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POLIMERY

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WITOLD KURAN
Warsaw University of Technology
Chemistry Department
Division of Polymer Synthesis & Processing
3, Noakowskiego Street, 00-664 Warsaw

Chain- and step-growth polymerizations mediated by late transition metal complexes*)

Summary — A review with 86 references covering chain-growth (insertion, metathesis) polymerization and step-growth (metathesis polycondensation of acyclic dienes, Heck-type polycondensation of haloarene derivatives, *etc.*) polymerization, promoted by catalysts based on late transition metals and each dicsussed in relation to monomer and catalyst type. The nature of catalyst's active sites is described and polymerization mechanisms are discussed. The most representative Pd-based catalysts are duly emphasized. The chain- and the step-growth models of propagation of polymerization are intercompared in terms of the oxidation state of the Pd species in the catalysts. The former mode keeps the oxidation state of palladium [Pd(II)] unaffected; the latter mode allows the oxidation state to vary from Pd(II) to Pd(0) (and back).

Key words: chain polymerization, step-growth polymerization, late transition metal complexes, palladium-based catalysts.

Ziegler—Natta catalysts based on early transition metal complexes are commonly known to be unique promoters for the coordination polymerization and copolymerization of ethylene and α-olefins, non-conjugated and conjugated diolefins, vinylaromatic compounds, cycloolefins and acetylenic monomers [1—5]. These catalysts greatly expand the range and versatility of technically feasible types of polymeric materials derived from addition polymerizations of unsaturated hydrocarbon monomers. Again, mention should be made of coordination copolymerization of olefins with functionalized olefins or polar monomers [6] which might afford copolymers exhibiting some advantageous properties superior to those characteristic of non-polar polyolefins.

Recent years have featured a dramatic progress in the design and application of organometallic coordination polymerization catalysts. Especially group 4 (Ti, Zr, Hf) metallocenes have been at the forefront of polyolefin developments. However, driven by industry's desire for more robust, functional group tolerant catalysts and for a greater and greater control over the resultant polymeric products, the search for new catalyst families has grown apace. Some most significant developments include late transition metal-based catalysts.

Late transition metal-based catalysts differ from most of the common coordination catalysts and usually igno-

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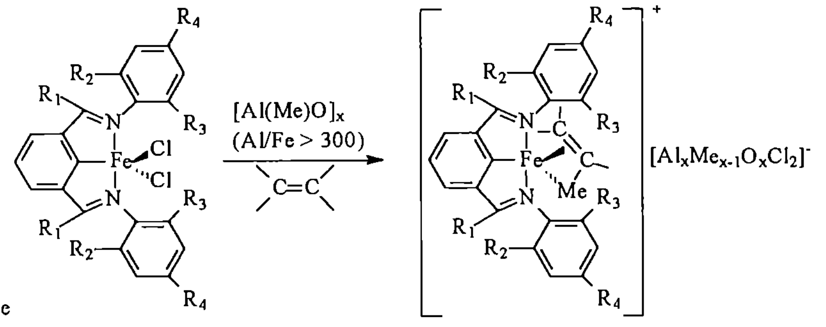


(1)

R_1 = H, Me
$R_2 = R_3$ = *i*-Pr, R_4 = H
$R_2 = R_3$ = Me, R_4 = H
$R_2 = R_4$ = Me, R_3 = H

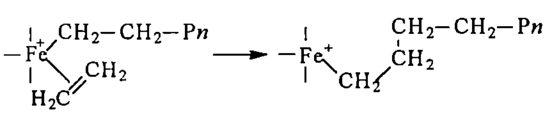
re the presence of functional polar groups or heteroatoms in the monomer molecule (and/or the polymerization medium) as the moieties which might deactivate catalyst's active sites. These catalysts appeared to be capable of promoting chain-growth addition polymerizations [7—11] as well as step-growth condensation polymerizations [12—14] of hydrocarbon and functionalized unsaturated hydrocarbon monomers.

CHAIN-GROWTH POLYMERIZATION

Insertion polymerization

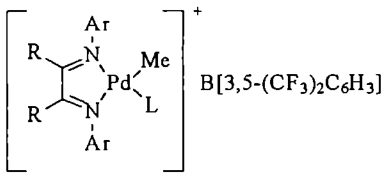
Recently, a new catalyst family has been described [15, 16], based on Fe(II) and Co(II) complexes having neutral 6-electron donor 2,6-*bis*(imino)pyridine ligands which are activated with methylaluminoxane (eqn. 1).

The cationic 14 electron Fe(II) species formed according to eqn. (1) shows an exceptionally high activity in the polymerization of ethylene (16-electron Fe(II) species with coordinated olefin), higher even than that of a metallocene catalyst under comparable conditions, and, in addition with a substantially isotactic microstructure of polypropylene (induced through chain-end stereocontrol). As a mechanism of olefin polymerization over an iron-*bis*-iminepyridine catalyst, the *cis*-insertion of coordinated alkene into the Fe-C bond has been postulated (eqn. 2) [17], analogously to the polymerizations run in the presence of other olefin polymerization catalysts.



(2)

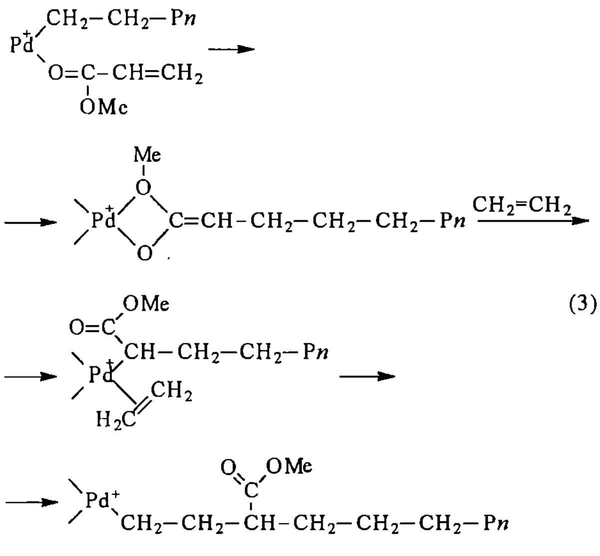
The cationic Pd(II) and Ni(II) complexes bearing bulky α-diimine ligands were the first examples of late transition metal-based catalysts capable of polymerizing ethylene and higher α-olefins to high-molecular-weight polymers [18] as well as able to copolymerize ethylene and α-olefins with polar comonomers like methyl acrylate in a random manner (1) [19].



