular mass of the resulting copolymers revealed the optimal conditions (a temperature of 40 °C, a 4 MPa pressure of CO, Pd complexes with P-P- and N-N-bidentate ligands) for the synthesis of a high-molecular-weight isotactic copolymer (the ratio $l:m > 9$).[5, 95] It should be noted that irrespective of the reaction conditions, groups of types **A** – **D** are the major terminal groups of the copolymers.



A **B** **C** **D**

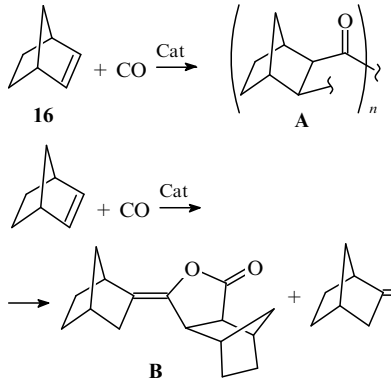
P is polymer.

The synthesis of a carbon monoxide – cyclohexene copolymer under the action of the $[Pd(MeCN)_4](BF_4)_2 - PPh_3$ complex has been reported.[96]

Of cyclic olefins used in copolymerisation with carbon monoxide, norbornene (**16**) is mentioned most often in the literature. Carbon monoxide copolymers with norbornene have been prepared in the presence of various Pd complexes, in particular,

$Pd(PPh_3)_4$, $PdCl_2-PPh_3-HCl$, and $[(bipy)Pd(MeCN)_2](BF_4)_2$, *etc.*[5,37,97–105]

It is known that norbornene can polymerise either with C—C bond cleavage, or with C—C bond cleavage and transfer of the reaction centre, or with ring opening. Depending on the catalyst used, copolymerisation can furnish polymers with a ketone (**A**) or lactone (**B**, **C**) structure.



The data on the influence of the nature of the ligands in the palladium complex on the copolymerisation rate and the glass transition temperature of the carbon monoxide copolymer with norbornene are summarised in Table 1.[106]

Copolymerisation of norbornene and carbon monoxide carried out with the $Pd(OAc)_2-Ph_2P(CH_2)_3PPh_2-p\text{-}MeC_6H_5SO_3H$ catalyst system in methanol in the presence of an oxidant (1,4-naphthoquinone or 1,4-benzoquinone) has been reported.[107] The researchers note that an increase in the *p*-toluenesulfonic acid to $Pd(OAc)_2$ molar ratio from 10 to 30 decreases the molecular mass of the co-oligomer with 8000 to 5000, while the replacement of 1,4-naphthoquinone by 1,4-benzoquinone decreases the copolymer yield and solubility in common organic solvents.

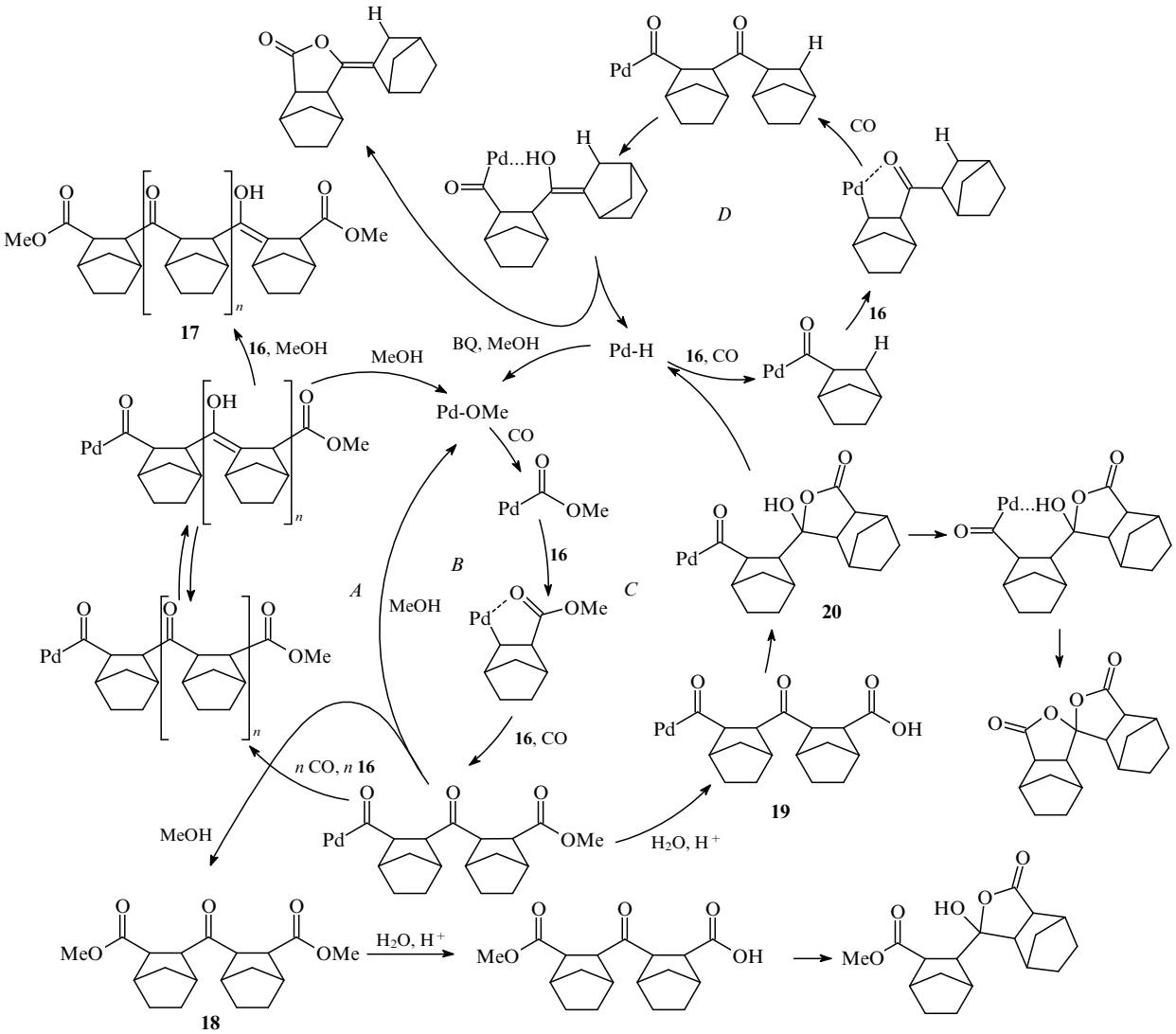
Table 1. Influence of the ligand nature on the rate of copolymerisation and glass transition temperature (T_g) of the CO – norbornene copolymer.

Ligand	Copolymerisation rate /g g_{Pd}^{-1} h^{-1}	T_g/°C
bipy	334	111
phen	371	113
5-NO_2-1,10-phen	282	112
$Ph_2P(CH_2)_3PPh_2$	58	126
PPh_3	31	120
$AsPh_3$	28	100
NPh_3	23	105

Note. Reaction conditions: $[Pd(OAc)_2] = 0.01$ mol litre^{-1}, [norbornene] = 10 mol litre^{-1}, temperature 90 °C.

Scheme 1 shows a reaction mechanism proposed on the basis of the data from ^{13}C and ^1H NMR and IR spectroscopy and the molecular-mass characteristics of the products of carbon monoxide co-oligomerisation with norbornene (**16**) under various

Scheme 1



BQ is 1,4-benzoquinone.

conditions.[107] The mechanism explains the formation of co-oligomers with different structures. Catalytic cycle *A* (the major cycle) affords high-molecular-weight and oligomeric structures (both ketone and spiroketal structures may appear). Chain termination (*via* methanolysis) results mainly in diester co-oligomers **17**.

Cycle *B* is analogous to cycle *A* but chain termination occurs after the formation of di- (**18**) and trimeric structures. The presence of trace amounts of water in the reaction medium (as a rule, methanol is used without dehydration and *p*-toluenesulfonic acid, often present as a component of the catalyst, contains water of crystallisation) initiates one more catalytic cycle *C*. In this cycle, hydrolysis affords monocarboxylic acid **19** and lactol **20** (due to tautometric transformations). When nitrogen-containing ligands are used (instead of phosphines), the reaction mixture must contain an oxidant, which facilitates the formation of catalytically active Pd-OMe sites. In this case, apart from catalytic cycles *A*, *B*, and *C*, one more cycle *D* is realised in which the Pd-H centres are the active sites.

The synthesis of block copolymers of norbornene with the $(CO/CH_2=CH_2)_n$ oligomer has been described.[108] The reaction was catalysed by time-stable complex *trans*-$Pd(PPh_3)_2.(Cl)(COC_6H_4Me\text{-}p)$ and carried out in an aprotic medium. This gave block copolymers containing long $(CO/C_2H_4)_n$ blocks alternating with norbornene.

Alternating copolymers of carbon monoxide with norbornene derivatives containing ester groups RC(O)O with different lengths of the hydrocarbon chain (acetate, pentanoate, octanoate, decanoate, dodecanoate) have been synthesised.[109] The reaction was carried out at 60 °C and at a carbon monoxide pressure of 3.4 MPa for 24 h in a $MeNO_2$–MeOH (5 : 1) mixture in the presence of the $[(bipy)Pd(MeCN)_2)](BF_4)_2$ catalyst. Table 2 presents some properties of the resulting copolymers. These copolymers were better soluble than those formed by carbon monoxide and norbornene (the former were soluble in DMSO, DMF, *N*,*N*-dimethylacetamide, pyridine and acetone but insoluble in benzene, toluene, chloroform, chlorobenzene or ether). An increase in the length of the hydrocarbon chain entailed a lower degree of crystallinity of the resulting copolymers and a higher solubility in organic solvents.

Table 2 Physicochemical properties of carbon monoxide copolymers with the ester derivatives of norbornene.

R	M_n	T_g /°C	T_m /°C	T^1_{dec} /°C	T^2_{dec} /°C
Me	3800	117	–	310	424
n-C_4H_9	4500	84	–	210	401
n-C_7H_{15}	5000	54	–	205	240
n-C_9H_{19}	4900	26	125	195	230
n-$C_{11}H_{23}$	5300	−32	99	180	230
Ph	4600	93	–	341	406

Note. T_g and T_m were determined by differential scanning calorimetry (DSC) at a heating rate of 20 °C min^{-1}. T^1_{dec} and T^2_{dec} are the temperatures of 10% loss of the polymer mass and the maximum decomposition, respectively determined by thermogravimetric analysis (TGA) at a heating rate of 10 °C min^{-1}.

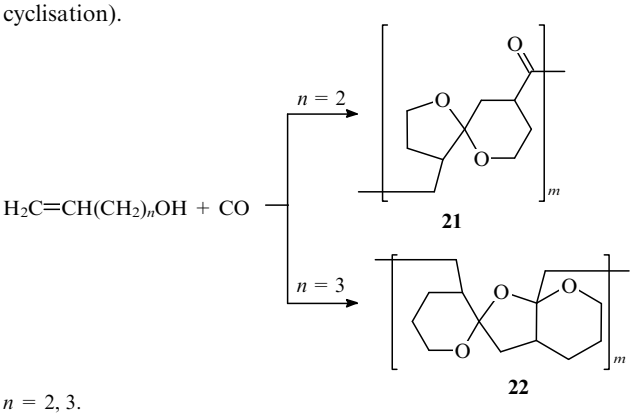
The data on the structure and properties of such copolymers are scarce. Photolysis of carbon monoxide copolymers with *exo*-norbornene having $M_n = 3200–4900$ and $M_w : M_n = 1.75–2.0$ has been studied by time-resolved EPR spectroscopy.[110] The EPR spectra of the copolymers exhibited weak signals for the *endo*-2-substituted norbornyl§ radicals, which attested to incomplete stereoregularity of this copolymer.

§ These radicals are produced by the Norrish-I mechanism on rupture of the polymer chain.

Copolymerisation of carbon monoxide with norbornene, cyclopentadiene or bicyclo[2.2.2]oct-2-ene in the presence of $[Pd(MeCN)_2(PPh_3)_2](BF_4)_2$ at 100 °C in acetonitrile yields low-molecular-weight polymers (M = 600–1000) containing lactone (**B** and **C**) and ketone (**A**) groups.[111] Copolymerisation of strained olefins with CO has been considered in detail in a review.[7]

4. Carbon monoxide – functional α-olefins and other monomers

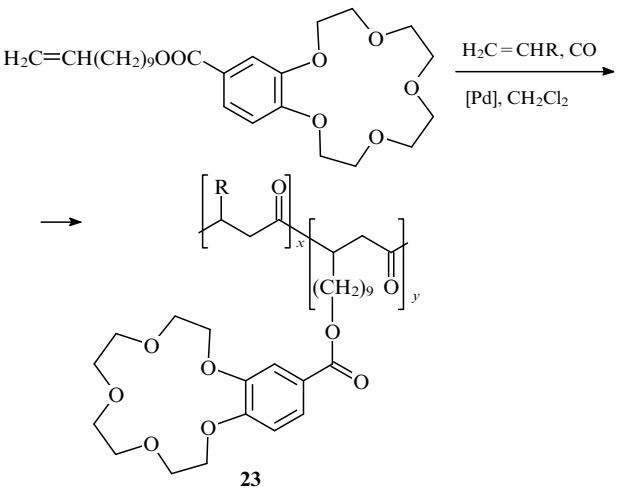
Of obvious scientific and practical interest are the products of alternating copolymerisation of carbon monoxide with various functionally substituted monomers. It has been reported [112] that carbon monoxide undergoes alternating copolymerisation with unsaturated alcohols $CH_2=CH(CH_2)_nOH$ (n = 2, 3, 5, 9) and acids $CH_2=CH(CH_2)_nCOOH$ (n = 1, 2, 4, 8) in the presence of $[Pd(Me\text{-}DUPHOS)(MeCN)_2](BF_4)_2$. The copolymers thus formed had molecular masses of $(10–45)\times10^3$ and $(12–100)\times10^4$, polydispersities of 1.5–2 and 2.9–5.8 for the alcohols and the acids, respectively. They exist as poly(1,4-ketone) and/or polyspiroketal structures and are optically active. Exceptions are provided by the copolymers based on but-3-en-1-ol (copolymer **21**) and pent-4-en-1-ol (copolymer **22**), which have an unusual polycyclic spiroketal structure. They are formed upon the interaction of the hydroxy group in the side chain with the nearest carbonyl group of the polymer chain (intramolecular cyclisation).



n = 2, 3.

The synthesis of the carbon monoxide copolymer with hepta-1,6-dien-4-ol ($M_w = 16\times10^3$ and T_g = 7 °C) has been reported.[113]

In the terpolymerisation of carbon monoxide with various α-olefins (C_3, C_6, C_{12} and C_{18}), a benzo-15-crown-5-functionalised α-olefin, undec-10-enyl[(benzo-15-crown-5)-4′-carboxylate], can be used as a comonomer.[114] It was found that an increase in the molecular mass of the α-olefin results in a decrease in the molecular mass of copolymer **23** from 12 800 (with C_6 α-olefin) to

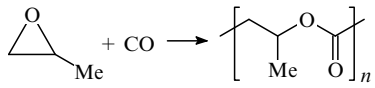


R = Me, Bu^n, n-$C_{10}H_{21}$, n-$C_{16}H_{33}$.

5 300 (for C_{18} α-olefin) and a decrease in T_g from 20 °C (for C_3) and −18 °C (for C_6) to −76 °C (for C_{12}). The polydispersities of the resulting terpolymers were 1.5–2.0. Despite the relatively low molecular mass of copolymers **23**, they were used to produce thin films suitable as ion selective membranes.

The synthesis of alternating copolymers of carbon monoxide with fluorinated alkenes $(C_nF_{2n+1})(CH_2)_mCH=CH_2$ ($m \geqslant 2$) has been described.[115] (see ¶). The resulting copolymers mainly had the spiroketal (rather than ketone) structure of the backbone.

