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Ruthenium complexes in the controlled synthesis of macromolecules

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Abstract. The use of ruthenium complexes in the catalysis of controlled radical polymerisation is surveyed. The main classes of ruthenium catalysts are described and the relationship between the electronic and spatial structure of metal complexes and their efficiency in polymerisation is analysed. Attention is focused on the ways of increasing the catalytic activity of systems based on ruthenium compounds in the controlled synthesis of macromolecules and also on the analysis of possibilities of their use in the synthesis of new polymeric materials. The bibliography includes 110 references.

I. Introduction

Contemporary synthetic chemistry of polymers is first of all aimed at the synthesis of new materials with preset properties and characteristics and also at the development of highly efficient methods for their synthesis. At present, the most active studies are carried out in the field of the so-called controlled radical polymerisation or polymerisation in the 'living' chain mode.[1–4] The major advantage of controlled radical polymerisation over conventional methods lies in the possibility of synthesising homo- and co-polymers with narrow molecular weight distributions (MWD). The other important merits of this method include degeneration of the undesired self-acceleration of this process at high degrees of conversion and the possibility of synthesising graft and block co-polymers.

The mentioned advantages of controlled radical polymerisation open up wide prospects for the macromolecular design, particularly, the synthesis of hybrid organic – inorganic materials with nanosized structures,[5] which explains the keen attention paid by scientists all over the world to this direction of polymer chemistry. Suffice is to say that in the past 14 years, more than 9000 papers were published and over 1300 patents were granted in this extremely topical and practically promising field of synthetic chemistry of polymers. The more so as at present the stream of publications does not slow down but on the contrary gradually increases, actively shifting towards the development of new promising chain-growth controllers based on metal complexes. The latter can effectively affect both the molecular-weight characteristics of polymers and the structure of synthesised macromolecules, which opens up wide prospects for synthesising new unique polymeric materials and nanostructures.

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II. Specific features of controlled radical polymerisation

Conditions for controlled radical polymerisation and its main mechanisms were described in detail in several recent reviews by Russian[6–9] and foreign[2–4,10] authors. It should be noted that the term 'living polymerisation' was first introduced by Szwarc[11,12] as applied to anionic polymerisation that included only reversible reactions of the chain termination through its interaction with a counter-ion.

The mechanism of 'living' radical polymerisation also implies the presence of the reversible chain termination, where a chain is repeatedly terminated ('dies') and then 'revives' again. However, in this case, in contrast to the truly non-terminating anionic polymerisation, not only reversible but also irreversible termination is possible, leading to the gradual decay of this reaction; this is why the mentioned process does not fully match the description of 'living'.

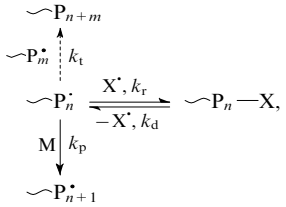
In the literature, the terms 'living', 'pseudoliving', 'quasi-living', controlled polymerisation, *etc*. were used in characterising this type of reactions. From our viewpoint, all these terms reflect more or less the essence of processes that occur in polymerisation systems. The IUPAC Commission have recommended to use the term 'living'/controlled radical polymerisation[13] as the name that describes most thoroughly the mechanism of synthesis of macromolecules under these conditions.

As noted above, the controlled radical polymerisation differs from the conventional polymerisation by simple replacement of the reaction of quadratic chain termination (interaction between two growing macroradicals $\sim P_n^{\bullet}$ and $\sim P_m^{\bullet}$) by a reversible reaction of chain termination or transfer

to yield a macromolecule with a labile end group ($\sim P_n-X$) where the newly formed bond can easily dissociate under the action of temperature, radiation or in its reaction with another species. This is accompanied by regeneration of the original macroradical, which continues the chain propagation.

The mechanism of this process may be illustrated by Scheme 1.

Scheme 1



where M is a monomer molecule; k_r, k_d, k_p, k_t are the rate constants for reactions of recombination, dissociation, chain propagation and termination.

The synthesis of polymers in the controlled mode may proceed only if the reversible chain termination substantially prevails over the quadratic termination. This is possible only where the content of active macroradicals in the reaction mixture is relatively low. An increase in the number of growing radicals increases the contribution of quadratic chain termination the probability of which is proportional to the square of radical concentration.[14] Hence, at the controlled radical polymerisation, the number of active chains at any moment should amount to merely a small fraction of their total number.