(I)

R = H, Me; Ar = 2,6-(*i*-Pr)$_2C_6H_3$; L = Et_2O, MeCN

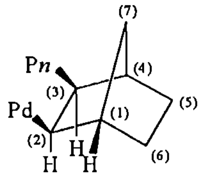
The insertion mechanism operates in the case of olefin polymerization. The propagation reaction of methyl acrylate during the copolymerization involves 2,1-insertion of the acrylate and chelate ring expansion, followed by insertion of ethylene unit (eqn. 3).



(3)

Late transition metal-based catalysts are known to promote the ring-retaining polymerization of cycloolefins.

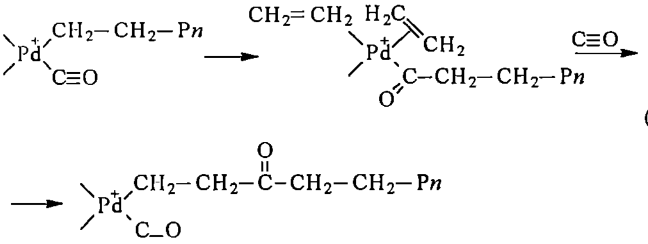
Cationic Pd(II) complexes with weakly coordinating ligands, *e.g.* $[Pd(EtCN)_4][BF_4]_2$, used as catalysts for polymerizations of strained bicyclic olefins like norbornene, have allowed to prepare an atactic high-molecular-weight polymer: poly(2,3-bicyclo[2.2.1]hept-2-ene) [8]. The polymerization of norbornene exhibits the features of a "living" process. It occurs *via* the *cis*-insertion involving predominantly the *exo* face of the monomer.



(II)

Decomposition of the Pd-M-Pn species *via* β-hydrogen elimination is unfavorable, since both of H_β atoms, H_3 and H_1, are not easily accessible for the Pd bond-forming process. Suppression of β-hydrogen abstraction is a prerequisite for the monomer undergoing *cis*-insertion polymerization leading, in this case, to poly(2,3-bicyclo[2.2.1]hept-2-ene) (II) [8].

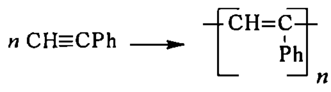
Cationic Pd(II) complexes like $[Pd(PPh_3)_n(MeCN)_{4-n}][BF_4]_2$ (n = 1, 2, 3) catalyze the alternating copolymerization of ethylene and carbon monoxide leading to high-molecular-weight polyketones (eqn. 4) [9, 10].



(4)

The Pd-based catalyst promotes rapid dimerization of ethylene in the absence of carbon monoxide, indicating β-hydrogen abstraction [20]. If carbon monoxide is present, an alternating insertion of ethylene and carbon monoxide occurs; the competing β-hydrogen abstraction is suppressed by the faster insertion of CO into a Pd-C bond.

Late transition metal catalysts, especially Rh complexes such as *e.g.* $(norbornadiene)_2RhCl_2$ [21, 22] promote polymerization of acetylene and non-crowded terminal alkynes like phenylacetylene (eqn. 5).

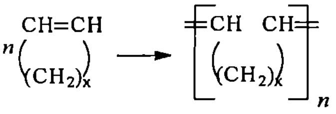


$$n\,CH{\equiv}CPh \longrightarrow \left[CH{=}\underset{Ph}{C} \right]_n \qquad (5)$$

The mechanism which operates in those polymerizations involves *cis*-insertion of the monomer (coordinating at the cationic metal species) into the Rh-C bond.

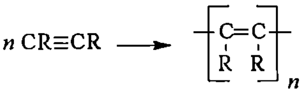
Metathesis polymerization

It is commonly known [11] that late transition metal complexes such as Mo, W (group 6) and Ru (group 8), promote ring-opening polymerization of cycloolefins (eqn. 6).



(6)

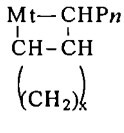
Late transition metal-based catalysts are also active in the metathesis polymerization of mono alkynes with bulky substituents and even disubstituted acetylenes (eqn. 7) [23—27].



$$n\,CR{\equiv}CR \longrightarrow \left[\underset{R}{C}{=}\underset{R}{C} \right]_n \qquad (7)$$

Such a polymerization proceeds according to the metathesis mechanism involving metal alkylidene and metallacyclobutane species:

$$Mt{=}CH-(CH_2)_x-CH{=}CHPn \qquad (III)$$



(IV)

In late transition metal-catalyzed chain-growth polymerizations, irrespectively of the insertion or the trans-alkylidenation mechanism, the conservation of the oxidation state of the metal is typical.

STEP-GROWTH POLYMERIZATION

Strikingly, relatively little attention has been paid to polymers which may be obtained by the coordination polycondensation of hydrocarbon and functionalized unsaturated hydrocarbon monomers. The polycondensations catalyzed by transition metal complexes, especially those involving the acyclic diene metathesis and the Heck coupling reaction, have been shown to be versatile methods for synthesizing new high-molecular-weight polymers with well-defined structures and functionalities. It is to be noted that catalysts capable of promoting such step-growth polymerizations differ from most common coordination catalysts and usually ignore the presence of functional polar groups or heteroatoms in the monomer molecule as the moieties which might deactivate catalyst's active sites. In many cases these catalysts are also useful for inducing chain-growth polymerization of hydrocarbon monomers such as ring-opening metathesis polymerization of cycloolefins (polyalkenamers derived from this polymerization are commercially available) and copolymerization of hydrocarbon and non-hydrocarbon monomers such as alternating copolymerization of ethylene and carbon monoxide (polyketones derived from this copolymerization are commercially available). The most representative coordination catalysts capable of promoting both the chain-growth and the step-growth polymerizations of various monomers are those based on molybdenum, tungsten and ruthenium complexes (ring-opening metathesis polymerization of cycloolefins, and acyclic diene metathesis polycondensation) and on palladium complexes (ethylene/carbon monoxide copolymerization and Heck coupling type polycondensation).

Step-growth reactions involving homo- and hetero-polycondensation of various bifunctional unsaturated monomers in the presence of late transition metal-based coordination catalysts have appeared to be very useful synthetic tools to prepare low- and high-molecular-weight polymers with an unsaturation in the polymer backbone. These reactions lead to unsaturated hydrocarbon and non-hydrocarbon polymers in which polymeric chains are formed by carbon-carbon [12—14, 28] and carbon-heteroatom [14, 29] couplings, respectively.

Essentially, two types of bifunctional unsaturated compounds show the capability of being condensed in high yield, *via* a late transition metal-catalyzed carbon-carbon coupling reaction, into their requisite generic high-molecular weight polymers plus a small molecule: non-conjugated acylic dialkenes and haloaromatic derivatives. The former monomers undergo metathesis polycondensation whereas the latter condense *via* the Heck-type and related coupling reactions.