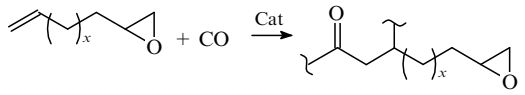
Copolymerisation of carbon monoxide with epoxides occurs with opening of the epoxide ring. The possibility of alternating copolymerisation of epoxides with carbon monoxide was first demonstrated in 1965.[117] Copolymerisation was carried out in the presence of the $Co(acac)_3$ – $AlEt_3$ catalyst system (acac is acetylacetonate). The alternating copolymerisation of carbon monoxide with epoxides induced by the $Co_2(CO)_8$ – pyridine catalyst system and resulting in polyesters **24** with a regular structure has been described.[118, 119]



24

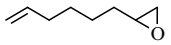
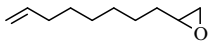
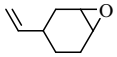
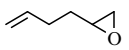
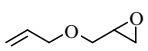
The $Co_2(CO)_8$ – $Ru_3(CO)_{12}$ system has also been used to catalyse this reaction.[120] The researchers showed that the Ru : Co ratio affects the yield, the molecular mass and the structure of the product.

Polyketones containing epoxide groups in the side chain were obtained by copolymerisation of carbon monoxide with vinyl epoxides (for example, 1,2-epoxyhex-5-ene, 1,2-epoxyoct-7-ene, 1,2-epoxydec-9-ene) in the presence of the [Pd{(*R*,*R*)-Me-DUPHOS}$(MeCN)_2$]$(BF_4)_2$ – $C_{10}H_6O_2$ – HCOOH catalyst system (Table 3).[121]



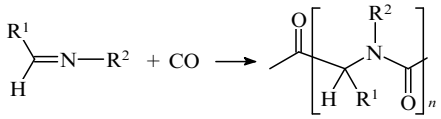
The copolymers formed have $M = (1-3) \times 10^4$ and a narrow molecular-mass distribution. They are soluble in CH_2Cl_2, THF, DMSO.

Table 3. Copolymerisation of CO with epoxides in the presence of the [Pd{(*R*,*R*)-Me-DUPHOS}$(MeCN)_2$]$(BF_4)_2$ – $C_{10}H_6O_2$ – HCOOH catalyst system.[121]

Epoxide	Time /h	Copolymer yield (%)	M_w	$M_w : M_n$
	40	3.58	30 500	1.97
	40	4.52	33 600	1.41
	18	5.41	28 500	3.40
	18	6.3	12 300	1.72
	48	6.77	3 350	1.28
	24	–	–	–

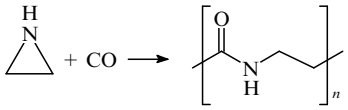
¶ The synthesis and study of the properties of alternating copolymers of carbon monoxide with fluorinated allylbenzenes have been considered in the literature.[116]

In 1998, it was shown that carbon monoxide copolymerisation with imines gives polypeptides, which can be of interest as biomimetic materials.[122, 123]



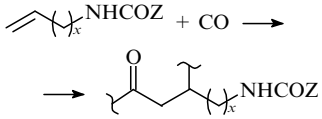
R^1, R^2 = H, Alk, Ar.

Later,[124] a crystalline polymer soluble in hot water, poly-β-alanine ($M = 14.1 \times 10^3$), has been prepared by copolymerisation of aziridine with carbon monoxide in the presence of the $CR_3C(O)Co(CO)_3PPh_3$ (R = H, D) and $HCo(CO)_3PPh_3$ complexes



It was found that, when the catalyst concentration is low, the polymer formed contains ethyleneimine units apart from β-alanine units.

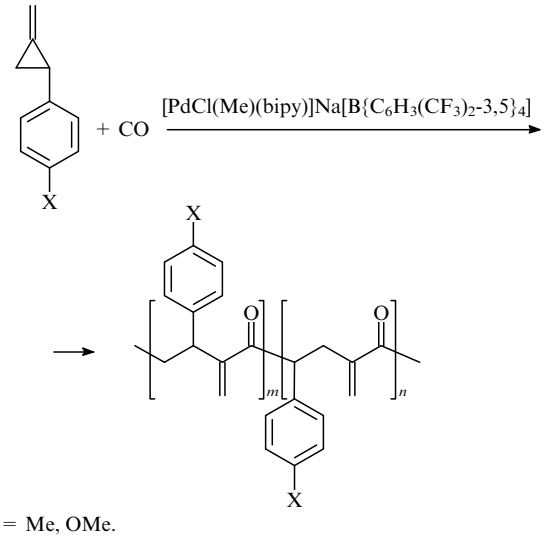
The synthesis of carbon monoxide copolymers with functionalised alkene monomers containing a carbamate or amide group has been described.[125] The [Pd(Me-DUPHOS)$(MeCN)_2$]$(BF_4)_2$ complex was used as the catalyst.



Z = OMe, OPh, Me, Ph; x = 1, 2.

This reaction carried out in CH_2Cl_2 or in a $MeNO_2$ – MeOH (2 : 1) solvent mixture gave copolymers with M_w ranging from 1×10^4 to 3×10^4, while in the absence of a solvent, $M_w = 6 \times 10^4$. Copolymerisation of carbon monoxide with *N*-(but-3-enyl)benzamide in CH_2Cl_2 or a $MeNO_2$ – MeOH (2 : 1) mixture gave two chiral copolymers, characterised by opposite signs of optical rotation.

The synthesis of alternating copolymers of carbon monoxide with cyclopropane derivatives has been described.[126–128] It has been proposed [127, 128] to carry out copolymerisation of 2-aryl-1-methylenecyclopropanes with CO in the presence of palladium diimine complexes such as [PdCl(R)(bipy)], [PdCl(R).(ArN=CHCH=NAr)] and [Pd(η^3-R′CHCHCH$_2$).(ArN=CHCH=NAr)] (R = Cl, Me; R′ = H, Ph; Ar = 4-MeC_6H_4, 4-$MeOC_6H_4$, 2,6-$Pr^i_2C_6H_3$).



X = Me, OMe.

The yields of copolymers obtained in the presence of π-allyl palladium complex are lower than the yields of copolymers synthesised using the [PdCl(R)(ArN=CHCH=NAr)] and [PdCl(R)(bipy)] complexes; however, in the presence of the π-allyl complex, regular copolymers are formed.

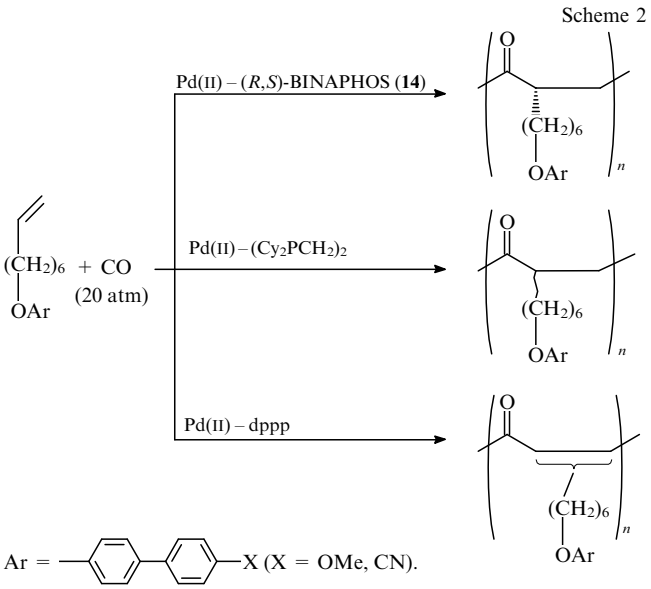
Recently, using copolymerisation of carbon monoxide, propylene and polyalcohol (polyethylene glycol, polyvinyl alcohol or monomethyl ether of ethylene glycol), the possibility of obtaining linear and branched poly(1,4-ketone)–polyalcohol block copolymers was demonstrated.[129]

Some vinyl monomers that cannot copolymerise with carbon monoxide can nevertheless be inserted as single units into the polymeric chain during terpolymerisation with ethylene and carbon monoxide. The content of these units in the product depends on the monomer concentration, the type of the catalyst used, temperature, *etc*. In particular, terpolymerisation proceeds rather vigorously when isobutylene,[130] methyl acrylate,[130,131] chlorohex-1-ene,[131] undec-10-enoic acid and its methyl ester, undec-10-enyl alcohol,[108] maleic acid anhydride,[132,133] allyl acetate[131,134] and vinyl acetate[131,135] are used as the third components.

Polymeric materials that possess anisotropic properties are valuable for practical purposes. One way of creating anisotropy in polymers during the synthesis is incorporation of mesogenic groups in the side chain. At present, copolymers and terpolymers (with hex-1-ene as the third component) of carbon monoxide with α-olefins containing methoxybiphenyl mesogenic groups have been prepared. These copolymers exist as smectic E-mesophases with a periodicity corresponding to S_A. Their thermal stability is comparable to that of the CO/MeCH=CH_2 alternating copolymer whose thermal decomposition starts at 270 °C. The isotropiosation temperature of copolymers decreases with an increase in the length of the spacer,† while that for terpolymers decreases with an increase in the content of hex-1-ene.[136]

The aliphatic α-alkenes containing mesogenic substituents enter into copolymerisation with carbon monoxide in the presence of Pd(II) complexes. Depending on the type of the ligand (L), products with different stereo- and regioregularities are formed in the palladium complex (Scheme 2).

Scheme 2



The properties of the resulting liquid-crystal polyketones[137] were studied by DSC and by polarisation optical microscopy.

† The length of the methylene chain that connects the polymer chain to the mesogenic group.

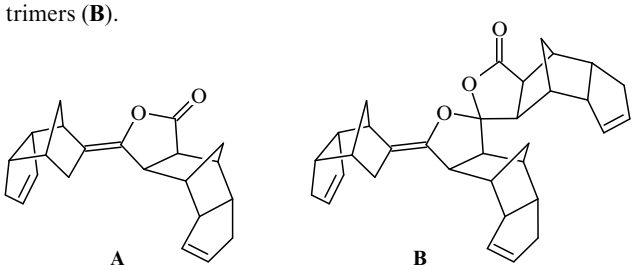
5. Carbon monoxide – linear dienes

Copolymerisation of carbon monoxide with butadiene in the presence of the $Pd(OAc)_2-Ph_2P(CH_2)_3PPh_2$ (or bipy)–CF_3COOH (or TsOH) catalyst system gives rise to low-molecular-mass copolymers in low yields.[5,138–140] On the basis of hexa-1,5-diene,[5,141,142] hepta-1,6-diene or octa-1,7-diene[5,113,142] and carbon monoxide, binary alternating copolyketones and terpolymers with ethylene have been synthesised. Hexa-1,5-diene[5,141,142] and hepta-1,6-diene react with carbon monoxide to give cyclic copolymers, whereas octa-1,7-diene copolymerises with CO to yield a linear alternating copolymer containing $CH_2CH=CH_2$ side groups.[5,113,141]

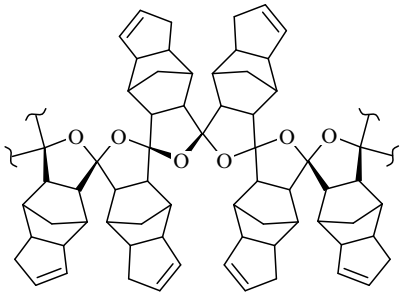
Data on the synthesis of the following terpolymers have been reported: hepta-1,6-dien-4-ol–carbon monoxide–propylene (T_g = 19 °C), propylene–carbon monoxide–methylenecyclopropane, propylene–carbon monoxide–octa-1,7-diene, hexa-1,5-diene–carbon monoxide–propylene,[113] ethylene–carbon monoxide–butadiene,[138–140] and ethylene–carbon monoxide–hexadiene.[141,142]

6. Carbon monoxide – cyclic dienes

The possibility of synthesis of an alternating copolymer of dicyclopentadiene (DCPD) with carbon monoxide was first mentioned in a patent.[98] Dicyclopentadiene is formed as a side product in the pyrolysis of petroleum products and represents a tricyclic hydrocarbon with two inequivalent C=C bonds, one highly reactive bond in the norbornene ring and one less reactive bond in the substituted cyclopentene ring. In the synthesis of DCPD/CO copolymers, the $Pd(OAc)_2$–bipy–TsOH–$C_6H_4O_2$ catalyst system was used. The copolymer is formed in a good yield even at room temperature, the presence of air in the reaction mixture being favourable for higher copolymer yield. When the $Pd(OAc)_2-Ph_2P(CH_2)_3PPh_2-CF_3COOH$ catalyst system is used, copolymerisation should be carried out at a temperature above 80–90 °C.[143] The synthesis of the CO copolymer with DCPD catalysed by $[Pd(MeCN)_2(PPh_3)_2](BF_4)_2$ (100 °C, carbon monoxide pressure of 1.0 MPa, 5 h) furnishes a solid white-coloured product, which is a mixture of CO/DCPD di- (**A**) and trimers (**B**).

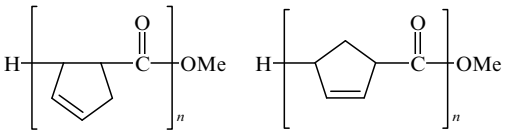


The copolymers of DCPD and carbon monoxide have, most often, a spiroketal structure, which is not tansformed into the ketone structure even on long-term heating.



Copolymerisation of carbon monoxide and cyclopentadiene in the presence of $[Pd(MeCN)_4](BF_4)_2$ (60 °C, pressure 5.6 MPa, 24 h) and various monodentate ligands [PPh_3, $AsPh_3$, NPh_3, $PMePh_2$, $P(OPh)_3$] has been described.[96] The process gives a partially crystalline copolymer with T_m > 180 °C, soluble in

THF. The M_n values of the copolymer increase from 570 to 2750 following an increase in the carbon monoxide pressure from 2.1 to 5.6 MPa. The highest yield of the copolymer is attained when PPh_3 is used as the ligand and MeOH is used as the reaction medium. According to ^1H NMR, the resulting copolymer consists of macromolecules having 1,2- and 1,4-structures,



1,2-structure 1,4-structure

the content of 1,2-structures markedly increasing for copolymerisation carried out in polar solvents (MeOH, MeCN). The resulting copolymer is thermally unstable: a partial mass loss is observed at 120 °C. The activity of cyclohexadiene in this reaction is about 60 times lower.

Using the $PdCl_2$ – 1,4:3,6-dianhydro-2,5-dideoxy-2,5-bis(diphenylphosphino)-L-idite – $CuCl_2$ – 2,6-$Me_2C_6H_2O_2$ – TsOH catalyst system (45 °C, 24 h, carbon monoxide pressure 6 MPa), alternating copolymers of carbon monoxide with DCPD and methylcyclopentadiene with an isotactic (1,4-ketone) structure and molecular masses of 1300 ($M_w : M_n = 1.7$ for DCPD) and 944 ($M_w : M_n = 2.88$ for methylcyclopentadiene) have been obtained.[144]

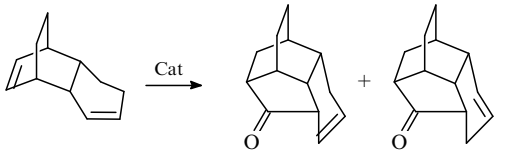
A study[145] of the influence of the solvent on the yield of carbon monoxide copolymer with 4-vinylcyclohexene obtained in the presence of the $[Pd(MeCN)_4](BF_4)_2$ – L catalyst system (L = PPh_3, bipy, phen or 5-NO_2-phen) (60 °C, carbon monoxide pressure 5.5 MPa, 12 h) has shown that copolymerisation rate is higher (1.45 and 0.82 g g_{Pd}^{-1} h^{-1}) in polar solvents (MeOH and $MeNO_2$) than in $CHCl_3$ (0.53 g g_{Pd}^{-1} h^{-1}). The copolymer thus formed had a relatively low molecular mass (1070 – 6910) and contained both ketone and cyclic (cyclohexyl and norbornane) structures in the chain. The copolymer was soluble in DMSO, *N*,*N*-dimethylacetamide, DMF, pyridine, acetonitrile, THF, nitromethane, acetone, chloroform and 1-methyl-2-pyrrolidone but insoluble in benzene, toluene, 1,2-dichloroethane, chlorobenzene, methanol, ether, 1,4-dioxane or ethyl acetate. According to DTG analysis, the loss of copolymer mass starts at 190 °C. Treatment of the copolymer with a solution of $LiAlH_4$ in THF results in polyalcohol, which is soluble in chloroform, THF, DMSO and methanol but insoluble in benzene, n-hexane or ether.