Controlled polymerisation is accompanied by a decrease in the polydispersity index and the linear increase in the polymer molecular weight with the increase in the degree of conversion. This is explained by the fact that under the conditions of initiation in the absence of irreversible chain termination, the fast exchange occurs between active and 'dormant' radical sites, ultimately leading to simultaneous chain propagation throughout the polymerisation process.

All the processes of controlled radical polymerisation known so far can be divided into the following three types according to the nature of the chain termination agent X:

— dissociation – recombination processes (Stable Free Radical Polymerisation, SFRP);[15]

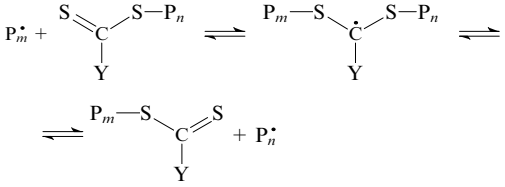
— processes with degenerate chain transfer or processes of addition – fragmentation (Reversible Addition Fragmentation Chain Transfer, RAFT);[16]

— processes accompanied by the transfer of an atom (Atom Transfer Radical Polymerisation, ATRP).[17, 18]

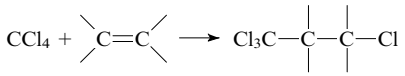
The controlled radical polymerisation according to the dissociation – recombination mechanism involves the use of stable radicals, namely, iminoxyl, carbon- or metal-centred radicals, *etc*., as the reagents X (see Scheme 1). One peculiarity of mentioned radicals is their ability to reversibly interact with the propagation sites converting them into the 'dormant' state. Moreover, it is extremely important for stable radicals to be intrinsically incapable of initiating propagation of new polymeric chains. Recently, the dissociation – recombination processes with transition metal complexes serving as the regulators of polymeric chain propagation have been conventionally called the Organometallic Mediated Radical Polymerisation (OMRP).[19] The origin of this term lies in the fact that such processes can be regulated not only by stable radicals, but also by diamagnetic metal complexes that are not intrinsically radicals.

Kinetic aspects of controlled polymerisation according to the dissociation – recombination mechanism were described in detail in several reviews.[6, 8–10]

Polymerisation according to the mechanism of reversible addition – fragmentation (RAFT) was discovered by Rizzardo and co-workers.[16, 20, 21] Here, the main reaction that sustains the 'pseudoliving' polymerisation represents the multiple chain transfer *via* dithioesters.

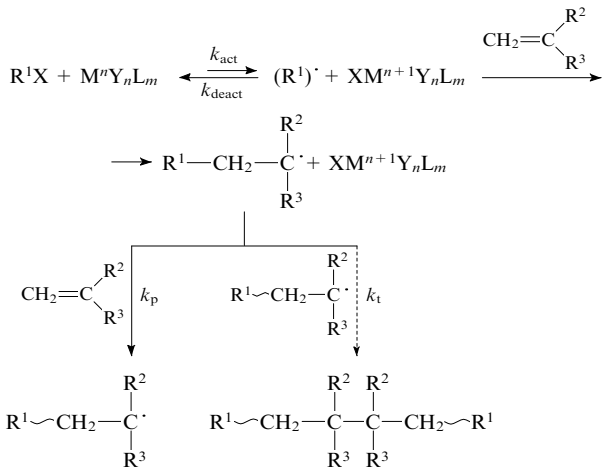


The concept of the controlled atom-transfer radical polymerisation (ATRP) has appeared due to the independent studies by Sawamoto[18, 22] and Matyiaszewski[1, 4, 17, 23] who actually relied on the Kharasch[24] reaction of radical addition of carbon tetrachloride to the double bond of alkenes, catalysed by transition metal complexes with the general composition $M^nY_nL_m$ (where M is a transition metal in a lower oxidation state $n+$, Y is a halogen atom, L is an organic ligand).



Sawamoto and Matyjaszewski extended this reaction to the synthesis of macromolecules. They have shown that in the reversible reaction of metal complexes $M^nY_nL_m$ with alkyl halides, a halogen atom is transferred from the alkyl halide to a metal complex, which is accompanied by metal oxidation and the appearance of alkyl radicals in the system. This reaction when carried out in the monomer medium allows chain propagation fragment after fragment, *i.e*., conduct radical polymerisation in the 'living' chain mode.

Scheme 2



where k_{act} and k_{deact} are the reaction rate constants for activation and deactivation, respectively.