High-molecular-weight polymers can also be prepared by a step-growth polymerization of acyclic and cyclic dialkynes with monofunctional monomers such as heterocumulenes, hetero-unsaturated monomers, and carbene-like monomers; these polyreactions proceed without the formation of any low-molecular-weight by-products (coordination polyaddition) [14].

Metathesis polycondensation of acyclic dienes

Acyclic dienes undergo metathesis polycondensation (*acyclic diene metathesis* — *"admet"*) to poly(alkylene)s in the presence of group 6 (Mo, W) and group 8 (Rh) metal alkylidene complexes as catalysts (eqn. 8) [30].

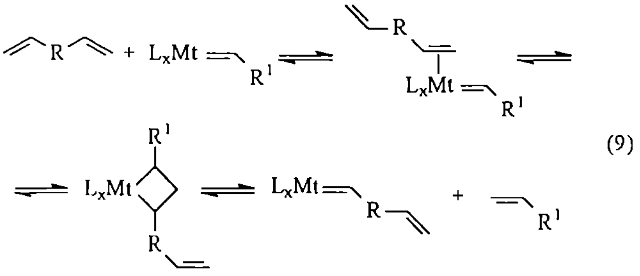
$$n\,CH_2{=}CH{-}R{-}CH{=}CH_2 \rightleftharpoons$$
$$\rightleftharpoons CH_2{=}\!\left[CH{-}R{-}CH{=}\right]_n\!CH_2 + (n-1)\,CH_2{=}CH_2 \qquad (8)$$

In the metathesis polycondensation terminal dienes (α,ω-dialkenes), $CH_2{=}CH{-}(CH_2)_x{-}CH{=}CH_2$ (x = 1—7), and divinylarenes $CH_2{=}CH{-}Ar{-}CH{=}CH_2$, are the monomers preferred for both entropic and steric considerations. The metathesis of terminal diene units yields ethylene as a small molecule: this is initially removed from the reaction medium by simply passing into the gas phase and can be completely removed from the polycondensation system by evacuation (under reduced pressure). The release and removal of a small condensate molecule is the driving force for the acyclic diene metathesis. The polycondensation is performed preferably under bulk conditions (no solvent used), since the acyclic diene metathesis is thermally neutral and there is no need to remove the heat of the reaction, in contrast to the exothermic cyclic olefin ring-opening metathesis polymerization.

Metathesis polycondensation of acyclic dienes has not been successful with conventional catalysts used for ring-opening metathesis polymerization of cycloolefins, because Lewis acids which are usually present give rise to adverse side reactions [12, 31]. Only Lewis acid-free well-defined catalysts have been successfully applied in the acyclic diene metathesis polycondensation; the key of the success has been to choose the catalysts that obviate pathways not involving metathesis mechanism [30, 32, 33].

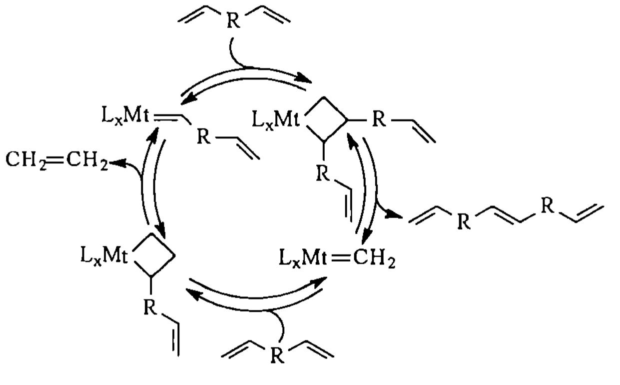
Wagener *et al.* [12, 32] were the first to convert acyclic α,ω-diene (1,9-decadiene) by using an acid-free metal alkylidene catalyst into a high-molecular weight polymer, poly(1-octenylene), with a number-average molecular weight of *ca.* 50 000 and polydispersity of 2.0.

The acyclic diene metathesis is peculiar in that it proceeds as a typical equilibrium condensation polymerization process, but is governed by the mechanism characterized by the occurrence of metal carbene and metallacyclobutane species; these species have been found to occur both in the ring-opening metathesis polymerization of cycloolefins and in the ring-closing metathesis of acyclic dienes [34, 35]. The initial step of the acyclic diene metathesis promoted by metal alkylidene ($L_xMt{=}CHR^1$) involves the formation of a π-complex between the olefin groups of the diene monomer and the metal, followed by the collapse to a corresponding metallacyclobutane ring [36]. In productive metathesis, this ring undergoes cleavage in such a monomer so as to place the metal center on the end of the monomer (eqn. 9).



(9)

The new metal alkylidene species, $L_xMt{=}CHRCH{=}CH_2$, initiates the polycondensation cycle which is illustrated in scheme 1 [37].

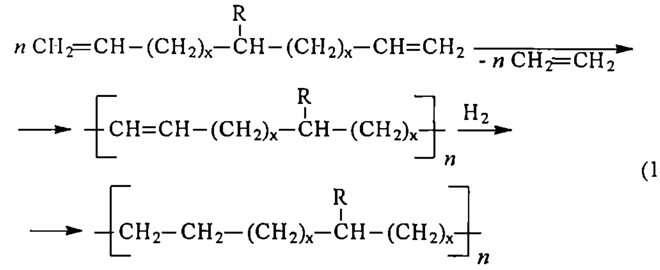


Scheme 1. The catalytic cycle for acyclic diene metathesis polycondensation

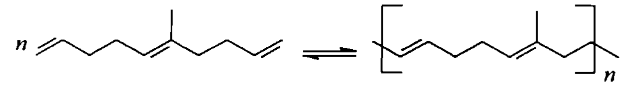
The polycondensation cycle is started in a way analogous to that shown in eqn. 9; one of the double bonds in a monomeric diene or in a polymer chain end forms a π-complex with the metal, which leads to another metallacyclobutane ring. In the next step, this ring collapses to form an internal olefin within a polymer chain and generates the true catalyst, a methylidene

$L_xMt{=}CH_2$, for the metathesis polycondensation. The cycle continues by the formation of a metallacyclobutane ring again *via* the same π complexation as described above. Cleavage of this metallacyclobutane ring evolves ethylene, and the cycle is repeated, with the polymer growing from a stepwise monomer in every cycle.