The first mention of the synthesis of the alternating copolymer of carbon monoxide and norbornadiene appeared more than 30 years ago.[146, 147] Palladium chloride was used as the catalyst. The copolymer formed had $M_n = 2900$, $T_m < 300$ °C; it was soluble in benzene, chloroform and THF. However, on storage in air, the solubility of the copolymer decreased, apparently, due to oxidation processes. The use of palladium complexes with bidentate P-P and N-N ligands as catalysts resulted in a higher yield of the copolymer.[98, 148] Copolymerisation carried out in the presence of $[Pd(MeCN)(PPh_3)_3](BF_4)_2$ at a temperature of 60 °C and a carbon monoxide pressure of 5.6 MPa gave a carbon monoxide – norbornadiene copolymer with $M_n = 3380$ soluble in $CHCl_3$ and C_6H_6,[97] while at 100 °C, a copolymer with $M_n = 800 – 1200$ was formed.[111] The IR spectra of the polymer exhibit characteristic bands at 1778, 1722 and 1702 cm^{-1}, indicating the presence of γ-lactone, ester, vinyl, and ketone groups in the polymer chain.

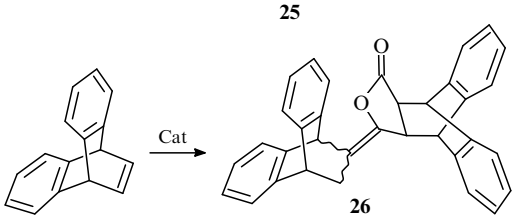
The influence of the nature of the catalyst, the temperature, the nature of the solvent and the concentrations of carbon monoxide, *p*-toluenesulfonic acid and 1,4-benzoquinone on the yield and the molecular mass of carbon monoxide – norbornadiene copolymer has been studied.[148] The highest catalytic activity in this reaction was found for $[Pd(MeCN)_4](BF_4)_2$ in the presence of bidentate N-N-ligands such as bipy or phen (in this case, copolymerisation rate reached 60 g g_{Pd}^{-1} h^{-1}). The presence of diphosphine $PPh_2(CH_2)_3PPh_2$ in the reaction medium decreases the catalyst activity about 1.5-fold and in the presence of monodentate ligands PPh_3, $AsPh_3$, NPh_3, or $P(OPh)_3$, the activity decreases 5 – 20 fold; simultaneously, the copolymer molecular mass decreases from 9000 to 1250. The replacement of polar protic solvents (for example, MeOH) by less polar solvents (THF or benzene) results, on the one hand, in a decrease in the catalyst activity and, on the other hand, in an increase in the copolymer molecular mass to 16 000, indicating the participation of the solvent in a chain termination reaction. An increase in the concentrations of carbon monoxide, TsOH or 1,4-benzoquinone results in a higher yield of the copolymer. Upon the increase in the carbon monoxide concentration, the molecular mass of the copolymer also increases (upon an increase in the TsOH or 1,4-benzoquinone concentration, the molecular mass decreases). The DTG data show that the copolymer starts to lose mass at 167 °C (at 356 °C, the mass loss is 24.5%). Hydrogenation of this copolymer affords polyalcohol, which is completely soluble in chloroform, THF, DMSO and *m*-cresol, partially soluble in acetone and methanol and insoluble in benzene, n-hexane or water.

The characteristic features of synthesis and the structure of alternating co-oligomers of carbon monoxide with norbornadiene and the mechanism of formation of various structural units in the polymer chain in the presence of the $Pd(MeC_6H_4PPh_3)(Tp^{Ph})$ catalyst in an aprotic medium and methanol have been considered.[149]

The copolymerisation of carbon monoxide with *endo*-tricyclo[6.2.2.$0^{2,7}$]dodeca-3,9-diene gives rise to oil-like dimers (mainly, dimer **25**) and that with dibenzobicyclo[2.2.2]octatriene affords solid dimer **26**.[111]

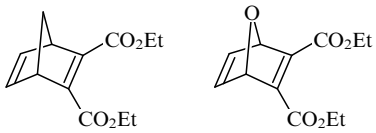


25



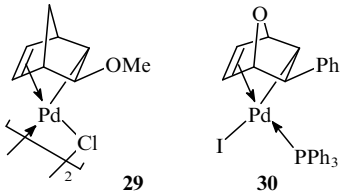
26

In the presence of Pd(II) complexes with σ,π-alkenyl ligands and a stabilising pyridine or triphenylphosphine ligand, alternating copolymers of carbon monoxide with diethylbicyclo-[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**27**) and diethyl 7-oxabicyclo[2.2.1]hepta-2,5-diene-2,3-dicarboxylate (**28**) have been obtained according to the living polymerisation mechanism.[150]



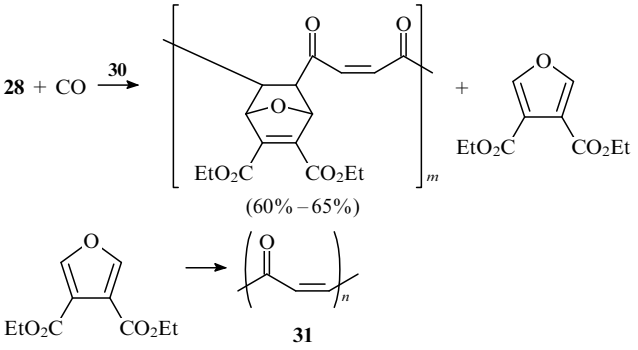
27 **28**

In the former case, dimeric palladium chloride complex was used as the catalyst (**29**), while in the latter case, this was triphenylphosphine complex **30**.

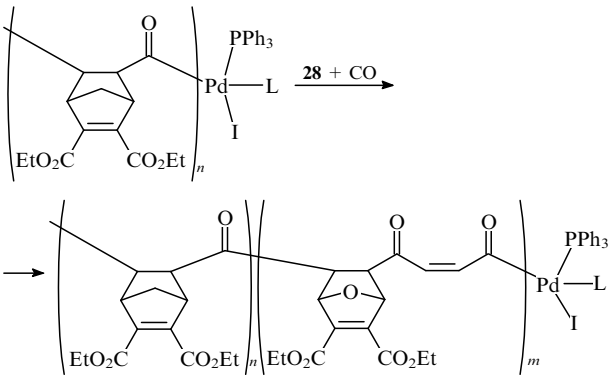


29 **30**

In the copolymerisation of carbon monoxide with diene **27**, the yield of the copolymer is nearly 100%, while in the copolymerisation with diene **28**, the yield was 60% – 65%. In the latter case, diethyl furan-3,4-dicarboxylate is formed as a side product. This side product can be isolated from the copolymer by heating at 70 °C. Diethyl furan-3,4-dicarboxylate is converted, in turn, into a polyconjugated polymer, polyketovinylene (**31**).



Study of the effect of the monomer and Pd complex concentrations on the kinetics of carbon monoxide copolymerisation with diene **27** has shown that the reaction is first order ($k = 8.2 \times 10^{-3}$ litre mol^{-1} s^{-1}) with respect to CO and Pd and a zero order with respect to diene. In all cases, the concentration of diene **27** was approximately two orders of magnitude higher than the carbon monoxide concentration. If monomer **28** is added to the CO/**27** copolymer, alternating block copolymer (CO/**27**)/(CO/**28**) can be obtained.



7. Carbon monoxide – allene derivatives

Although insertion of carbon mono- and dioxide and sulfur dioxide into the palladium – allyl bond has been mentioned in the literature,[151 – 155] no data on the synthesis of a binary copolymer of carbon monoxide with unsubstituted allene has been reported. Copolymers of carbon monoxide with 1,1-dimethylallene (1,2- and 2,3-isomers), 1,1,3,3-tetramethylallene [5, 156] and a large number of arylallenes *p*-$XC_6H_4CH=C=CH_2$ (X = H, Me, MeO, Cl, F, Bu^n, Bu^t) have now been prepared. The reaction with arylallenes was carried out at 25 °C, a CO pressure of 0.1 MPa (21 h) in the presence of a Rh complex, $Rh[\eta^3\text{-}CH(Ar)C\{C(=CHAr)CH_2C(=CHAr)CH_2CH_2CH=CHAr\}CH_2](PPh_3)_2$ (Ar = C_6H_4OMe-*p*).[5, 157] The reaction follows the living polymerisation mechanism. The alternating copolymers thus formed have $M = 10^4 – 10^5$, $M_w : M_n = 1.06 – 1.16$. Copolymerisation of phenylallene and carbon monoxide with subsequent addition of 4-methoxyphenylallene to the reaction mixture gives the block copolyketone $[CO-C(=CHPh)CH_2]_m/[CO-C(=CHC_6H_4OMe\text{-}p)CH_2]_n$; meanwhile, terpolymerisation of carbon monoxide with an equimolar mixture of phenylallene and 4-methoxyphenylallene yields a statistical copolymer. The same rhodium complex was used for terpolymerisation of carbon monoxide with 4-hexylphenylallene and 4-dodecylphenylallene. The T_m and T_g values of the $[CO/C(=CHC_6H_4Alk\text{-}p)CH_2]_n$ polyketones were found to increase in the series of alkyl radicals $C_{12}H_{25} < C_6H_{13} < Bu^n < Me < H$ from 65 to 170 °C and from 30 to 125 °C, respectively. By terpolymerisation of carbon monoxide with a mixture of phenylallene and 4-alkylphenylallene (Alk ≠ Me), statistical and block terpolymers were obtained, whereas the use of a mixture of 4-methylphenylallene and bisallenylbenzene results in cross-linked polyketones.[158, 159] The copolymerisation rate decreases in the sequence of comonomers: 1,1-dimethylallene > phenylallene > cyclohexylallene. Terpolymerisation of carbon monoxide with a mixture of 4-(allenyloxy)-azobenzene and 4-(methoxyphenyl)allene [or 4-(*tert*-butyl)-phenyloxyallene] resulted in statistical polyketones.[160]

The synthesis of new functional polyketones soluble in dichloromethane, THF and toluene was accomplished by terpolymerisation of propylene and carbon monoxide with 2-allylphenol, 2-allylmethoxybenzene, 4-allylmethoxybenzene and 4-allyl-2-methoxyphenol in the presence of the $[Pd(dppp)(MeCN)_2](BF_4)_2$ complex as the catalyst [160] and by carbon monoxide copolymerisation with 4-allylanisole catalysed by $[Pd\{(R,R)\text{-Me-DUPHOS}\}(MeCN)_2](BF_4)_2$.[5, 112]

Analysis of the state-of-the-art studies dealing with the synthesis of alternating copolymers of carbon monoxide with dienes shows that the search for effective catalysts is only at an early stage, unlike that for the synthesis of copolymers of carbon monoxide with alkenes. The obtained copolymers have a relatively low molecular mass ($10^3 – 10^4$) and only the use of some Pd complexes enables living copolymerisation mechanism; in this case, it is possible to obtain alternating copolymers with a molecular mass of $\sim 10^5$. Undoubtedly, effective catalysts for the synthesis of carbon monoxide copolymers with dienes would be found in the near future and these polymers would find extensive use.

8. Copolymers of carbon monoxide with styrene and its derivatives

Copolymerisation of carbon monoxide with styrene and its derivatives takes place only in the presence of nitrogen N-N- or hybrid P-X-ligands (X = N, O). In the presence of the $[(MeCO)Pd(MeCN)\{(R,S)\text{-BINAPHOS}\}][B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]$ complex,[161] the chain initiation and propagation involved in the copolymerisation of carbon monoxide with *tert*-butylstyrene take place by the 1,2-inclusion mechanism.

Milani *et al.* [162] have studied the influence of the nature of the solvent [methanol or 2,2,2-trifluoroethanol (TFE)], the temperature, the carbon monoxide pressure and the concentration of 1,4-benzoquinone on the CO – styrene copolymerisation rate and on the molecular mass of the resulting copolymer. It was found that in TFE, the copolymerisation catalysed by the $[Pd(bipy)_2](PF_6)_2$ system is a quasi-steady-state process, whereas in methanol, the rate decreases with time. As the temperature is raised from 60 to 80 °C, the rate of copolymerisation increases from 271 to 1134 g g_{Pd}^{-1} h^{-1}, and the $[\eta]$ value decreases from 0.27 to 0.14 dl g^{-1}. The reaction time (7 – 48 h) and the carbon monoxide pressure have a little influence on the molecular mass of the resulting copolymer but influence the copolymerisation rate. Thus an increase in the carbon monoxide pressure from 1 to 4 MPa results in a sharp decrease in the reaction rate from 1081 to 290 g g_{Pd}^{-1} h^{-1}.

Interesting results have been obtained by Milani *et al.*,[163] who attained a rate of carbon monoxide – styrene copolymerisation equal to $\sim 17\,000$ g g_{Pd}^{-1} h^{-1} by using the $[Pd(bipy)_2](PF_6)_2 – C_6H_4O_2$ catalyst system, the reaction being conducted in TFE. The researchers noted that the catalyst system did not lose activity for at least 48 h. The presence of 1,4-benzoquinone influences not only the catalyst activity but also the molecular mass of the copolymer. With the molar ratio $C_6H_4O_2 : Pd = 5 : 1$, a copolymer with $M_w = 71\,710$ was obtained ($M_w : M_n = 2$), and in the absence of 1,4-benzoquinone, with $M_w = 84\,860$ ($M_w : M_n = 1.8$). It is noteworthy that this is the first example of synthesis of a carbon

monoxide copolymer with styrene with such a high molecular mass.

By varying the styrene : ethylene monomer ratio, one can prepare $C_2H_4/CO/H_2C=CHPh$ terpolymers in a high yield and with different contents of styrene. Recently, it has been shown [164] that the use of the palladium complex with the (*S*)-3-(1,2,2-$Me_3C_3H_4$)-1,10-phen ligand allows one to carry out carbon monoxide copolymerisation with styrene (or 4-methylstyrene) in TFE for 80 h almost without a decrease in the reaction rate and to obtain copolymers with a molecular mass of 20×10^4 (or 30×10^4). An increase in the styrene : Pd molar ratio (from 48 000 to 96 000) increases the yield and the molecular mass of product approximately twofold. The terminal groups present in the copolymers synthesised in TFE are PhCH=CH, Me(Ph)CH or CF_3CH_2O.[165] It has been shown [166] that the content of TFE should not exceed 3 mass % – 5 mass %.

The catalytic activity of the $[Pd(\eta^1,\eta^2\text{-}C_8H_{12}OMe).(bipy)]^+X^-$ complex [where $X = BPh_4$, CF_3SO_3, BF_4, PF_6, SbF_6, $B\{3,5\text{-}(CF_3)_2C_6H_3\}_4$] in the carbon monoxide copolymerisation with styrene in dichloromethane has been studied as a function of the activity of the counter-ion used.[167] The following activity series was elucidated: $BPh_4 \ll CF_3SO_3 < BF_4 < PF_6 < SbF_6 < B\{3,5\text{-}(CF_3)_2C_6H_3\}_4$. With an excess of the bipyridine ligand, the activity series changes to give $BPh_4 \ll CF_3SO_3 < BF_4 \approx B\{3,5\text{-}(CF_3)_2C_6H_3\}_4 \approx PF_6 \approx SbF_6$.