To date, several ways of conducting controlled polymerisation in the presence of transition metal complexes are known. Among them, the ATRP and Reverse ATRP processes

were studied most thoroughly.[22] In the former process, an alkyl halide or any other compound containing a labile carbon–halogen bond serves as the initiator and a complex formed by a transition metal in a lower oxidation state acts as the catalyst. The latter process employs a conventional radical initiator and a complex formed by a metal in a higher oxidation state as the catalyst. In this case, a reverse sequence of transformations is observed, namely, first of all, the destruction of initiator (I) generates active radicals that react with the monomer to produce growing macroradicals; later, these macroradicals react with the complex formed by the metal in a higher oxidation state.

Scheme 3

$$I \longrightarrow 2\,R^{\bullet},$$

$$R^{\bullet} + n\,M \longrightarrow \sim P_n^{\bullet},$$

$$\sim P_n^{\bullet} + X{-}M^{n+1}Y_nL_m \rightleftharpoons \sim P_n{-}X + M^nY_nL_m.$$

The controlled nature of this process is due to the reversible reaction of a growing macroradical with the complex formed by the transition metal in a higher oxidation state.

At present, the controlled synthesis of polymers in the presence of metal complexes according to the ATRP mechanism is the most actively developing and promising method for the production of macromolecules with fixed molecular-weight characteristics. Compounds of copper,[4,17,22,25–27] ruthenium,[18,22] iron,[28] nickel[29,30] and several other metals were employed most often as the catalysts of the ATRP process.

This review analyses the available publications on the use of ruthenium complexes in the controlled synthesis of macromolecules.

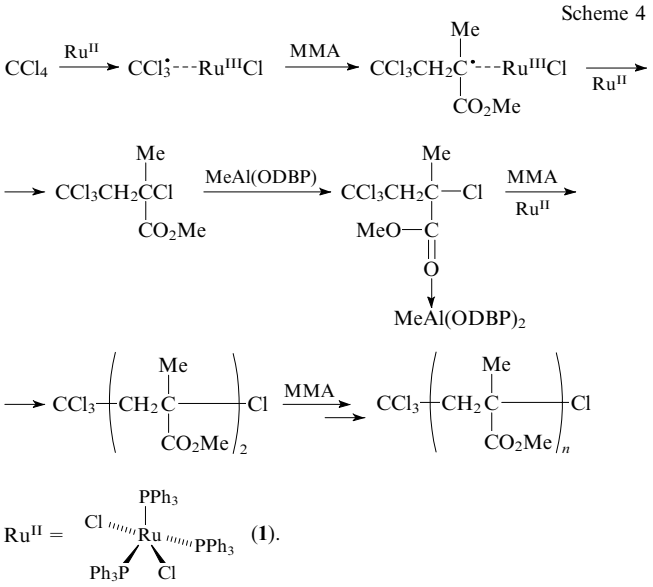
III. Ruthenium compounds as the catalysts of atom-transfer radical polymerisation

Ruthenium complexes were among the first metal complexes to be used in the atom-transfer radical polymerisation.[22] On the one hand, this is due to the fact that the ATRP process was developed based on the Kharasch reaction,[24] which is most often catalysed by complexes of this metal.[31,32] On the other hand, this is associated with unique properties of ruthenium, particularly, its ability to form complexes in different oxidation states where the transition of a ruthenium atom from one oxidation state to another [for example, Ru(II) $\rightleftharpoons$ Ru(III)] occurs sufficiently easily and, what is more important, reversibly. The wide spectrum of stable oxidation states of ruthenium and the reversibility of its redox transitions are responsible for the wide use of ruthenium complexes in the catalysis of many reactions involving organic compounds.[33,34] To date, a large number of catalytic systems based on complexes of this metal are known that are capable of initiating and regulating the synthesis of homo- and co-polymers.

1. Ruthenium phosphine complexes

The priority in the use of ruthenium compounds for synthesising macromolecules in the 'living' chain mode belongs to Sawamoto and co-workers[18] who back in 1995 reported on the possibility of performing controlled polymerisation of methyl methacrylate (MMA) in the presence of a three-component initiating system that involved carbon tetrachloride (initiator), tris(triphenylphosphine)ruthenium dichloride (**1**) (Ru^{II}, catalyst) and methylaluminium bis[2,6-di(*tert*-butyl)-phenoxiole] [$MeAl(ODBP)_2$ as the activator and the co-catalyst] (Scheme 4).[18]

Scheme 4



Ru^{II} = $Cl_2Ru(PPh_3)_2$ (**1**).

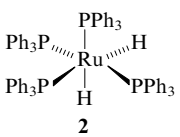
Poly(methyl methacrylate) synthesised by Sawamoto demonstrated a rather narrow MWD ($M_w/M_n = 1.32$).