The catalyst and monomer development in acyclic diene metathesis remains the subject of interest directed on preparing high-molecular-weight polymers with a well-defined backbone from a variety of non-functionalized and functionalized dienes by easily accessible and less expensive means. It is possible now to produce both conjugated aliphatic and aliphatic-aromatic hydrocarbon polymers [37—40] and saturated hydrocarbon polymers, *e.g.* a strictly linear polyethylene [41] and a perfectly branched polyethylene (eqn. 10) [42] including those identical in structure with perfectly alternating copolymers [*e.g.* butadiene/isoprene (eqn. 11)] [40].



$$n\,CH_2{=}CH{-}(CH_2)_x{-}\overset{R}{CH}{-}(CH_2)_x{-}CH{=}CH_2 \xrightarrow[-\,n\,CH_2=CH_2]{} \left[CH{=}CH{-}(CH_2)_x{-}\overset{R}{CH}{-}(CH_2)_x\right]_n \xrightarrow{H_2} \left[CH_2{-}CH_2{-}(CH_2)_x{-}\overset{R}{CH}{-}(CH_2)_x\right]_n \qquad (10)$$



(11)

The technique illustrated by eqn. 10 gives control over of the number of methylene groups between the branching points as well as the length and the identity of the branch itself.

By applying acyclic diene monomers containing functional groups for the metathesis polycondensation, a wide variety of functionalized unsaturated and saturated high-molecular-weight polymers have been obtained; among them, polyethers [42—45], polythioethers [43], polyesters [46, 47], polycarbonates [48], polyketones [49], polysiloxanes [50, 51], polycarbosiloxanes [52], polycarbosilanes [53, 54], and polymers with a conjugated π system [55] deserve attention. It has also been possible to design a series of segmented functionalized copolymers by using, for the metathesis polycondensation, α,ω-dienyl telechelic oligomers containing functional groups such as those in alcohols, esters, carboxylic acids, and amides [56, 57].

Heck-type polycondensation of haloarene derivatives

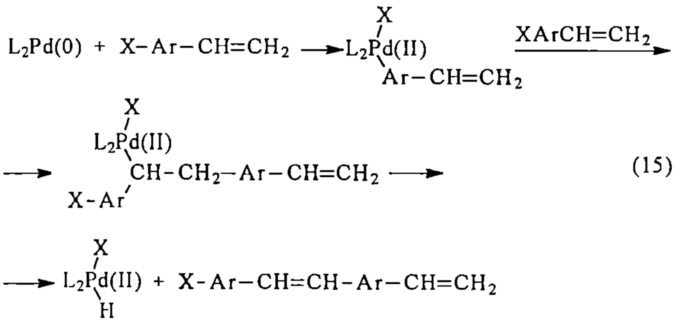
The transition metal-catalyzed coupling of aryl halides with alkenes (alkenylation of aromatic halides) is referred to as the Heck reaction [58]. Heitz *et al.* [59—63] were the first to utilize the Heck reaction to synthesize high-molecular-weight poly(arylene vinylene)s by self-coupling of *p*-bromostyrene (eqn. 12) or cross-coupling of 1,4-dibromobenzene with ethylene (eqn. 13) or with 1,4-divinylbenzene (eqn. 14).

$$n\,X{-}Ar{-}CH{=}CH_2 \longrightarrow X\left[Ar{-}CH{=}CH\right]_n H + (n\text{-}1)\,HX \qquad (12)$$

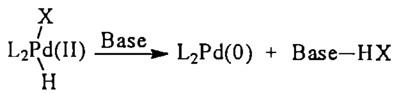
$$n\,X{-}Ar{-}X + n\,CH_2{=}CH_2 \longrightarrow X\left[Ar{-}CH{=}CH\right]_n H + (2n\text{-}1)\,HX \qquad (13)$$

$$n\,X{-}Ar^1{-}X + n\,CH_2{=}CH{-}Ar^2{-}CH{=}CH_2 \longrightarrow X\left[Ar^1{-}CH{=}CH{-}Ar^2{-}CH{=}CH\right]_n H + (2n\text{ - }1)\,HX \qquad (14)$$

The Heck type step-growth condensation polymerization is readily catalyzed by palladium-based catalysts, although nickel-based catalysts are effective, too. This coordination polycondensation requires the oxidation state of the metal (eqns. 15 and 16) to be changed in contrast with the chain-growth polymerization for which preservation of the oxidation state of the metal (*e.g.* Pd(II)) is typical [9].



$$L_2Pd(0) + X{-}Ar{-}CH{=}CH_2 \longrightarrow L_2\overset{X}{\underset{Ar-CH=CH_2}{Pd}}(II) \xrightarrow{XArCH=CH_2} L_2\overset{X}{Pd}(II){-}\underset{X-Ar}{CH}{-}CH_2{-}Ar{-}CH{=}CH_2 \longrightarrow L_2\overset{X}{\underset{H}{Pd}}(II) + X{-}Ar{-}CH{=}CH{-}Ar{-}CH{=}CH_2 \qquad (15)$$



$$L_2\overset{X}{\underset{H}{Pd}}(II) \xrightarrow{Base} L_2Pd(0) + Base{-}HX \qquad (16)$$

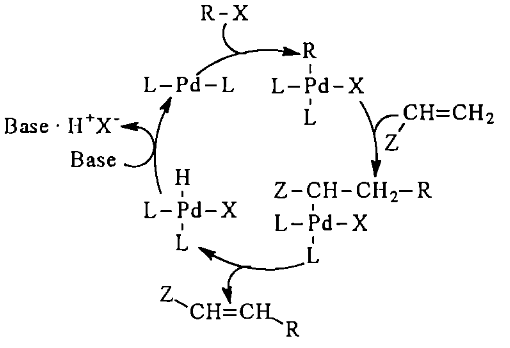
The first step in the Heck type catalytic reactions is the oxidative addition of the aryl halide to Pd(0) species to form an intermediate organopalladium halide constituting the Pd(II) species. This is followed by insertion of the olefinic bond and a subsequent β-hydrogen elimination with the formation of the polymeric chain (eqn. 15). Palladium species, $L_2(X)Pd{-}CH(ArX)CH_2ArCH{=}CH_2$, do not propagate the chain-growth polymerization of the $CH_2{=}CHArX$ monomer *via* its olefinic bond. The catalyst is recycled by the reaction of the Pd(II)-hydride species with a base (eqn. 16).