A new class of catalysts based on the Pd(II) bipyridyl complex containing $[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]^-$ as the counter-ion have been prepared. These catalysts were found to be more active in the carbon monoxide copolymerisation with styrene or *tert*-butylstyrene than catalysts with the PF_6 counter-ion.

A study [168, 169] of terpolymerisation in the $C_2H_4/CO/CH_2=CHPh$ system at high carbon monoxide pressures in the presence of various P-N-ligands as parts of the [Pd(COMe).(P-N)(solv)]O_3SCF_3 palladium complex [P-N is phosphino(dihydrooxazole) ligand, solv is solvent] has shown that a decrease in the carbon monoxide pressure from 29 to 14 MPa entails a decrease in the reaction rate from 27 to 12.9 mmol g_{Pd}^{-1} h^{-1}; simultaneously, the $(-C_2H_4-CO-):(-CH_2CHPh-CO-)$ ratio of copolymer units changes from 80 : 20 to 90 : 10. For $C_2H_4/CO/CH_2=CHPh$ terpolymers, the dependence of T_g on the composition $(C_2H_4/CO)/(CH_2=CHPh/CO)$ was determined. The copolymer containing 27 mol.% of the $-CH_2CHPhCO-$ units has $T_g = 37$ °C, a rupture resistance (σ_p) of 62 MPa, and a relative elongation at rupture (ε) of 270%.[170]

It was found that by varying the nature of the aryl substituent at the phosphorus atom in (*S*)-2-[2-(diarylphosphino)phenyl]-4-benzyl-4,5-dihydrooxazole (Ar = Ph, *p*-$MeOC_6H_4$, *o*-$MeOC_6H_4$, *o*-MeC_6H_4), one can affect the copolymerisation rate and the tacticity of the $CO/CH_2=CHPh$ copolymer.[171]

Ar	w /mmol g_{Pd}^{-1} h^{-1}	T_m /°C
Ph	81	228
p-$MeOC_6H_4$	28	175
o-$MeOC_6H_4$	71	127
o-MeC_6H_4	11.7	80

New homogeneous bismethoxycarbonyl complexes [Pd(L-L).$(MeOCO)_2$] (L-L are substituted phenanthroline ligands) have been used to synthesise the syndiotactic $CO/CH_2=CHPh$ copolymer.[172] In the $[Pd(L\text{-}L)(MeOCO)_2](X)_2$ – oxidant catalyst system, PF_6^- acts as the weakly coordinated counter-ion and 1,4-naphthoquinone acts as the oxidant. The rate of copolymerisation of carbon monoxide with styrene at 65 °C and at a carbon monoxide pressure of 4 MPa is ~194 g g_{Pd}^{-1} h^{-1}. The rate depends on the pK_a of the phenanthroline ligand. With an increase in the pK_a (caused by the introduction of substituents in the phenanthroline ring), the copolymerisation rate and the copolymer molecular mass decrease 2 – 6-fold with simultaneous decrease in the copolymer tacticity. A decrease in the copolymerisation rate following an increase in the pK_a of the N-N-ligand from 4.44 (bipy) to 6.31 (tetramethylphenanthroline) has also been reported in the study [46] describing styrene – carbon monoxide copolymerisation catalysed by the $[Pd(N\text{-}N)(MeCO_2)_2]$ and $[Pd(N\text{-}N)(CF_3CO_2)_2]$ complexes (N-N is bipy, 1,10-phenanthroline or their derivatives). The degree of polymerisation of the copolymer increases with time and after 6 h, it reaches 160. The copolymer thus obtained has $T_g = 99$ °C and $T_m = 273$ °C. On short-term (5 min) heating of the copolymer at temperatures of 200 °C and 220 °C, the number of terminal vinyl groups substantially increases, while the number of methoxycarbonyl groups decreases (their ratio in the initial copolymer is 1 : 1).

The syntheses of carbon monoxide – styrene and carbon monoxide – *p*-methylstyrene copolymers as well as styrene – carbon monoxide – ethylene, styrene – carbon monoxide – propylene, styrene – carbon monoxide – ω-undecyl alcohol and styrene – carbon monoxide – ω-methyl undecenecarboxylate terpolymers have been carried out using the $[Pd(5\text{-}Me\text{-}1,10\text{-}phen).(MeCN)_2](BF_4)_2 - C_6H_4O_2$ catalyst system.[173] The $CO/CH_2=CHPh$ copolymer is poorly soluble in 2-chlorophenol and in hexafluoroisopropyl alcohol and has $T_g = 94$ °C and $T_m = 290$ °C. The crystallinity of the copolymer sharply decreases after it has been dissolved and reprecipitated. For example, reprecipitation of the $CO/CH_2=CHC_6H_4Me\text{-}p$ copolymer from a solution in 2-chlorophenol by methanol gave an amorphous polymer, which was soluble in chloroform and dichloromethane.

The solubility of the $C_2H_4/CO/CH_2=CHPh$ and $CH_2=CHMe/CO/CH_2=CHPh$ terpolymers depends on the styrene : olefin ratio. For example, a terpolymer containing 11 mol.% – 12 mol.% of the $-C_2H_4CO-$ units is soluble in chloroform and dichloromethane but insoluble in acetone, whereas the material containing 80 mol.% of the $-C_2H_4CO-$ units is insoluble in common organic solvents but is soluble in 2-chlorophenol and hexafluoroisopropyl alcohol.

Japanese researchers ‡ have studied the asymmetric terpolymerisation of propylene and hex-1-ene with 4-(*tert*-butyl)styrene and carbon monoxide in the presence of the Pd complex with the phosphine phosphite ligand BINAPHOS (**14**). It was shown that the glass transition temperature of the copolymers depends on the olefin content in the copolymer.

In the copolymerisation of carbon monoxide and styrene in the presence of the $Pd(OAc)_2$ – bipy – TsOH catalyst system, the maximum copolymerisation rate (68 g g_{Pd}^{-1} h^{-1}) is observed at a bipy : Pd molar ratio of 15 : 1. The replacement of methanol used as the reaction medium by acetone, THF, DMSO, aniline or DMF results in a sharp decrease in the copolymerisation rate and the reduction of Pd(II) to Pd(0). When copolymerisation is carried out in petroleum ether, cyclohexane, nitrobenzene, ethyl acetate or phenyl ethyl ether, the rate decreases 3 – 4-fold compared to the copolymerisation rate in methanol.[174]

The effect of the nature of the bidentate N-N ligand on the structure of the resulting copolymer of carbon monoxide with styrene was demonstrated using two ligands: diazabutadiene and bioxazoline. It was found that in the former case, an isotactic copolymer is formed, while in the latter case, the product is a syndiotactic polymer.[175] When the Pd(II) acetonitrile complex with 2,2-bis[4-(*S*)-methyl-1,3-oxazolin-2-yl]propane [176] and (4*S*,4′*S*)-(−)-4,4′,5,5′-tetrahydro-4,4′-diisopropyl-2,2′-bioxazole,[177] which are ligands with C_2-symmetry, was used as the catalyst, the isotactic $CO/CH_2=CHPh$ copolymer and partially isotactic $CO/CH_2=CHC_6H_4Me\text{-}p$ copolymer with high optical activity were obtained. Using C_2-symmetric Pd complexes, (*R*,*R*/*S*,*S*)-*trans*-1,2-$[C_6H_{10}\{N=CH\text{-}2\text{-}C_5H_4N(PdMe(NCMe)_2)\}_2][B\{3,5\text{-}(CF_3)_2.C_6H_3\}_4]_2$ and $[C_2H_4\{N=CH\text{-}2\text{-}C_5H_4N(PdMe(NCMe)_2)\}_2].[B\{3,5\text{-}(CF_3)_2C_6H_3\}_4]_2$, syndiotactic copolymers of carbon monoxide with styrene and 4-methylstyrene were obtained.[178] Palladium complexes with C_s-symmetry with asymmetric chelating ligands on the basis of 2-(pyrazol-1-yl)pyridine, 2-(pyrazol-1-

‡ Y Kawashima, K Nozaki, T Hiyama *Inorg. Chim. Acta* **350** 577 (2003).

yl)pyrimidine and 2-[(3,5-dimethyl)pyrazol-1-yl]pyrimidine have been used for copolymerisation of carbon monoxide with 4-(*tert*-butyl)styrene. This gave syndiotactic copolymers.[179] The use of C_1-symmetric pyridinylimidazole ligands with different hydrocarbon substituents provides carbon monoxide–4-(*tert*-butyl)-styrene copolymers with different tacticities depending on the substituent.[180]

The synthesis of a stereoregular carbon monoxide–4-(*tert*-butyl)styrene block copolymer using the 2,2′-bipyridyl–bioxazoline Pd(II) complex catalyst system has been reported.[176] Bipyridyl is added to the palladium complex during the synthesis; as a result, fast ligand exchange takes place. The produced copolymer contains macromolecules of both isotactic and syndiotactic structures. Depending on the symmetry of the phosphino(dihydrooxazole) ligand used, both isotactic and atactic polymers were obtained.[181, 182] The synthesis of alternating copolymers of carbon monoxide with hydroxystyrene and its formate and acetate has been described.[183] It is noteworthy that $Pd(OAc)_2$ can be replaced by rare earth metal (Y, La, Nd, Sm, Dy) acetates or their mixtures with $Cu(OAc)_2$. For example, copolymerisation of carbon monoxide with styrene in the presence of rare earth metal acetates has been reported.[184]

III. The mechanism of alternating copolymerisation of carbon monoxide

In a study of the alternating copolymerisation of carbon monoxide with olefins, the ethylene–carbon monoxide system studied most comprehensively was chosen as the model system and the $Pd(OAc)_2$–diphosphine–acid system used most often was chosen as the catalyst.

When the catalyst is formed *in situ* under homogeneous conditions, depending on the nature of the solvent (alcohol, water or a less polar solvent), reactions (1)–(8) can take place between the catalyst components and the medium. If copolymerisation is carried out in methanol, L_2PdOMe^+ would act as the catalytically active species [reaction (2)].[185]

In water and in moist solvents, Pd hydride complexes may form [reactions (4), (8)]. In addition, palladium hydride species can be formed by reactions (3), (5) and (6).

$$Pd^{2+} + L_2 \longrightarrow L_2Pd^{2+} \text{ } (L_2 \text{ is a bidentate phosphine ligand}) \quad (1),$$

$$L_2Pd^{2+} + MeOH \longrightarrow L_2PdOMe^+ + H^+, \quad (2)$$

$$L_2PdOMe^+ \longrightarrow L_2PdH^+ + CH_2O, \quad (3)$$

$$L_2Pd^{2+} + CO + H_2O \longrightarrow L_2PdH^+ + CO_2 + H^+, \quad (4)$$

$$L_2Pd^{2+} + C_2H_4 + MeOH \longrightarrow L_2PdH^+ + CH_2{=}CHOMe + H^+, \quad (5)$$

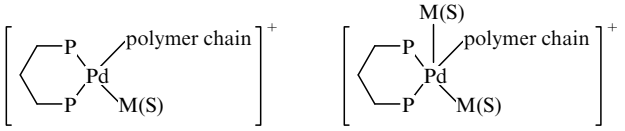
$$L_2Pd^{2+} + H_2 \longrightarrow L_2PdH^+ + H^+. \quad (6)$$

In an aqueous medium, apart from L_2PdH^+, the L_2PdOH^+ species are also present; they react with CO by reactions (7) and (8).

$$L_2PdOH^+ + CO \longrightarrow L_2PdCOOH^+, \quad (7)$$

$$L_2PdCOOH^+ \longrightarrow L_2PdH^+ + CO_2. \quad (8)$$

Initiation and propagation of the polymer chain. The chain initiation in a solution (*i.e.*, primary insertion of a CO or C_2H_4 molecule into a Pd–alkyl or Pd–acyl complex) has been studied rather comprehensively by various physicochemical and theoretical methods.[25, 185–202] In a number of studies,[25, 186, 187, 200–202] the structure of the catalytically active species that run the copolymerisation process has been proposed on the basis of data from EXAFS, UV, IR and ^1H and ^{31}P NMR spectroscopy and mass spectrometry. In particular, it was found that the monochelate complex of diphosphine and palladium acetate is the active site of the copolymerisation. As the diphosphine : palladium molar ratio increases to 2 or more, the monochelate complex is transformed into an inert bischelate complex, which is unable to participate in copolymerisation. When the inert palladium complex is exposed to atmospheric oxygen, the equilibrium shifts toward the formation of the catalytically active monochelate palladium complex. The relationship between the contents of these complexes in the catalyst system and the rate and the induction period of copolymerisation has been established.[185] On the basis of ^1H NMR data, it was shown that the $CO-C_2H_4$ copolymerisation in protic (alcohols) and aprotic solvents is initiated by the insertion of the CO and C_2H_4 molecules into the Pd–OMe and Pd–H bonds, respectively. It should be noted that protic solvents not only serve as the reaction medium; they are also involved in chain initiation and termination reactions and also stabilise the Pd^{2+} cation. It was found [25] that in addition to the catalytically active 16-electron four-coordinate square planar $Pd(d^8)$ species (**A**), a five-coordinate 18-electron pyramidal $Pd(d^8)$ species is also present in the reaction area (**B**).



A **B**

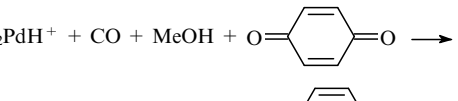
M is monomer (CO or C_2H_4), S is solvent.