For the Heck-type polycondensation of haloarene vinyl derivatives diverse Pd(0) complexes are most widely used, usually with weak donor ligands like tertiary phosphines. A coordinatively unsaturated Pd(0) complex endowed with the 14-electron structure has meanwhile been proven to be the catalytically active species. This complex is most often generated *in situ* [64]. Tetrakis(triphenylphosphine) palladium(0) which exists at equilibrium with tris(triphenyl-phosphine) palladium(0) and free triphenyl-phosphine in the solution, is frequently employed. The loss of the second phosphine ligand [25, 65] leads to the catalytically active bis(triphenylphosphine) palladium(0) (eqn. 17).

$$\mathrm{Pd(PPh_3)_4} \underset{+\,\mathrm{PPh_3}}{\overset{-\,\mathrm{PPh_3}}{\rightleftharpoons}} \mathrm{Pd(PPh_3)_3} \underset{+\,\mathrm{PPh_3}}{\overset{-\,\mathrm{PPh_3}}{\rightleftharpoons}} \mathrm{Pd(PPh_3)_2} \qquad (17)$$

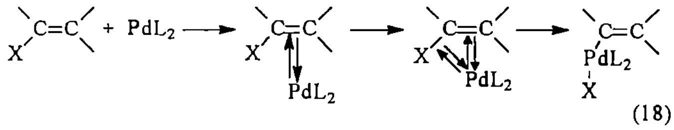
A number of sterically encumbered bis(phosphine) palladium(0) complexes have been known [26, 27, 66], but the $Pd(PPh_3)_2$ complex is exclusive. Also Pd(II) complexes, *e.g.* bis(triphenylphosphine) palladium dichloride, which in the reaction medium are easily reduced to the $Pd(PPh_3)_2$ complex, are commonly employed [67].

Scheme 2 shows the general catalytic cycle in the Heck-type polycondensation which consists in oxidative addition of aryl halide olefin insertion, polymeric chain elimination, and reductive elimination with the formation of a small molecule [13].



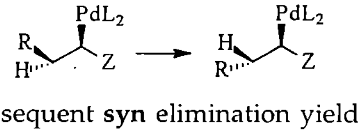
Scheme 2. The catalytic cycle the aryl-vinyl coupling reactions

At the crucial stage of oxidative addition of the electrophile to the zero-valent palladium, the double synergistic interaction is shown (eqn. 18) to take place.



(18)

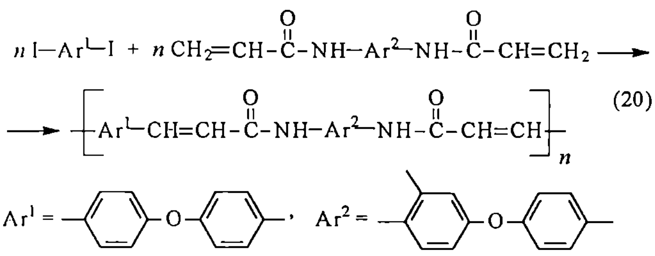
The π complex Pd(0) species undergoes a concerted synergistic interaction with the carbon-halogen bond, which proceeds with the configuration retained [68]. At the next stage, which follows the insertion of olefinic bond into the Pd-C bond, the β-hydride elimination takes place, but only after an internal rotation around the former double bond (eqn. 19) as it requires at least one H_β atom to be oriented synperiplanar with respect to the halopalladium moiety [68].



(19)

The subsequent **syn** elimination yields a 1,2-substituted alkene, RCH=CHZ, and a hydridopalladium halide $L_2Pd(H)X$. Finally, reductive elimination of HX from the hydridopalladium halide, aided by the base added, regenerates the active catalyst species and thereby completes the catalytic cycle presented in Scheme 2.

Application of the Heck coupling polycondensation is not limited to the simple systems but includes a variety of self- and cross-coupling reactions involving reactants with various functionalities. For instance, polycondensation of diiodoarene with bis-acrylamidoarene, run over the $Pd(OOCCH_3)_2$-$P(o\text{-}C_6H_4CH_3)_3$ catalyst, yields a corresponding aromatic high-molecular-weight polycinnamamide (eqn. 20) [69].



$$n\,\mathrm{I{-}Ar^1{-}I} + n\,\mathrm{CH_2{=}CH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}Ar^2{-}NH{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH_2} \longrightarrow \left[\mathrm{Ar^1{-}CH{=}CH{-}\overset{\overset{O}{\|}}{C}{-}NH{-}Ar^2{-}NH{-}\overset{\overset{O}{\|}}{C}{-}CH{=}CH}\right]_n \qquad (20)$$

Polymers with the cinnamoyl backbone were also prepared by Heck's coupling of dihaloarenes and acrylates [70].

Other examples of functionalized poly(arylene vinylene)s comprise polymers with alkyl, aryl, fluoroalkyl, nitro, alkoxy, porphyrin and metalloporphyrin moieties [13].

The late transition metal-catalyzed coupling reaction of aryl halides with alkynes (alkynylation of aryl halides) is frequently also considered to be the Heck reaction [71]. Polymers containing arylacetylene and diarylacetylene units in the backbone have been obtained by the self-coupling of ethynylaryl halides (eqn. 21) and the cross-coupling of aromatic dihalides with acetylene (eqn. 22) or with diethynylbenzenes (eqn. 23) [28].

$$n\,\mathrm{X{-}Ar{-}C{\equiv}CH} \longrightarrow \mathrm{X}\!\left[\mathrm{Ar{-}C{\equiv}C}\right]_n\!\mathrm{H} + (n-1)\,\mathrm{HX} \qquad (21)$$

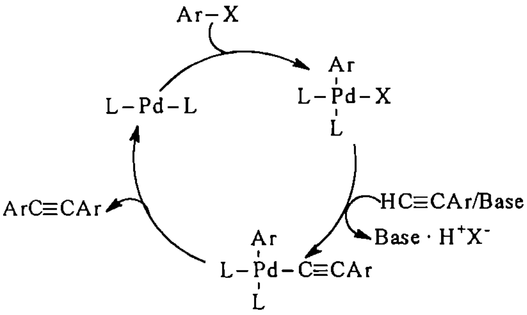
$$n\,\mathrm{X{-}Ar{-}X} + n\,\mathrm{CH{\equiv}CH} \longrightarrow \mathrm{X}\!\left[\mathrm{Ar{-}C{\equiv}C}\right]_n\!\mathrm{H} + (2n-1)\,\mathrm{HX} \qquad (22)$$

$$n\,\mathrm{X{-}Ar^1{-}X} + n\,\mathrm{CH{\equiv}C{-}Ar^2{-}C{\equiv}CH} \longrightarrow \mathrm{X}\!\left[\mathrm{Ar^1{-}C{\equiv}C{-}Ar^2{-}C{\equiv}C}\right]_n\!\mathrm{H} + (2n-1)\,\mathrm{HX} \qquad (23)$$

The aryl-acetylene coupling polycondensation is performed mainly in the presence of Pd-based catalysts under normal Heck reaction conditions (at temperatures within the region of 50—100°C). However, the most effective coupling reaction is achieved by combining Pd(0) complexes with Cu(I) compound, whereby the reaction is enabled to run at ambient temperature [72].