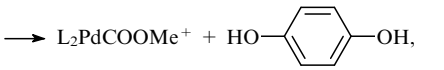
Studies of the initiation and propagation of the polymer chain have been carried out using a heterogeneous single-centre Pd complex, $[\{Ph_2P(CH_2)_3PPh_2\}Pd(Me)(OSO_2CF_3)]$. The polarisation-modulated absorption IR spectroscopy technique has been used [186] to observe the changes taking place in the IR spectra on the successive insertion of the CO and C_2H_4 molecules into the Pd–OMe bond in the active catalytic species [reactions (9), (10)]. It was found that the hydride species L_2PdH^+, formed during the formation of the catalyst and in the subsequent chain termination and transfer steps, can be transformed again into catalytically active species by reaction (14).

$$L_2PdOMe^+ + CO \longrightarrow L_2PdCOOMe^+, \quad (9)$$

$$L_2PdOMe^+ + C_2H_4 \longrightarrow L_2PdCH_2CH_2OMe^+, \quad (10)$$

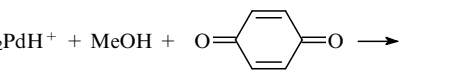
$$L_2PdH^+ + C_2H_4 \longrightarrow L_2PdC_2H_5^+, \quad (11)$$

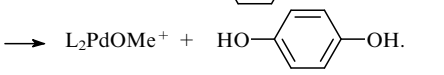
$$L_2PdH^+ + CO + MeOH + \text{} \longrightarrow \quad (12)$$

$$\longrightarrow L_2PdCOOMe^+ + \text{}$$

$$L_2Pd^{2+} + CO \longrightarrow L_2PdCO^{2+}, \quad (13)$$

$$L_2PdCO^{2+} + MeOH \longrightarrow L_2PdCOOMe^+ + H^+, \quad (13')$$

$$L_2PdH^+ + MeOH + \text{} \longrightarrow \quad (14)$$

$$\longrightarrow L_2PdOMe^+ + \text{}$$

It should be noted that, depending on the nature of the initiating species (L_2PdOMe^+ or L_2PdH^+), the growing polymer chain would have a methoxyl or ethyl group at one end [reactions (15)–(17)].

$$L_2PdCOOMe^+ + C_2H_4 \longrightarrow L_2PdCH_2CH_2COOMe^+, \quad (15)$$

$$L_2PdCH_2CH_2OMe^+ + CO \longrightarrow L_2PdCOCH_2CH_2OMe^+, \quad (16)$$

$$L_2PdC_2H_5^+ + CO \longrightarrow L_2PdCOC_2H_5^+. \quad (17)$$

Chain restriction (termination and transfer). When the chain is transferred to the alcohol (by a protolysis or alcoholosis reaction), either methoxy or ethyl group is located at the end of the chain. In these cases, diester [reaction (18)], ketoester [reaction (19)] or diketone [reaction (20)] type copolymers are formed. Recently, it has been shown [203] that in a homogeneous medium (when the

length of the growing polymer chain does not exceed 500), chain termination and transfer occur mainly *via* protolysis of the active site, whereas in a heterogeneous medium (when the polymer chain is long and the polymer precipitates), both protolysis and alcoholysis reactions take place. (For determining the rates of these reactions depending on the type of catalyst and conditions of copolymerisation, further systematic research is required.)

$$L_2PdCO(CH_2CH_2CO)_nOMe^+ + MeOH \longrightarrow \quad (18)$$

$$\longrightarrow L_2PdH^+ + \underset{\text{diester}}{MeOCO(CH_2CH_2CO)_nOMe}$$

$$L_2PdCO(CH_2CH_2CO)_nOMe^+ + MeOH \longrightarrow \quad (19)$$

$$\longrightarrow L_2PdOMe^+ + \underset{\text{ketoester}}{HCO(CH_2CH_2CO)_nOMe}$$

$$L_2PdCO(CH_2CH_2CO)_nC_2H_5^+ + MeOH \longrightarrow \quad (20)$$

$$\longrightarrow L_2PdOMe^+ + \underset{\text{diketone}}{HCO(CH_2CH_2CO)_nC_2H_5}$$

During copolymerisation of CO and C_2H_4 in water or in water-containing solvents, the following reaction can take place:

$$L_2PdCO(CH_2CH_2CO)_nC_2H_5^+ + HOH \longrightarrow \quad (21)$$

$$\longrightarrow L_2PdOH^+ + \underset{\text{diketone}}{HCO(CH_2CH_2CO)_nC_2H_5}$$

Spontaneous chain termination. When copolymerisation is carried out in aprotic solvents, spontaneous chain termination takes place by β-elimination mechanism [reactions (22), (23)]. In this case, one end of the polymer chain would bear the vinyl group.

$$L_2Pd(CH_2CH_2CO)_nOMe^+ \longrightarrow$$

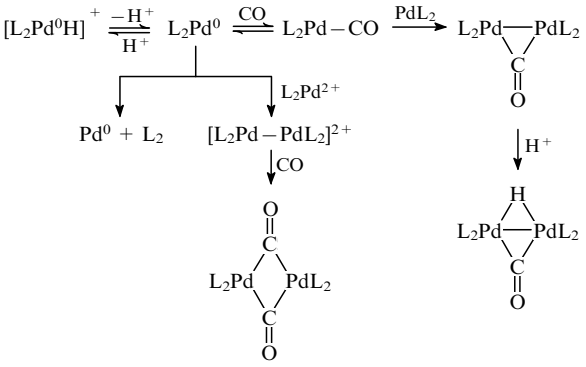
$$\longrightarrow L_2PdH^+ + CH_2{=}CHCO(CH_2CH_2CO)_{n-1}OMe, \quad (22)$$

$$L_2Pd(CH_2CH_2CO)_nC_2H_5^+ \longrightarrow$$

$$\longrightarrow L_2PdH^+ + CH_2{=}CHCO(CH_2CH_2CO)_{n-1}C_2H_5. \quad (23)$$

Irreversible destruction of the potential L_2PdH^+ active sites. The kinetic studies[21,22] show that, despite the steady-state copolymerisation character, the reaction rate decreases with time, due to the decrease in the concentration of catalytically active sites. Scheme 3 presents the most probable ways of destruction of the potentially active L_2PdH^+ sites.[7]

Scheme 3

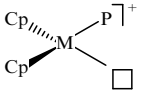
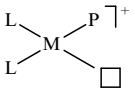


In terms of the above kinetic scheme, the inverse kinetic problem was solved and the rate constants for individual copolymerisation steps were estimated. This model describes quantitatively the dependence of the initial process rate on the comonomer pressure, the kinetic curves for the consumption of comonomers and the molecular-mass characteristics of the copolymers at different pressures of the $CO/CH_2{=}CH_2$ monomer mixture.[203]

* * *

It is worth noting that although the Pd complexes used in the alternating copolymerisation of carbon monoxide with various monomers seem to differ from the known Ziegler–Natta catalysts (including metallocene type catalysts) used in the synthesis of polyolefins, they still have much in common with these catalysts (Table 4). Both the palladium complexes and the Ziegler–Natta catalysts contain an electrophilic metal cation and a weakly coordinated anion. In both types of catalyst, the metal cations have a coordination number equal to four. However, the metal cations in the Ziegler–Natta catalyst are most often tetravalent and contain four anionic ligands [two strongly coordinated (for example, Cp ligands) and two weakly coordinated Z^- anions], whereas in Pd complexes, the Pd cation is divalent and contains two neutral (L) and two weakly coordinated (Z^-) anionic ligand. The active sites in both types of catalyst have a *cis*-structure during the growth of the polymer chain and monomer coordination. In the d^0-metallocene complex, the *cis*-structure involves the pseudotetragonal coordination environment of the metal, while in the square planar Pd(d^8) complex, the *cis*-structure is ensured by the presence of neutral ligands.

Table 4. Comparison of the catalysts used in the synthesis of polyolefins (**A**) and polyketones (**B**).[3]

Catalyst structure	**A**	**B**
Metal ion	Ti^{IV}, Zr^{IV}, Hf^{IV}	Pd^{II}
Ligands	2 Cp^-, 2 Z^-	2 L, 2 Z^-
Anions	non-coordinated	weakly coordinated or non-coordinated
Geometry	tetrahedral	square planar
Active site structure		

Note. Cp is cyclopentadienyl.

IV. Structure and properties of polyketones

1. Study of the structure and properties of polyketones

Copolymers of ethylene with carbon monoxide were described by NMR and IR spectroscopy. The IR spectra of low-molecular-weight aliphatic polyketones exhibit an intense characteristic absorption band in the region of 1715–1720 cm^{-1} due to the CO group.[204] The IR spectra of random ethylene–carbon monoxide copolymers containing ~1 mol.% of carbon monoxide[205] also contain an absorption band in this region. However, in the IR spectrum of the alternating C_2H_4/CO copolymer, this band is shifted to 1695 cm^{-1}. The vibration frequencies of some functional groups of the CO/C_2H_4 copolymer at room temperature are lower than those observed for low-molecular-weight model analogues.

A study of the IR spectra of solid samples of model ketoesters $MeO(COCH_2CH_2)_nH$ ($n = 1-5$) has shown that the absorption band due to CO shifts from 1720 to 1700 cm^{-1} with an increase in n (see Ref. 206). The IR absorption bands of the alternating copolymer of carbon monoxide with ethylene are listed in Table 5.[207]

Table 5. Absorption bands in the IR spectra of the $CO/CH_2=CH_2$ copolymer (25 °C, KBr pellet).[207]

ν /cm^{-1}	Type of vibration [a]
3250 – 3680	traces of H_2O
3392 w	$2\nu(C=O)$
2912 s	$\nu_{as}(CH_2)$
1692 vs	$\nu_{as}(C=O)$
1408 s	$\delta_s(CH_2)$
1334 s	δ_w, $\delta_{tw}(CH_2)$
1260 m	δ_w, $\delta_{tw}(CH_2)$
1057 s	$\nu(CH_2-CO-CH_2)$
810 m	skeletal vibrations
594 m	skeletal vibrations

[a] ν_{as} are asymmetric, δ_w are rocking; δ_{tw} are twisting, and δ_s are scissoring vibrations.

A study of the temperature variation of the IR spectra of the carbon monoxide – ethylene copolymer has shown that in the temperature range of 20 – 260 °C, the CO vibration frequency shifts from 1692 to 1709 cm^{-1} (Fig. 1 *a*), and the band for the CH_2COCH_2 groups shifts from 1055 to 1062 cm^{-1} (Fig. 1 *b*). The vibrational spectra of thin films (60 μm) of the ethylene – carbon monoxide copolymer deposited on gold-coated silicon substrates have been reported.[208, 209]

Investigations of 5 – 12-nm thick films from CO/C_2H_4-based polyketones deposited on the surface of gold by Raman (120 – 3300 cm^{-1}), IR (10 – 3300 cm^{-1}), reflection absorption IR (500 – 3300 cm^{-1}) and surface electromagnetic wave absorption (1000 – 1450 cm^{-1}) spectra have shown that 8 – 12 nm thick films are predominantly lamellar crystals with a complex conformation of chains, while in the 5-nm thick films, crystals with stretched chains predominate.[210]

By using ^1H and ^{13}C NMR spectroscopy, not only the composition of the random CO/C_2H_4 copolymer but also the distribution of the monomer units along the chain, the terminal groups, branchings and conformational transitions have been determined.[211]

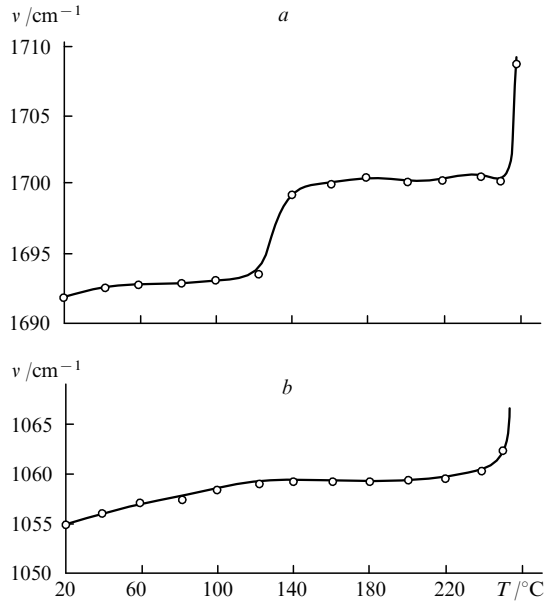


Figure 1. Effect of temperature on the shift of the absorption bands of the CO (*a*) and CH_2COCH_2 (*b*) groups in the IR spectra of the carbon monoxide – ethylene copolymer.

Belov *et al*.[212] reported the results of a ^1H and ^{13}C NMR study of the microsctructure of CO/C_2H_4 copolymers. The molecular-mass characteristics of the copolymers were determined by osmometry and gel permeation chromatography (GPC); in addition, the constants K and α of the Mark – Kuhn – Howink equation in the range of molecular mass from 10^3 to 10^6 were found.

The crystal structure of the ethylene – carbon monoxide copolymer with different ratios of the monomer units in the polymer chain has been studied.[213 – 215] In 1961, the crystal structure parameters of an alternating copolymer of ethylene and carbon monoxide (T_m = 175 – 185 °C), obtained by radiation copolymerisation were determined for the first time while studying the properties of oriented films.[213] More recently it has been shown [215] that this alternating copolymer has a β-structure, the *ab* projection of the orthorhombic cell of this structure being similar to that of polyethylene (PE). The alternating copolymer of ethylene and carbon monoxide obtained in a catalytic process has T_m = 250 – 260 °C and has the so-called α-structure. The conformations of the polymer backbone in these two structures are identical; however, the chain packings are different. This difference can be attributed to different orientations of the carbonyl groups relative to the chains arranged in the unit cell corners. The angles between the plane of the macromolecule and the *bc* plane are 26° and 40° in the α- and β-structures, respectively.

In the α-structure, the symmetry transformation that relates the corner and the central chains is $1/2-x$, $1/2+y$, z; while in the β-structure, this transformation is given by $1/2+x$, $1/2-y$, z. Thus, the difference between the two structures is described by rotation of the central chain through an angle of ~180° around the axis of this chain or by a translation of the central chain by half the unit cell dimension along the axis of the macromolecule. In the α-structure, the dipoles of all the carbonyl groups are oriented toward the same direction, whereas in the β-structure, the dipoles of the carbonyl groups of the corner and central chains point to different directions. As a consequence, the chain packing in the α-structure is less dense than that in the β-structure (the calculated densities are 1.383 and 1.297 g cm^{-3}, respectively). The cross section of the unit cell is perpendicular to the fiber axis and has an area of 35.2 Å^2, which is somewhat smaller than the area of the PE unit cell (36.2 Å^2). Table 6 presents data on the CO and CH_2 vibration frequencies for three forms [α, β and the amorphous form (or a melt)] of the co-polyketone based on $CH_2=CH_2$ and CO.

Table 6. Vibration frequencies of the main groups of the $CO/CH_2=CH_2$ copolymer in the IR spectrum.[208]

Type of vibration	ν /cm^{-1}		
	α-form	β-form	amorphous form or melt
$\nu_{as}(CH_2)$	2910 – 2912	2917	2911
$\nu(C=O)$	1692 – 1694	1697 – 1700	1708
$\delta_s(CH_2)$	1408	1415	1410
δ_w, $\delta_{tw}(CH_2)$	1334	1336	1358
$\nu(CH_2-CO)$	1056	1059	1079
Skeletal	811	804	835, 811, 794 [a]
Skeletal	591 – 594	603	616, 580, 558 [a]

[a] Vibration frequencies caused by the possible destructive processes in the polymer.

Table 7 contains the experimental densities of the alternating copolymer of ethylene and carbon monoxide (polyketone, POK), the unit cell parameters and T_m; the same characteristics for other polymers are given for comparison.

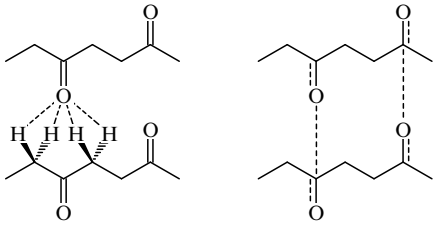
The α-form of POK has a greater density and a shorter $CH_2\cdots C=O$ distance (3 Å) than the β-form (3.41 Å). This is due

Table 7. Melting point, density and unit cell parameters for various polymers.[216]

Polymer	T_m /°C	d /g cm^{-3}	Sructure	a /Å	b /Å	c /Å
α-Form of POK	see [a]	1.38	ortho-rhombic	6.91	5.12	7.60 [b]
β-Form of POK	550	1.30		7.97	4.76	7.57 [b]
Polyalcohol prepared from POK	410	1.08	–	8.78	5.47	7.47 [b]
PVA [c]	540	1.35	monoclinic (β = 91.7°)	7.81	2.52	5.51
PE	414	1.00	ortho-rhombic	7.40	4.93	2.54 [b]

[a] The α-structure passes to the β-structure prior to the onset of melting of polyketone (at 110 – 130 °C). [b] Along the fibre axis. [c] PVA is poly(vinyl alcohol).

to the formation of intermolecular bonds between the CO and CH_2 groups. At room temperature, the α-form is more stable, whereas at a temperature of > 140 °C, only the β-form exists. The α→β temperature transition lies at about 113 °C (for the fibre) and 120 – 140 °C (for the film). The β→α transition takes place only upon drawing of POK samples. Thus, it can be concluded that the α- and β-forms of the copolymer are characterised by different strength of intermolecular cohesion caused by the presence of hydrogen bonds and dipole – dipole interactions.



A 3D computer model of polyketone was constructed using the molecular dynamics method. The calculated values for density and crystal lattice parameters coincided almost entirely with experimental data over a broad temperature range. Using the 3D model, it was shown that the crystal structure of the α- and β-phases is largely determined by the Coulomb interaction between the polar carbonyl groups.[217]

The ethylene – carbon monoxide – α-olefin terpolymers (α-olefin is propylene,[218, 219] but-1-ene or hex-1-ene [218]) were studied by

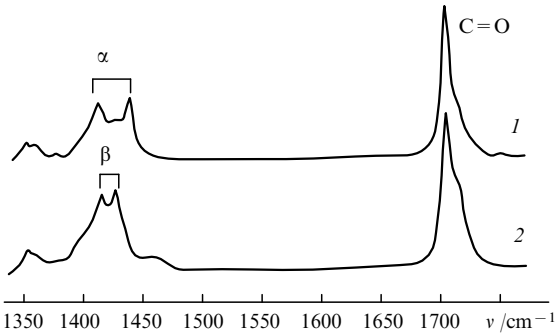


Figure 2. Raman spectra of the alternating ethylene – carbon monoxide – propylene terpolymers containing macromolecules of the α- (curve *1*) and β-form (curve *2*).

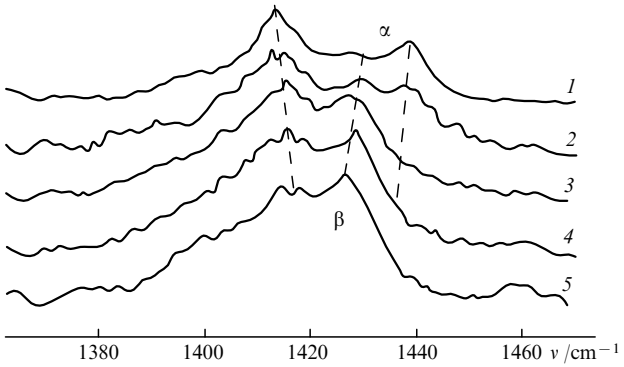


Figure 3. Raman spectra of the alternating ethylene – carbon monoxide – propylene terpolymers with different contents of propylene. [C_3H_6] (mol %): 0 (*1*), 1.2 (*2*), 2.9 (*3*), 4.6 (*4*), 7.2 (*5*).

wide-angle and small-angle X-ray diffraction, DSC and Raman spectroscopy. Copolymers containing hex-1-ene have a higher crystallinity than copolymers containing propylene and but-1-ene. The relative content of the α-form macromolecules in the terpolymers decreases in the sequence hex-1-ene > but-1-ene > propylene.[218] Figures 2 and 3 show the Raman spectra of the ethylene – carbon monoxide – propylene terpolymers which contain both α- and β-forms. It can be seen from Fig. 3 that the content of α-form macromolecules in the copolymer decreases with an increase in the propylene content.

The crystal structure of the CO/C_2H_4 copolymer and the $C_2H_4/CO/C_3H_6$ terpolymer (1.2 mol.%, 2.9 mol.%, 4.6 mol.% and 7.2 mol.% of propylene) was studied by DSC, Raman spectroscopy and wide-angle X-ray diffraction and the contents of α- and β-forms were determined.[220] The influence of the stereo- and regio-regularity of the propylene – carbon monoxide copolymer on its crystal structure and macroscopic properties was studied.[§]

Using X-ray examination and optical and electronic microscopy, the structure and morphology of the ethylene – carbon monoxide copolymer crystals prepared by crystallisation of the polymer from a mixture of hexafluoroisopropyl alcohol and hydroquinone have been studied.[221]

The crystal structure of iso- and syndiotactic copolymers of CO with styrene and some its derivatives has been studied.[222 – 224] The key crystallographic characteristics of these copolymers are listed in Table 8.

Table 8. Crystallographic parameters of copolymers of carbon monoxide with styrene or its derivatives.

Parameter	Copolymer $CO/CH_2=CHPh$		Copolymer $CO/CH_2=CHC_6H_4R$ (see [222])		
	isotactic [224]	syndiotactic [222]	R = *p*-F	R = *m*-Me	R = *p*-Me
a /Å	8.367	15.20	15.59	16.14	35.54
b /Å	7.574	6.166	6.168	6.816	6.262
c /Å	5.47	7.590	7.551	7.580	7.536
β /deg	100.0	102.5	98.8	100.3	96.0
d_{calc} /g cm^{-3}	1.347	1.262	1.388	–	–

The syndiotactic carbon monoxide copolymer with styrene (or *tert*-butylstyrene) can be converted into the atactic copolymer by heating in an organic base (for example, in a tertiary amine,

§ D V Anokhin, V M Neverov, S N Chvalun, N P Bessonova, Yu K Godovsky, F Hollmann, U Merer, B Rieger *Vysokomol. Soedin., Ser. A* **46** 69 (2004); [*Polym. Sci. (Engl. Transl.)*].

N-alkylamide or alkali metal phenoxide) at 40–200 °C [225] or by treatment of the copolymer in the NaOH–MeOH–THF medium.[226]

The IR spectra of carbon monoxide–DCPD copolymers exhibit high-intensity absorption bands in the regions of 1790 and 1721 cm^{-1} (for dimers **A**), indicating the presence of an enol lactone structure, and 1775, 1710–1735 cm^{-1} (for trimers **B**), indicating the presence of γ-lactone and ester vinyl groups.[111] The ^{13}C NMR spectra of these copolymers show signals at about 178–179 ppm (the carbonyl-group carbon atom in the lactone structure **A**), 147–149 (the carbon atoms of the ester vinyl group in structure **B**), 130–136 ppm (the C_{sp}^2 atoms of the cyclopentene ring) and 116–120 ppm (the carbon atom of the spiroketal structure **B**). The formation of terminal lactone groups can be regarded as intramolecular chain termination due to the reaction with methanol (methanolysis), usually resulting in the formation of terminal ester groups.

2. Thermal and thermodynamic properties

In a study of melting of ethylene–carbon monoxide copolymers, it was suggested that the increase in T_m for random carbon monoxide–ethylene copolymers with respect to PE is due to restriction of the rotation caused by the presence of carbonyl groups.[213] Determination of the heats of melting for random copolymers of ethylene and carbon monoxide has shown that the alternating copolymer has $T_m = 244$ °C and a low melting entropy.[227] Study of the melting of low- and high-molecular-weight alternating carbon monoxide–ethylene copolymers showed that their maximum melting points are 278 °C, the heats of melting are 4 and 6.2 kJ mol^{-1}, and the melting entropies are 7.3 and 11.3 J mol^{-1} K^{-1}, respectively.[214] In the case of $MeCH=CH_2/CO$ or $EtCH=CH_2/CO$ copolymers, the presence of side substituents in the position neighbouring to the carbonyl group promotes the formation of macromolecules with less regular structures. These copolymers have lower T_m values and lower solubilities in common solvents. The inclusion of propylene in the polymer chain on passing to the terpolymerisation of ethylene, propylene and carbon monoxide results in a noticeable decrease in T_m values of the terpolymer formed, which has a beneficial effect on the processing conditions. Figure 4 presents the dependences of the heat of melting (Fig. 4 *a*), the degree of crystallinity (Fig. 4 *b*) and T_m (Fig. 4 *c*) for the ethylene–carbon monoxide–α-olefin terpolymers (the α-olefin is propylene, but-1-ene, hex-1-ene) on the α-olefin concentration.[228]

As noted above, copolymerisation of propylene and α-olefins with carbon monoxide may yield macromolecules with the polyspiroketal structure. In the case of the propylene–carbon monoxide copolymer, the polyspiroketal structure is transformed into the usual ketone structure when the copolymer has been dissolved in hexafluoroiopropyl alcohol or heated to 70 °C (the process enthalpy is −11.8 to −10.5 kJ mol^{-1}). This value is close to the calculated enthalpy for the polymerisation of acetone (−10.0 kJ mol^{-1}).[229] The polyspiroketal structures of the but-1-ene–carbon monoxide and hept-1-ene–carbon monoxide copolymers are more stable than the polyspiroketal structure of the propylene–CO copolymer. The polyspiroketal structure of the hept-1-ene–carbon monoxide copolymer does not pass to the ketone structure even upon dissolution in chloroform. It is noteworthy that copolymers containing the spiroketal structure differ in physicochemical properties from copolymers with the ketone structure. For example, copolymers of carbon monoxide with but-1-ene and hept-1-ene having the ketone structure are completely soluble in acetone, while the same copolymers containing both spiroketal and ketone macromolecules are insoluble in acetone.[83]

The crystallisation kinetics of two samples of the ethylene–propylene–carbon monoxide terpolymer containing 3 mol.% and 6 mol.% of propylene has been studied.[230] In the epitaxial crystallisation of the ethylene–carbon monoxide copolymer carried out by the hypoeutectic growth technique on hydroquinone crystals, the axes of the polymeric chains are arranged parallel to the hydroquinone surface.[221] Tunnelling electron microscopy (TEM) has been used to study epitaxial crystallisation (at temperatures of 150–190 °C) of the carbon monoxide–ethylene copolymer on NaCl and KI crystals from a nitrobenzene solution. It was shown that the shape and orientation of macromolecular chains on the substrate surface depend on its nature.[231–233] The copolymer crystals grown under isothermal conditions (at 139 °C for 24 h) from a 0.01 mass % solution in nitrobenzene contained only macromolecules of the α-form (they were characterised by TEM and small-angle X-ray diffraction), whereas the copolymer crystals grown on the surface of alkali metals contained macromolecules of both (α and β) forms.[234]

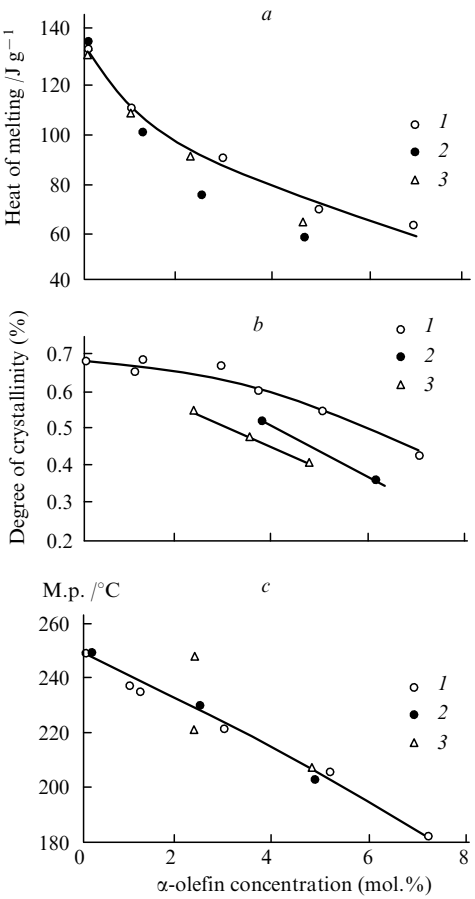


Figure 4. Effect of the α-olefin concentration on the heat of melting (*a*), degree of crystallinity (*b*) and T_m (*c*) of ethylene–CO–propylene (*1*), ethylene–CO–but-1-ene (*2*), ethylene–CO–hex-1-ene (*3*) terpolymers.[228]

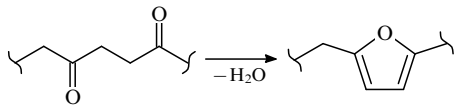
Detailed study of the characteristic features of the crystallisation and melting of three samples of the ethylene–carbon monoxide–propylene terpolymer (I–III) by DSC, wide-angle and small-angle X-ray and optical spectroscopies has been reported.[235]

Sample	$[C_3H_6]$ /mol.%	M_w	$M_w : M_n$
I	0	4×10^4	3.09
II	6	8×10^4	2.99
III	6	4×10^4	2.32

It was noted that T_m decreases by about 1 °C, the heats of melting decrease by 2 J g^{-1} and the sample crystallinity also decreases after every heating to T_m, which is due to cross-linking reactions. The heats of melting for the crystalline (100%) C_2H_4/CO copolymer (β-form) and $C_2H_4/CO/C_3H_6$ terpolymer (β-form) were determined to be 239±11 and 226±16 J g^{-1}, respectively. The thickness of the lamellae increases linearly with an increase in the

crystallisation temperature. The isothermal crystallisation of the copolymer proceeds faster than that for the terpolymer. On the basis of comprehensive analysis, it was concluded that the equilibrium T_m for the high-molecular mass copolymer and terpolymer and that for the low-molecular-mass copolymer are 278, 252 and 249.5 °C, respectively.

The high T_m values of ethylene–carbon monoxide copolymers bring about difficulties in the material processing into articles. This is due to the fact that at elevated temperatures, in addition to thermal destruction, condensation may take place, giving rise to furan structures in the polymer chain according to the following scheme:

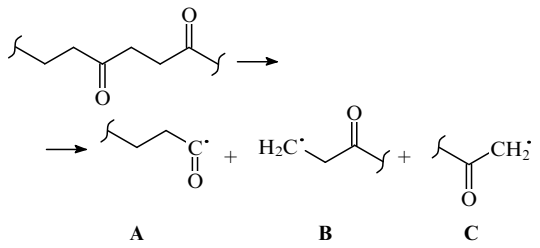


The thermal destruction of the carbon monoxide–ethylene copolymer at 500 °C to give linear polyketones, diketones and low-molecular-mass products has been studied.[236] A study of the thermal destruction of this polymer *in vacuo* at temperatures above T_m by flash pyrolysis–gas chromatography–mass spectrometry (FP-GCMS) has identified the formation of vinyl ketones with different molecular masses.[237]

The destruction of samples of the carbon monoxide–ethylene copolymers containing 70 ($[\eta] = 0.41$ dl g^{-1}) and 15 ppm Pd ($[\eta] = 2.5$ dl g^{-1}) has been studied by DTG, mass spectrometry, and UV and IR spectroscopy. The copolymer starts to lose mass at approximately 290 °C; the maximum mass loss is observed at 370–410 °C. The main decomposition products at temperatures of up to 215 °C are polyfuran structures and water. The residue obtained after the pyrolysis in an inert atmosphere and *in vacuo* amounts to 30 mass % and 10 mass %, respectively. After the pyrolysis, the polymer completely loses its solubility in hexafluoroisopropyl alcohol and crystallinity estimated based on the absorption bands in the region of 1082–1056 cm^{-1}. Cross-linking of polymer chains starts at 230 °C and is accompanied by the formation of ethylene, carbon monoxide and low-molecular-mass ketones. The rupture of polymer chains at this relatively low temperature affords macroradicals, which can be destroyed both upon intermolecular chain transfer and in bimolecular processes.

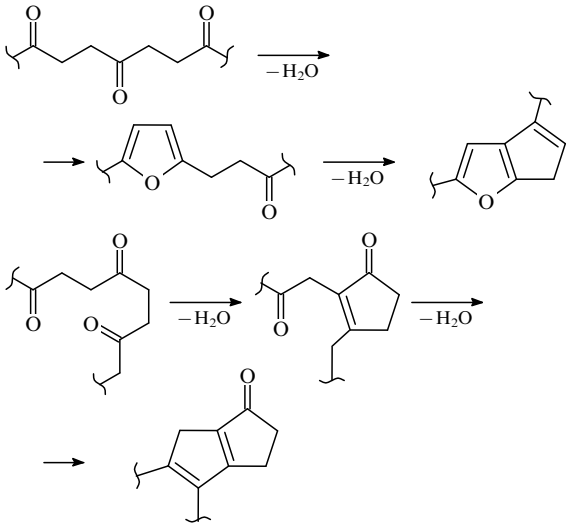
The pyrolysis products obtained at 500 °C were found to include CO, CO_2, water, linear low-molecular-mass polyketones, cyclopentanone derivatives, aromatic compounds (phenols, aromatic ketones and hydrocarbons having bi- and polycyclic structures). Pyrolysis of preliminarily 'aged' copolymer gives large amounts of water and CO_2 as well as furan, phenolic and aromatic derivatives, and linear polyketones. The thermal decomposition of the copolymer can be described as aldol condensation and/or dehydration to give furan structures at temperatures below 260 °C. On the basis of the DSC data, it was suggested that destruction starts in the amorphous regions of the copolymer.[238, 239]

The pyrolysis at 550 °C and thermal decomposition of the ethylene–carbon monoxide copolymer at 350 and 400 °C have been studied.[239] The volatile products of thermal decomposition were studied by GC and mass spectrometry, while the structural changes in the copolymer were examined by IR, UV and visible spectroscopy. It was found that all the volatile products are formed from **A**–**C** type radicals



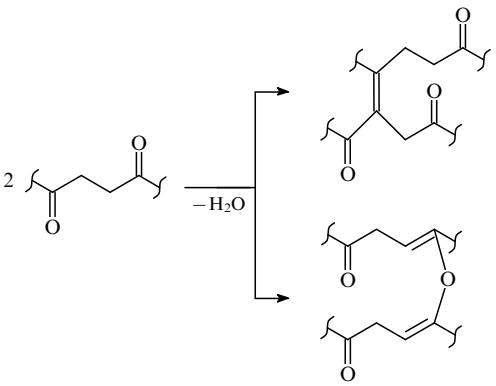
Depending on the temperature and duration of maintenance, the copolymer colour changes from while to pale yellow and dark brown; simultaneously, the polymer loses, either completely or partially, the solubility in hexafluoroisopropyl alcohol (due to cross-linking of polymer chains). Analysis of the IR spectra of thermally aged copolymers of carbon monoxide with ethylene shows that ageing is accompanied by the formation of new functional groups (Scheme 4).