The general catalytic cycle in the Pd(0)/Cu(I)-promoted aryl-acetylene coupling reaction is shown in Scheme 3 [28].

The $Pd(PPh_3)_2$ complex (PdL_2) has two vacant coordination sites and easily undergoes a Cu(I)-promoted oxidative addition with aryl halide (Ar-X) to generate a



Scheme 3. The catalytic for the aryl-alkynyl coupling reaction

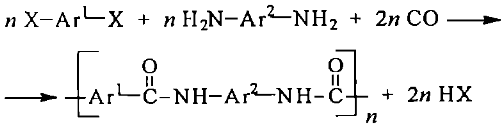
Pd(II) complex. This is followed by substitution of the halide with an acetylide, and reductive elimination of the diarylacetylene to regenerate Pd(0) active sites. A base is required to deprotonate acetylene [28]. In the absence of a base, coordination of acetylene to a Pd(II) species would be through the triple bond rather than through the acetylide carbon bond, thereby allowing oligomerization of the acetylene derivative to occur in a chain-growth manner [73].

Acetylene used for the coupling reaction with aromatic halides can be applied as an acetylene adduct with acetone, 2-methyl-3-butyn-2-ol ($HC{\equiv}C{-}(CH_3)_2OH$); this method allows to avoid complications with the purification and dosage of acetylene to perform a one-pot synthesis [74].

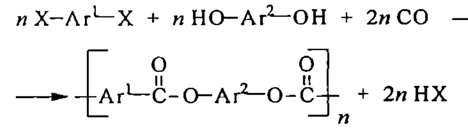
It should be added that also functionalized diacetylene monomers have been used for coupling reactions with haloarenes to prepare polyamides [75] and polysilanes [76].

Late transition metal-catalyzed polycondensation involving haloarene derivatives can also proceed *via* aryl-alkyl and aryl-aryl bond-forming coupling reactions to yield aliphatic-aromatic and aromatic polymers, respectively [28].

Palladium or nickel-catalyzed polycondensation of dihaloarenes with bifunctional nucleophilic monomers such as aromatic diamines and bisphenols in the presence of carbon monoxide, which represent carbon-heteroatom coupling reactions, appeared to be a new promising method for the synthesis of high-molecular-weight aromatic polyamides (eqn. 24) and polyesters (eqn. 25), respectively [29].

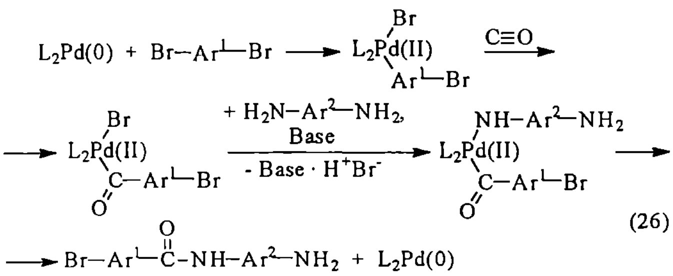


$$n\,X{-}Ar^{1}{-}X + n\,H_2N{-}Ar^{2}{-}NH_2 + 2n\,CO \longrightarrow \left[Ar^{1}{-}\overset{O}{\overset{\|}{C}}{-}NH{-}Ar^{2}{-}NH{-}\overset{O}{\overset{\|}{C}} \right]_n + 2n\,HX \qquad (24)$$



$$n\,X{-}Ar^{1}{-}X + n\,HO{-}Ar^{2}{-}OH + 2n\,CO \longrightarrow \left[Ar^{1}{-}\overset{O}{\overset{\|}{C}}{-}O{-}Ar^{2}{-}O{-}\overset{O}{\overset{\|}{C}} \right]_n + 2n\,HX \qquad (25)$$

The general catalytic cycle for the carbonylation polycondensation, *e.g.*, that according to eqn. 24, follows eqn. 26 [29].

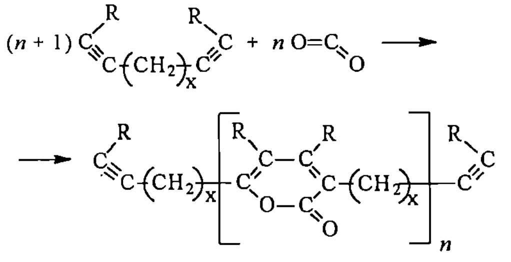


(26)

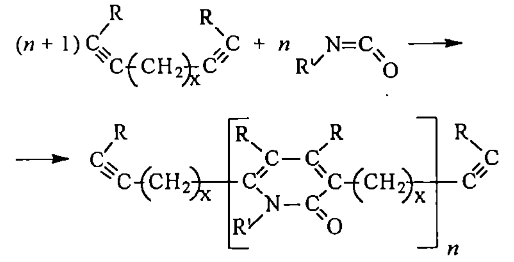
The coordination carbonylation polycondensation has been extended to include the reactions leading to other polymers like poly(imide-amide)s, poly(acylhydrazide)s, and poly(benzoxazole)s [77—79].

Polyaddition of dialkynes with heterocumulenes

Coordination polyaddition of internal dialkynes, $R{-}C{\equiv}C{-}(CH_2)_x{-}C{\equiv}C{-}R$ (R = Et; x ≤ 2, x ≥ 6) *e.g.*, 3,7-decadiyne and 3,11-tetradecadiyne, with heterocumulenes such as O=C=O and RN=C=O, in the presence of the $(R_3P)_2Ni(Cod)_2$ complex (R = $n{-}C_8H_{17}$, Cod = 1,5-cyclooctadiene), led to high-molecular-weight poly(2-pyrone) (eqn. 27) [80] and poly(2-pyridone) (eqn. 28) [81].



(27)



(28)

In the case of dialkynes with x = 3—5 methylene groups between unsaturations in the molecule, low-molecular-weight internal cyclization products are formed rather than polymers [82, 83]. Also aromatic diyenes like 1,4-diethynylbenzene and 1,4-bis(phenylethynyl)benzene, are useful for the synthesis of poly(2-pyridone)s in coordination polyadditions run with isocyanates [84, 85].

By the use of cyclic dialkynes in the Ni(0)-catalyzed polyaddition with carbon dioxide and alkylisocyanate gave the corresponding poly(2-pyrone)s and poly(2-pyridone)s [86].