Scheme 4

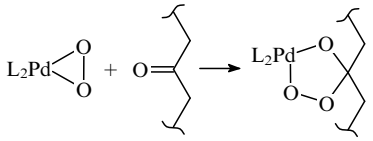


In addition, due to cross-linking of the polymer chains, copolymer loses crystallinity and becomes amorphous. The cross-linking of copolymer macromolecules can proceed according to Scheme 5.

Scheme 5



The influence of the remains of the Pd catalyst on the mass loss from the ethylene–carbon monoxide–propylene terpolymer in an inert atmosphere and in the presence of oxygen has been studied by TGA.[240, 241] On the basis of the DTG data, it was shown that under inert atmosphere, the maximum loss of mass (10%–30%) occurs at a Pd content of [Pd] ≈ 300 ppm (Fig. 5 *a*), while for the thermal destruction in air it barely depends on the Pd content up to 600–800 ppm and starts to decrease only at Pd > 800 ppm (Fig. 5 *b*). Thus, it was suggested that traces of palladium do not influence the temperature of the onset of thermal decomposition in the presence of oxygen, which is apparently related to the formation of stable palladium complexes with dioxygen, which subsequently react with the copolymer according to the following scheme:



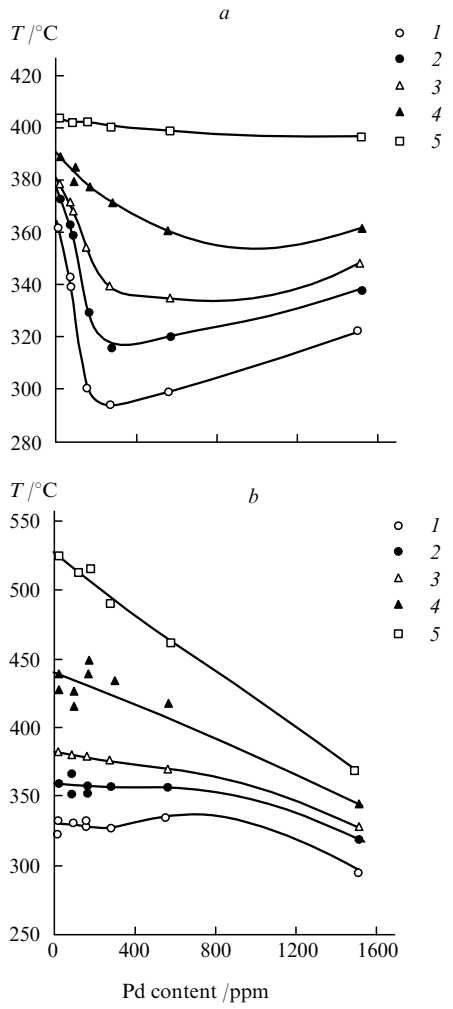


Figure 5. Effect of the palladium content in the ethylene–carbon monoxide–propylene terpolymer on the loss of its mass in an inert atmosphere (*a*) and in air (*b*).
Mass loss (%): 10 (*1*), 20 (*2*), 30 (*3*), 50 (*4*), 75 (*5*).

It was found that the oxidation state of palladium [Pd(II) or Pd(0)] has an influence on the destruction of copolymer. In the former case, destruction starts at a temperature lower by 60 °C than in the latter case.

Under an inert atmosphere, thermal decomposition is retarded with an increase in the palladium content (> 300 ppm). The higher the palladium content ¶ in the copolymer, the higher the degree of cross-linking.[240]

When the palladium content is less than 6 ppm, the ethylene–carbon monoxide–propylene terpolymer can be moulded to give transparent specimens which do not change their colour.[242]

A study of the uninhibited oxidation of the $CH_2=CH_2/CO$ copolymer (at 170–200 °C) and the $MeCH=CH_2/CO$ copolymer (at 80–180 °C) has shown that the patterns of oxidation of these copolymers are complex and differ considerably from each other.[243, 244] The kinetics of oxygen absorption during oxidation of the former copolymer shows two clear-cut steady-state sections with activation energies of 203 and 133 kJ mol^{-1}. For the second copolymer, the oxidation rate decreases with an increase in the temperature (> 140 °C) (negative temperature coefficient), the apparent activation energy being −59 kJ mol^{-1}. The mechanism of this phenomenon is related to switching from the standard oxidation mechanism [reactions (24), (25)] to a mechanism in which a significant role is played by decomposition of the $RO_2^{\bullet}$ radical [reaction (26)].

$$R^{\bullet} + O_2 \longrightarrow RO_2^{\bullet}, \quad (24)$$

$$RO_2^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}, \quad (25)$$

$$RO_2^{\bullet} \longrightarrow R_1^{\bullet} + \text{products}. \quad (26)$$

In the search for compounds that could stabilise polyketones during processing to manufacture articles, the best results were obtained for aromatic carbodiimides, mono- and polyepoxy compounds, β-diketones and cellulose ethers in combination with hydroxyapatite. The key criteria used to estimate the efficiency of stabilisers in the processing of polyketones included the degree of crystallinity (DC), the shift of the crystallisation temperature in the second heating–cooling cycle (ΔT), the heat of crystallisation (C_2) in the second cycle and the ratio of the peak height in the second crystallisation cycle to the peak width at the half-height ($C_{h/w}$) (Table 9).

Table 9. Efficiency of various stabilisers (according to DSC).[245]

Stabiliser [a]	Degree of crystallinity	ΔT /°C	C_2 /J g^{-1}	$C_{h/w}$
Stabaxol P (1%)	0.73	12.1	−77	3.2
Stabaxol P (2%) + CaHA (2%)	0.88	5.1	−95	5.7
Stabaxol P (1%) + CaHA (1%) + R50 (1%)	0.85	2.7	−98	5.6
R50 (2%) + CaHA (2%)	0.81	1.3	−92	7.7
R83 (2%) + CaHA (2%)	0.77	−1.2	−81	3.0
ERL 4221 (2%)	0.70	10.7	−72	1.8
ERL 4221 (1%) + CaHA (1%) + R50 (1%)	0.77	3.3	−86	6.7
ERL 4221 (1%) + CaHA (1%) + R83 (1%)	0.75	5.7	−84	4.1
ERL 4221 (1%) + Naugard 445 (1%)	0.71	14.0	−68	1.0
DEN 444 (2%)	0.71	13.2	−79	2.2
Limonene monoxide (2%)	0.68	14.0	−74	1.0
Ethylcellulose (1%)	0.62	19.0	−68	2.1
Hydroxypropylcellulose (1%)	0.62	21.0	−65	1.8
Irganox 1425 (2%)	0.57	25.2	−62.8	–
Naugard 445 (2%)	0.48	41.2	−47.9	–
Stabaxol P (2%)	0.38	53.0	−37.3	–

[a] **Notation**: Stabaxol P is 2,2′,6,6′-tetraisopropyldiphenylcarbodiimide, CaHA is hydroxyapatite, R50, R83 are β-diketones, ERL 4221, DEN 444 are epoxides, Naugard 445 is alkylated diphenylamine, Irganox 1425 is calcium bis[monoethyl(3,5-di-*tert*-butyl-4-hydroxybenzyl)]phosphonate.

The photodestruction of the $CH_2=CH_2/CO$ and $MeCH=CH_2/CO$ copolymers has been studied under anaerobic conditions. The rate of photooxidation at room temperature does not depend on the palladium content in the copolymer. The photostability of the $CO/MeCH=CH_2$ copolymer was found to be lower than that of the $CO/CH_2=CH_2$ copolymer due to oxidation reactions proceeding by the Norrish-I and Norrish-II mechanisms.[246] ($CO/CH_2=CH_2$ is oxidised only according to the Norrish-I mechanism.[247])

The photolysis and γ-radiolysis of the $CO/CH_2=CH_2$ copolymers and the subsequent thermal and chemical transformations of samples following an increase in the irradiation temperature (from

¶ Traces of transition metal ions are often used as catalysts for the destruction of polymeric materials both in the presence and in the absence of oxygen.[241]

−196 to 27 °C) have been studied.[248, 249] The main reaction in the photolysis is the rupture of the polymer chain to give alkyl and acyl radicals with the quantum yields $\varphi_R = 2 \times 10^{-4}$ at −196 °C and $\varphi_R = 2 \times 10^{-3}$ at 27 °C. The major products formed in the copolymer photolysis at 27 °C include ethane, ethylene and carbon monoxide. Radiolysis of the copolymer at −196 °C affords the same alkyl and acyl radicals as the photolysis. At a dose of $\leqslant 50$ kGy, these radicals account for ~50% of all paramagnetic centres.

The biodegradation of the $CO/CH_2=CH_2$ copolymer has been studied and the results have been compared with the data on biodegradation of PE and cellophane.[250] In terms of the susceptibility to biodestruction, the copolymer in question occupies an intermediate position between PE and cellophane.

The systematic research into the thermodynamic characteristics of alternating copolymers has been started. Using adiabatic vacuum and dynamic calorimetry, the temperature dependence of the heat capacity was determined and the temperatures and enthalpies of the physical transformations of carbon monoxide copolymers with ethylene,[251] propylene,[252] styrene,[253] *endo*-dicyclopentadiene[254] and norbornadiene† were found.

Of high practical value is the study of blends of polyketones with various polymers (as compatibilisers). It was found that the propylene–carbon monoxide copolymer forms homogeneous transparent blends with the styrene–acrylonitrile (SAN) copolymer containing 37 mass % of acrylonitrile.[86] As the content of SAN increases from 20 mass % to 90 mass %, the glass transition temperature increases from ~30 to 100 °C, which is in good agreement with the dependence of T_g on the composition of the polymer blend described by the Fox equation. However, blending of the propylene–carbon monoxide copolymer with polystyrene or the styrene–maleic anhydride copolymer gives brittle heterogeneous blends. The physicomechanical properties of the initial and glass fibre reinforced (30 mass %) ethylene–carbon monoxide–propylene terpolymer (with a propylene content of 5 mass %–6 mass %) obtained by injection moulding with controlled drawing have been compared.[255]

A TGA study of the thermal decomposition of syndiotactic carbon monoxide–styrene copolymer has shown that the process occurs in three stages. The activation energy of the fastest second stage of thermal decomposition, equal to 31 kcal mol^{-1}, is lower than the activation energy of the thermal decomposition of polystyrene (PS) (55 kcal mol^{-1}), which is indicative of a lower stability of $CO/CH_2=CHPh$. Photolysis of the copolymer entails a decrease in its molecular mass and loss of the sample mass. The macroradicals formed in the photolysis of the copolymer initiate polymerisation of methyl methacrylate (MMA) to give the CO–styrene block copolymer and poly(methyl methacrylate).[177] Photolysis of samples of the carbon monoxide–4-(*tert*-butyl)styrene copolymer (M_n = 44 000–53 000, $M_w : M_n$ = 1.2–1.4), in particular, a sample containing ^{13}CO, has been studied by time-resolved EPR spectroscopy at two frequencies, in the X (9.5 GHz) and Q (35.1 GHz) ranges.[97]

3. Mechanical and other properties of copolyketones

At present, the properties of terpolymers ($CH_2=CH_2/CO/MeCH=CH_2$) have been studied most comprehensively; the properties of alternating copolymers ($CH_2=CH_2/CO$) traded under the name Carilon (Shell Chemical Co) or Ketoneks (British Polymer Co) have been less studied.

Films of the $CH_2=CH_2/CO/MeCH=CH_2$ terpolymer containing 0 mol.%–14.6 mol.% of propylene before and after 3–6-fold drawing have been studied by X-ray diffraction and DSC. Drawing was found to promote the formation of units of the copolymer α-form; the lower the drawing velocity, the greater the number of the α-form units.[256] As the content of propylene in the copolymer increases from 0 to 14.6%, the temperature of the α → β transition decreases from 91 to 60 °C and simultaneously, the melting peak is broadened.

The effect of the temperature (0–80 °C) on the mechanical strength (tensile strength and the fracture pattern in uniaxial and biaxial tests) of solid and hollow cylindrical specimens of the $CH_2=CH_2/CO/MeCH=CH_2$ terpolymer containing 6 mol.% of propylene was studied. The data obtained in this study were compared with the results of calculations for a model anisotropic material.[257, 258]

Karttunen and Lesser[259] have studied the effect of extrusion conditions (shear rate, cooling rate) during moulding of hollow cylindrical specimens on the mechanical properties of the ethylene–carbon monoxide–propylene terpolymer containing 6 mol.% of propylene (T_m = 225 °C, T_g = 12 °C, molecular mass 1×10^5, degree of crystallinity 33%–35%, density 1.24 g cm^{-3}). The methods used included DSC, dynamic mechanical analysis (DMTA), IR spectroscopy, wide-angle X-ray diffraction and electron microscopy. The crystal structure and the morphology of this copolymer were studied by X-ray diffraction, DSC and TEM. It was found that T_m of the copolymer linearly decreases with an increase in the propylene content from 6 to 10 mol.%. Further increase in the content of propylene in the copolymer (10%–16%) barely influences its T_m.[260] The obtained results are in line with the data of other publications.[261, 262]

High-strength (1.1 GPa) and high-modulus (13 GPa) fibres of four specimens (I–IV) of the $CH_2=CH_2/CO/MeCH=CH_2$ terpolymer were produced by extrusion at temperatures of 250, 255 and 266 °C.

Specimen	$[C_3H_6]$ /mol.%	M_w	$M_w : M_n$
I	6.0	4×10^4	2.84
II	6.0	6×10^4	3.00
III	3.5	6×10^4	3.10
IV	0	4×10^4	3.10

The structure and morphology of the resulting fibres were studied by DSC, wide- and small-angle X-ray diffraction and scanning electron microscopy. It was found that in the $CH_2=CH_2/CO/MeCH=CH_2$ terpolymers, the crystalline phase is always represented by the β-form. In the $CH_2=CH_2/CO$ copolymer, depending on the cooling rate, α-form is also present in addition to the major β-form.[263] The dependences of the physicomechanical properties, the degree of crystallinity and T_m of the ethylene–CO–propylene terpolymers on the amount of propylene in specimens I–IV are shown in Figs 6, 7.