The mechanism of ring formation from monoalkyne and heterocumulenes, catalyzed by Ni(0) complexes like $L_xNi(0)$, has been proposed to involve one-step cycloaddition. The ring formed is then expanded *via* insertion of the acetylenic bond in the next monomer molecule into a Ni(II)-C bond; a metallocycle eliminates the corresponding product and the catalyst endowed with Ni(0) active sites is regenerated.

Interestingly, the catalytic cycles in the step-growth coordination polyaddition and polycondensation are similar in terms of oxidative addition, monomer insertion, and reductive elimination.

CONCLUDING REMARKS

The late transition metal complexes have appeared over the last decade or so to be versatile catalysts of very high productivity and selectivity for a vast number of various coordination polymerization processes proceeding by both the chain- and step-growth propagation mechanisms. These catalysts are especially likely to provide a fertile ground for future development. The greater functional group tolerance for the late transition metal complexes, as compared with that for the early transition metals, also offers attractive prospects for polar monomer enchainment in the addition and condensation coordination polymerizations. Recent progress has made the late transition metal-based catalysts find an increasingly extensive way into commercial operations. It is, however, clear that, for coordination polymerization and polycondensation (polyaddition), the process of catalyst discovery and development is far from completed. The speed of catalyst discovery is likely to be limited only by the flair and imagination of synthetic organometallic and coordination chemists for ligand design.

REFERENCES

[1] Kuran W.: *Polimery* 1994, **39**, 570. [2] Kuran W.: *Polimery* 1995, **40**, 137. [3] Kuran W.: *Polimery* 1995, **40**, 202. [4] Kuran W.: *Polimery* 1995, **40**, 391. [5] Kuran W.: *Wiad. Chem.* 1995, **49**, 375. [6] Kuran W.: *Polimery* 1997, **42**, 604. [7] Britovsek G. J. P., Gibson V. C., Wass D. F.: *Angew. Chem., Int. Ed. Engl.* 1999, **38**, 428. [8] Melia J., Connor E., Rush E., Breunig S., Mehler C., Risse W.: *Macromol. Symp.* 1995, **89**, 433. [9] Sen A., Lai T. W.: *J. Am. Chem. Soc.* 1982, **104**, 3520. [10] Kuran W., Florjańczyk Z., Sitkowska J.: *Polimery* 1991, **36**, 133.

[11] Ivin K. J.: "Encyclopedia of Polymer Science and Engineering", Vol. 9, Wiley-Interscience, New York 1987, p. 634. [12] Lindmark-Hamberg M., Wagener K. B.: *Macromolecules* 1987, **20**, 2949. [13] Heitz W., Greiner, A.: "The Polymeric Materials Encyclopedia", Vol. 7, CRC Press, Boca Raton, Florida 1996, p. 4865. [14] Tsuda T.: "The Polymeric Materials Encyclopedia", Vol. 3, CRC Press, Boca Raton, Florida 1996, p. 1905. [15] Britovsek G. J. P., Gibson V. C., Kimberley B. S., Maddox P. J., McTavish S. J., Solan G. A., White A. J. P., Williams D. J.: *J. Chem. Soc., Chem. Commun.* 1998, 849. [16] Small B. J., Brookhart M., Bennett A. M. A.: *J. Am. Chem. Soc.* 1998, **120**, 4049. [17] Deng L., Margl P., Ziegler T.: *J. Am. Chem. Soc.* 1999, **121**, 6749. [18] Johnson L. K., Killian C. M., Brookhart M.: *J. Am. Chem.Soc.* 1995, **117**, 6414. [19] Mecking S., Johnson L. K., Wang D. L., Brookhart M.: *J. Am. Chem. Soc.* 1998, **120**, 888. [20] Sen A., Lai T. V .: *J. Am. Chem. Soc.* 1981, **103**, 4627.

[21] Tabata M., Yang W., Yokota K.: *Polym. J.* 1990, **22**, 110. [22] Tabata M., Inaba Y., Yokota K., Nozaki Y.: *J. Macromol. Sci.-Pure Appl. Chem. A* 1994, **31**, 465. [23] Nakano M., Masuda T., Higashimura T.: *Macromolecules* 1994, **27**, 1344. [24] Masuda T., Higashimura T.: *Adv. Polym. Sci.* 1987, **81**, 121. [25] Kuran W., Musco A.: *J. Organometal. Chem.* 1972, **40**, C47. [26] Kuran W., Musco A.: *Inorg. Chim. Acta.* 1975, **12**, 187. [27] Musco A., Kuran W., Silvani A., Anker M. W.: *J. Chem. Soc., Chem. Commun.* **1973**, 938. [28] Percec V., Pugh C., Cramer E., Okita S., Weiss R.: *Makromol. Chem., Macromol. Symp.* 1992, **54/55**, 113. [29] Imai Y.: *Makromol. Chem., Macromol. Symp.* 1992, **54/55**, 151. [30] Brzezinska K., Wolfa P. S., Watson M. D., Wagener K. B.: *Macromol. Chem. Phys.* 1996, **197**, 2065.

[31] Wagener K. B., Nel J. G., Konzelman J., Boncella J. M.: *Macromolecules* 1990, **23**, 5155. [32] Wagener K. B., Nel J. G., Duttweiler R. P., Hillmyer M. A., Boncella J. M., Konzelman J., Y Smith D. W. Jr., Puts R. D., Willonghby L.: *Rubber Chem. Technol.* 1991, **64** (1), 83. [33] Schwab P. F., Marcia B., Ziller J. W., Grubbs R. H.: *Angew. Chem., Int. Ed. Eng.* 1995, **34**, 2039. [34] Ofstead E. A., Wagener K. B.: "New Methods for Polymer Synthesis", Plenum Press, New York 1992, Chapter 8. [35] Ivin K. J., Mol J. C.: "Olefin Metathesis and Metathesis Polymerization", Academic Press, San Diego-London 1997. [36] Wagener K. B., Boncella J. M., Nel J. G., Duttweiler R. P.: *Macromolecules* 1991, **24**, 2649. [37] Wagener K. B., Boncella J. M., Nel J. G., Duttweiler R. P., Hillmyer M. A.: *Makromol. Chem.* 1990, **191**, 365. [38] Tao D., Wagener K. B.: *Macromolecules* 1994, **27**, 1281. [39] Nel J. G., Wagener K. B., Boncella J. M., Duttweiler R. P.: *Polym. Prepr. Am. Chem. Soc., Div. Polym. Chem.* 1989, **30** (1), 283. [40] Konzelman J., Wagener K. B.: *Macromolecules* 1996, **29**, 7657.

[41] O'Gara J. E., Wagener K. B., Hahn S. F.: *Makromol. Chem., Rapid Commun.* 1993, **14**, 657. [42] Brzezinska K., Wagener K. B.: *Macromolecules* 1991, **24**, 5273. [43] O'Gara J. E., Portmess J. D., Wagener K. B.: *Macromolecules* 1993, **26**, 2837. [44] Wagener K. B., Brzezinska K., Bauch C. G.: *Makromol. Chem., Rapid Commun.* 1992, **13**, 75. [45] Brzezinska K., Wagener K. B.: *Macromolecules* 1992, **25**, 2094. [46] Wagener K. B., Patton J. T., Boncella J. M.: *Macromolecules* 1992, **25**, 3862. [47] Bauch C. G., Boncella J. M., Wagener K. B.: *Makromol. Chem., Rapid Commun.* 1991, **12**, 413. [48] Wagener K. B., Patton J. T.: *Macromolecules* 1993, **26**, 249. [49] Wagener K. B., Patton J. T., Forbes M. D., Myers T. L., Maynard H. D.: *Polym. Int.* 1993, **32**, 411.[50] Smith D. W. Jr., Wagener K. B.: *Macromolecules* 1991, **24**, 6073.

[51] Marciniec B., Lewandowski M.: *J. Inorg. Organomet. Polym.* 1995, **5**, 647. [52] Smith D. W. Jr., Wagener K. B.: *Macromolecules* 1993, **26**, 1633. [53] Marciniec B., Le-

wandowski M.: *J. Polym. Sci.: Part A, Polym. Chem.* 1996, **34**, 1443. [54] Cummings S. K., Smith D. W. Jr., Wagener K. B.: *Macromol. Commun.* 1995, **16**, 347. [55] Wagener K. B., Tao D.: *Macromolecules* 1994, **27**, 1281. [56] Wagener K. B., Brzezinska K., Anderson J. D., Dilocker S.: *J. Polym. Sci., Part A, Polym. Chem.* 1997, **35**, 3411. [57] Viswanathan T., Gomez F., Wagener K. B.: *J. Polym. Sci., Part A, Polym. Chem.* 1994, **32**, 2469. [58] Heck R. F., Nolley J. P. Jr.: *J. Org. Chem.* 1972, **37**, 2320. [59] Heitz W., Brügging W., Freund L., Gailberger M., Greiner A., Jung M., Kampschulte U., Niessner N., Osan F., Schmidt H. W., Wicker M.: *Makromol. Chem.* 1988, **189**, 119. [60] Greiner A., Heitz W.: *Makromol. Chem., Rapid Commun.* 1990, **9**, 581.

[61] Brenda M., Greiner A., Heitz W.: *Makromol. Chem.* 1990, **191**, 1083. [62] Greiner A., Martelock H., Noll A., Siegfried N., Heitz W.: *Polymer* 1991, **32**, 1857. [63] Martelock H., Greiner A., Heitz W.: *Makromol. Chem.* 1991, 192, 967. [64] Brown J. M., Hii K. K.: *Angew. Chem., Int. Ed. Engl.* 1996, **35**, 657. [65] Fauvarque J. F., Pflüger F., Troupel M.: *J. Organometal. Chem.* 1981, **208**, 419. [66] Otsuka S., Yoshida T., Matsumoto M., Nakatsu K.: *J. Am. Chem. Soc.* 1976, **98**, 5850. [67] Hartwig J. F., Patt J.: *J. Am. Chem. Soc.* 1995, **117**, 5373. [68] Friestad G. K., Branchand B. P: *Tetrahedron Lett.* 1995, **36**, 7047. [69] Yoneyama M., Tanaka M., Kakimoto M., Imai Y.: *Macromolecules* 1989, **22**, 4148. [70] Suzuki M., Sho K., Kim J. C., Saegusa T.: *Polym. Bull.* 1989, **21**, 415.

[71] Dieck H. A., Heck R. F.: *J. Organometal. Chem.* 1975, **93**, 259. [72] Takahashi S., Kuroyama Y., Sonogashira K., Hagihava N.: *Synthesis* 1980, 627. [73] Simionescu C. L, Percec V., Dimitrescu S.: *J. Polym. Sci., Polym. Chem. Ed.* 1997, **15**, 2497. [74] Pugh C., Percec V.: *J. Polym. Sci., Polym. Chem. Ed.* 1990, **28**, 1101. [75] Müller W. T., Ringsdorf H.: *Macromolecules* 1990, **23**, 2825. [76] Corrini R. J.-P., Douglas W. E., Yang Z.-X.: *Eur Polym. J.* 1993, **29**, 1563. [77] Yoneyama M., Kakimoto M., Imai Y.: *Macromolecules* 1989, **22**, 4152. [78] Perry R. J., Turner S. R., Blevins R. W.: *Macromolecules* 1993, **26**, 1509. [79] Perry R. J., Wilson B. D.: *Macromolecules* 1994, **27**, 40. [80] Tsuda T., Maruta K., Kitaike Y.: *J. Am. Chem. Soc.* 1992, **114**, 1498.

[81] Tsuda T., Hokazono H. Y.: *Macromolecules* 1993, **26**, 1796. [82] Tsuda T., Hokazono H. Y.: *Macromolecules* 1994, **27**, 1289. [83] Tsuda T.: *Gazz. Chim. Ital.* 1995, **125**, 101. [84] Tsuda T., Tobisawa A.: *Macromolecules* 1995, **28**, 1360. [85] Tsuda T., Tobisawa A.: *Macromolecules* 1994, **27**, 5943. [86] Tsuda T.: "The Polymeric Materials Encyclopedia", Vol. 5, CRC Press, Boca Raton, Florida 1996, p. 3525.

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c.d. z III str. okładki

3—7 czerwca 2002 r. Paryż (Francja). "12th International Plastics, Rubber and Composite Materials Show EUROPLAST 2002".

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Informacje: Dept. of Polymer Engineering, University of Minho, 4800-058 Guimaraes, Portugal. Tel.: +351 253 510 245, fax: +351 253 510 249; e-mail: pps18@dep.uminho.pt; internet: http://www.dep.uminho.pt/pps18.

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Informacje: Marie-Héléne Gulli. Laboratoire de Génie Chimique, Université Paul Sebatier, F-31062 Toulouse Cedex-France. Fax.: +33 (0) 561 55 6139; e-mail: icom@lgc.ups-tlse.fr, internet: http://www.ems.cict.fr.

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