The morphological features and the mechanisms of crack formation in specimens of the $CH_2=CH_2/CO/MeCH=CH_2$ terpolymer (Carilon DP P1000) with a degree of crystallinity of

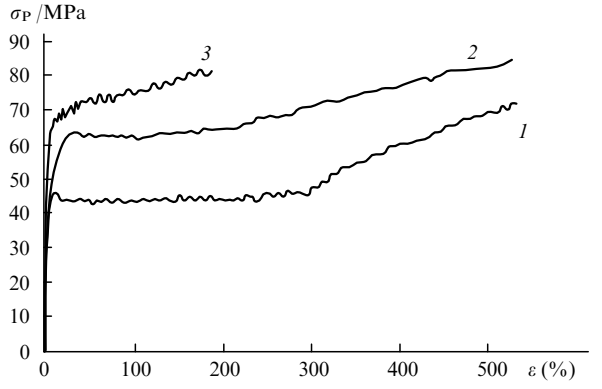


Figure 6. Load–elongation curve for specimens I (curve *1*), III (curve *2*) and IV (curve *3*).

† N N Smirnova, T A Bykova, T G Kulagina, L V Nikishchenkova, G P Belov, E V Novikova *Izv. Akad. Nauk, Ser. Khim.* (2004) (in the press) [*Russ. Chem. Bull., Int. Ed. (Engl. Transl.)*].

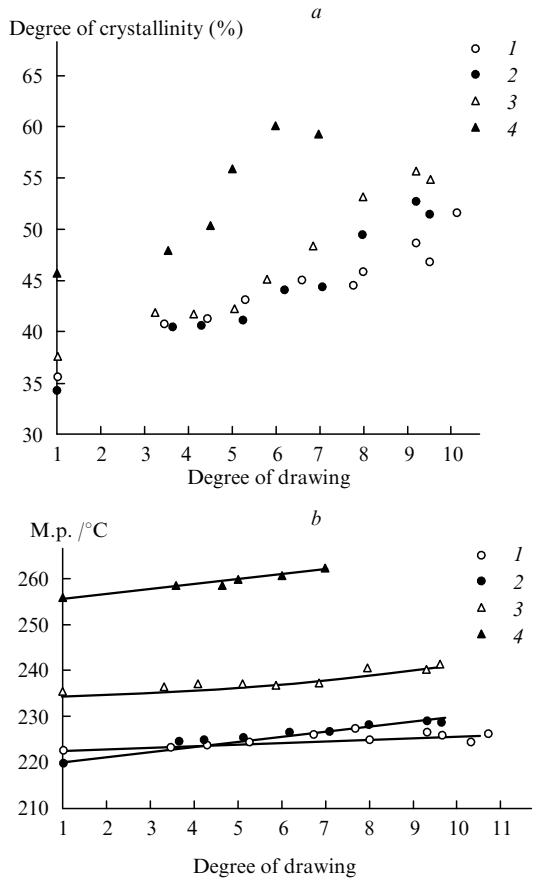


Figure 7. Degree of crystallinity (*a*) and T_m (*b*) of samples I–IV (points *1–4*, respectively) *vs.* degree of drawing.

38% obtained by injection moulding and mould pressing were studied by DSC, DMTA and optical microscopy.[264]

Studies of such copolymers carried out by thermoelastometry in the temperature range of 13–54 °C at pressures of 30–100 MPa have shown[265] that thermodynamic parameters of the terpolymers (specific volumes, thermal expansion and compression coefficients) are deteriorated with an increase in the content of the $(-C_2H_4CO-)_n$ blocks, whereas the thermal characteristics (heat and temperature conductivity, specific heat capacity) virtually do not depend on the polymer composition. The bell-shaped dependences of the Newton viscosity[266] and diamagnetic susceptibility[267] on the content of the $(-C_2H_4CO-)_n$ blocks in the ethylene–carbon monoxide–propylene terpolymer was described within the bounds of the classical copolymerisation theory taking the strictly alternating $CH_2=CH_2/CO$ and $MeCH=CH_2/CO$ copolymers as 'virtual homopolymers' and the strictly alternating $CH_2=CH_2/CO/MeCH=CH_2$ terpolymer, as a 'virtual copolymer.'

According to X-ray diffraction data,[266–268] the ethylene–CO–propylene terpolymers are amorphous to X-rays at room temperature; however, in the temperature range above the glass transition temperature ($T_g \approx 17$ °C), the heat capacity curves contain sections corresponding to slight endothermic effects. In the same temperature range, the intensity of the dielectric relaxation does not decrease with temperature but, conversely, increases. Moreover, hysteresis effects were found for the viscoelastic characteristics of the terpolymers in the melt on heating the specimens to 227 °C with subsequent cooling to 127 °C.[268] This set of data indicates that long-term storage of the terpolymers at room temperature promotes the formation of a network of $CH_2=CH_2/CO$ nanocrystallines with runs through the continuous phase of the noncrystalline $MeCH=CH_2/CO$ blocks. The low values of the shape parameter from the Kolmogorov–Avrami equation in combination with exceptionally long half-periods of nanocrystallisation[269] are consistent with the views stating that nanocrystallites are formed through lateral aggregation of the $CH_2=CH_2/CO$ blocks, which is retarded by the continuous $MeCH=CH_2/CO$ phase.

It was found that the activation energy of the relaxation processes at low temperatures equals 14 kcal mol^{-1}, while at elevated temperatures, this value is 38–61 kcal mol^{-1}. Young's modulus for the $CH_2=CH_2/CO/MeCH=CH_2$ terpolymer containing ~50% of the $-C_2H_4CO-$ units is three orders of magnitude lower than that of the $CH_2=CH_2/CO$ copolymer (1.6 GPa). As the content of the $-C_2H_4CO-$ units in the terpolymer increases, its melting heat increases, while T_g decreases from 22 °C (for the $MeCH=CH_2/CO$ copolymer) to 3 °C (for the terpolymer containing 80 mass % of the $-C_2H_4CO-$ units).[269]

Hollmann *et al.*[270] studied the dielectric (in the frequency range of 10^{-1}–10^6 Hz) and mechanical properties of terpolymers (with a content of the $-C_2H_4CO-$ units ranging from 0 mass % to 80 mass % and a molecular mass of 12×10^4–22.8×10^4) and determined their glass transition and melting temperatures. The structural changes taking place in the $CH_2=CH_2/CO/MeCH=CH_2$ specimens containing 47% and 69% of $-C_2H_4CO-$ units upon deformation were investigated by X-ray diffraction and DSC. It was shown that great reversible deformations are mainly due to the amorphous component of the terpolymer.[271]

The effect of the polyketone molecular mass and the conditions of surface formation (for example, during press moulding) on the energy characteristics of the surface has been studied.‡

Good adhesion of the alternating ethylene–CO copolymer to organic and inorganic materials allows the use of this copolymer in the production of composite materials without special adhesives. The properties of unfilled and glass fibre reinforced $CH_2=CH_2/CO$ copolymer are presented in Table 10. The influence of various types of surface treatment of glass fibre on the mechanical properties of the composites has been studied.§

Table 10. Properties of alternating $CO/CH_2=CH_2$ copolymer.[11]

Property	Unfilled copolymer	Glass fibre filled copolymer (30 mass %)
Density /g cm^{-3}	1.24	1.45
Melt index (240 °C, 2.16 kg) /g (10 min)$^{-1}$	6	5
Tensile strength /MPa	55	120
Elongation at rupture (%)	350	3
Vika softening temperature (5 kg) /°C	205	215
Shrinkage (%)	2	0.3–0.7

Owing to the specific structure of the polymer chain and the crystallinity (30%–50%), polyketones are not hydrolysed. Unlike other polymers such as PA, PC and polyesters, they are stable against aqueous solutions of weak acids and inorganic salts (Table 11).[272]

‡ S A Bogdanova, O R Shashkina, G P Belov, O N Golodkov, V P Barabanov, I A Starostina *Vysokomol. Soedin.* (2004) (in the press) [*Polym. Sci. (Engl. Transl.)*].

§ Yu N Smirnov, G P Belov, V V Barelko, O N Golodkov, E V Novikova, A D Pomogailo, K E Danilov *Plast. Massy*, (2004) (in the press).

Table 11. Effect of different media on the tensile strength of the alternating $CO/CH_2=CH_2$ copolymer [for comparison, data for polyamide (PA) are given].[272]

Medium	σ_p /MPa	
	polyketone	PA
Control run at 50% moisture content	57.7	57.2
Water	59.2	33.1
Sea water	60.0	33.1
Aqueous solutions		
MeCOOH (5 mass %)	57.9	33.8
$CaCl_2$ (5 mass %)	60.0	33.8
Antifreeze	59.2	35.8
H_2SO_4 (30 mass %)	59.3	dissolves
$ZnCl_2$ (50 mass %)	46.2	dissolves
HCl (10 mass %)	64.7	dissolves
NaOH (1 mass %)	58.6	28.2
NaOH (10 mass %)	60.0	28.9

Long-term keeping of polyketone in alcohols, ethyl acetate, benzene and methyl ethyl ketone has no effect on its properties, while keeping in chlorine-containing (trichloroethylene, dichloromethane, chloroform) and polar aprotic solvents (DMSO, *N*-methylpyrrolidone) results in swelling of the polymer (the gain in the mass is 8% to 35%) and a decrease in its strength (by up to 30%). The high hydrolytic and chemical stability of polyketone is combined with good barrier properties against hydrocarbons, oxygen and carbon dioxide (Table 12). Data on the permeability, diffusion coefficients and solubility of three gases (helium, oxygen and carbon dioxide) in the ethylene–propylene–carbon monoxide terpolymer (0.93 : 0.07 : 1) have been reported.[273]

The high crystallisation rate of polyketone ensures a short duration of the moulding cycle for articles based on this polymer (see Table 12) and eliminates the necessity for further conditioning, which substantially reduces the production costs.

V. Modification of polyketones

The chemical modification of polyketones at the carbonyl group allows one to create new classes of chiral and achiral polymers, which can serve themselves as the starting materials for the development of new low- and high-molecular-mass compounds *via* reactions in polymer chains.

The achiral $CH_2=CH_2/CO$ copolymer and atactic $MeCH=CH_2/CO$ copolymer can be converted into polyfurans,[275] polythiophenes,[275] polyoximes,[276–278] polycyanohydrins[1,276] and polyalcohols.[1,216,275–283] The reduction of isotactic $MeCH=CH_2/CO$ copolymer with lithium aluminium hydride gave polyalcohol whose stereochemistry has not been determined at that moment.[83] Later,[161] using tetrabutylammonium tetrahydroborate, the isotactic $MeCH=CH_2/CO$ copolymer was quantitatively reduced into the polyalcohol and the enantiomers present were identified by ^{13}C NMR spectroscopy ($S:R = 70:30$).

Other derivatives obtained include polyacetylenes,[284,285] polyamines,[1,286,287] poly(α-hydroxyphosphonic acids),[1,288] polythiols,[1,289] polyamides,[1,290] polyoximes,[1,290] polyketoesters,[291] polyketoximes,[278] dioxolane-containing derivatives,[292] nitrogen- and sulfur-containing heterocyclic derivatives of polyketone[293,294] and polymeric 1,2-diketones.[295] The molecular-topological structure of a polyketone modified by amines was studied.¶

VI. Applications

The alternating copolymers of olefins and CO can be used to manufacture high-strength fibres with a maximum strength of 3.8–3.9 GPa, which retain 85%–90% of their strength even at 140 °C. Due to the high polarity, these fibres possess a lower creep† than PE or PETF fibres. Highly oriented fibres have an elongation at rupture of 4%–5% and an initial modulus of 50–55 GPa.[216]

High-molecular-weight copolymers ($CO/MeCH=CH_2$) and terpolymers ($CH_2=CH_2/CO/MeCH=CH_2$) with the composition $(C_2H_4/CO):(C_3H_6/CO) = 1:1$ possess high elasticity and resemble poly(vinyl chloride) (PVC) in mechanical properties. As regards their barrier properties (N_2, O_2 and CO_2 permeability), they occupy an intermediate position between high-density polyethylene and PVC and in terms of water permeability, they are similar to polyurethane. Recently, the preparation of low-molecular-weight $CH_2=CH_2/CO/MeCH=CH_2$ terpolymers with $M_n = (1.5–5.0)\times10^3$ traded under the name Carilite Oligomer has been reported. These terpolymers can be cross-linked under the action of polyfunctional amines or converted into polyaminopyrroles by the reaction with asymmetrical diamines.[93]

As the chain length in the α-olefin increases, the glass transition temperature of α-olefin–carbon monoxide copolymers decreases from 25 °C (for $CO/MeCH=CH_2$) to −60 °C (for dodec-1-ene–carbon monoxide) and the contact angle increases from 65° (for $CO/MeCH=CH_2$) to 110° (for oct-1-ene–carbon monoxide); on further increase in the chain length in the α-olefin ($>C_6$), the contact angle almost does not change. In propylene–carbon monoxide–higher α-olefin terpolymerisation, a decrease

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† Creep is building-up of the deformation in the course of time under a constant load.

Table 12. Permeability with respect to O_2, CO_2 and moisture and other characteristics of the polymers used for packing foodstuffs.[274]

Polymer[a]	Permeability			Extrudability	Crystallisation rate	Duration of moulding
	O_2	CO_2	90% moisture (38 °C)			
PA (amorphous)	4–19	39	59–79	poor	see[b]	medium
PA (crystalline)	–	–	98	–	–	–
PETP (amorphous)	31–97	78–295	20–28	medium	see[b]	high
PETP (crystalline)	8.9–19	39–58	4.7–4.9	good	low	very high
PP	1170	3100	2.08	"	high	low
PC	777–970	1170	1239	medium	see[b]	medium
$CH_2=CH_2/CO/MeCH=CH_2$	8–19	93	12–47	very good	high	very low
$CH_2=CH_2/CO$	8–19	93	44–67	the same	"	the same

[a] Abbreviations: PA is polyamide, PETP is poly(ethylene terephthalate), PP is polypropylene, PC is polycarbonate. [b] Amorphous polymer.

in T_g can be attained by increasing the content of the higher α-olefin.

The ever-growing demand for thermally stable and easily processable polymers having specific gas permeability properties is due to the increased requirements for packaging of foodstuffs. The alternating copolymers of olefins and carbon monoxide are especially attractive in this respect because they are thermally and chemically stable. They are distinguished by good barrier characteristics (with respect to gases) not inferior to nylon or PETP; good compatibility with other polymeric packaging materials (*e.g.*, nylon, PC, PVC). The combination of high chemical stability and low permeability makes polyketones attractive also for the use as protective coatings and chemical containers especially in those cases where it is necessary to prevent the escape of organic compounds into the environment. Polyketones can be used for the manufacture of pipes and hoses meant for transfer of chemicals. In this case, in addition to chemical stability and low permeability, the polymers should possess high mechanical and abrasive strengths.

Due to the high adhesion to organic and inorganic materials, alternating copolymers can be used to design structural materials with high mechanical strength. Due to the low friction coefficient, high strength and relatively low specific gravity, these polymers can be advised for the use in mechanical engineering (gear units and other similar structures).

Low-molecular-mass polyketones are of interest for preparative small-tonnage chemistry. For example, ethyl vinyl ketone and 1,4-diketones can be used for the production of substituted cyclopentanones, which are structural elements of natural aromatic compounds possessing the jasmine odour.[296]

* * *

This review is an attempt to survey and analyse the key aspects of a new line of research promising for both scientific and practical purposes, namely, the synthesis of alternating copolymers and terpolymers of carbon monoxide with various monomers. The attention is focussed on the search of new Pd(II), Ni(II), Cu(II) and Ru(II) catalysts and new ligands and modification of known catalysts used in the synthesis of alternating copolymers based on carbon monoxide and olefins, dienes, styrene and their derivatives. Some properties and applications of the copolymers are considered.

The alternating terpolymers based on carbon monoxide, ethylene and propylene (so-called aliphatic polyketones) manufactured in industry refer to a new class of structural polymers that combine high melting points (220–260 °C), good adhesion to organic and inorganic materials, high strength, high chemical stability and so on.

It is clear that the research and industrial projects executed during the last 10–15 years (after the beginning of studies of the effective copolymerisation of carbon monoxide with ethylene) represent only an early stage of the comprehensive investigation of the alternating copolymerisation of CO with various monomers.

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