The above paper together with the known publication by Matyjaszewski[17] devoted to the use of copper complexes in the controlled synthesis of macromolecules have virtually laid foundations for the aforementioned concept of polymerisation according to the ATRP mechanism, the most topical modern direction in the synthetic chemistry of polymers.

Ruthenium compound **1** proposed by Sawamoto had already been known as an active catalyst of the Kharasch type radical addition of carbon tetrachloride to terminal alkenes.[31] It is noteworthy that the adduct $CCl_3CH_2CH(R)Cl$, which was formed in the addition of CCl_4 to $CH_2{=}CHR$ ($R = C_nH_{2n+1}$-n, where $n = 4-7$), demonstrated low efficiency in polymerisation processes. Under the reaction conditions (60 °C), this adduct did not react with the excess MMA. As the temperature increased to 80 °C, the MMA polymerisation became possible; however, the process was characterised by a low rate and a relatively high polydispersity index of synthesised samples (> 1.6).

It is possible to increase the degree of control over the living radical polymerisation of MMA initiated by carbon tetrachloride and catalysed by ruthenium triphenylphosphine complex **1** by adding the third component (co-catalyst, a weak Lewis acid) to the system. This components may be represented by alkoxides of aluminium,[18,35–41] titanium[41] or tin.[41] It was assumed that the reaction of mentioned compounds with the ruthenium complex should favour the enhancement in the stability of the metal in the higher oxidation state, *i.e.*, facilitate the Ru(II) → Ru(III) transition, thus making possible the cleavage of the carbon–chlorine bond in the adduct $CCl_3CH_2CCl(Me)CO_2Me$. Thus, the MMA polymerisation initiated by a three-component system $CCl_4 - RuCl_2(PPh_3)_3 - M(OR)_x$ proceeded much faster than in the absence of a Lewis acid to yield polymers with narrow distributions ($M_w/M_n = 1.1-1.3$).

The use of another ruthenium compound, namely, its hydride complex **2** (Ref. 39)



2

as the ATRP catalyst made it possible to carry out the polymerisation of MMA even at 30 °C and in the absence of a Lewis acid (for instance, an aluminium alkoxide) as a co-catalyst. Polymers thus formed were characterised by a rather narrow MWD (M_w/M_n = 1.17). Complex **2** is distinguished, on the one hand, by its high catalytic activity and, on the other hand, by its low stability. Thus during the polymer synthesis, the reaction mixture changed its colour, which indirectly pointed to side processes that lead to changes in the catalyst composition and its destruction. As the degree of conversion increased, the rate of MMA polymerisation involving complex **2** decreased, as evidenced by the presence of a break in the dependence of $\ln([M_0]/[M])$ on time.

Historically, the first halogen-containing compound used as the initiator of the ATRP processes was carbon tetrachloride. In subsequent studies, other compounds with a labile carbon–halogen bond were proposed for use, which included α-halocarbonyl compounds,[35] alkylaryl halides,[38] sulfonyl chlorides[42] and so on.[22,43] The following organic compounds were used most often as the initiators: Cl_3CX (X = H, Cl, Br, Ac), $CH_2{=}CHCH_2X$ (X = Cl, Br); MeCH(Ph)X (X = Cl, Br, I); $MeCH(CONMe_2)X$ (X = Cl, Br); $Me_2C(CO_2Me)CH_2-CMe(CO_2Me)X$ (X = Cl, Br); $Me_2C(CONMe_2)Br$; $Me_2C(CO_2Et)X$ (X = Cl, Br); PhC(O)CHClX (X = H, Cl).

It should be noted that the structure of an initiator substantially affects the initial polymerisation step, by governing the macroradical formation rate and thus determining the breadth of the MWD.

Polymers with the narrowest distribution were synthesised when compounds with the structure identical to that of 'dormant' polymeric chains were used as the initiators. In this case, the initiation was fast, allowing all polymeric chains to propagate simultaneously. A separate group includes polyfunctional initiators used in the production of star-like polymers.[44,45]

The second important factor that affects the molecular-weight distribution is the nature of the halogen atom reversibly transferred to the metal-complex catalysts. When bromine-containing initiators were used, the control over the MWD of polymers was more effective as compared with their chlorine-containing counterparts.[43,46] Probably, this was associated with the difference in the carbon–halogen bond energies, which affects the efficiency of the ATRP reaction (see Scheme 3).

Introduction of free radicals such as 1,1-diphenylpicrylhydrazyl, galvinoxyl, 2,2,6,6-tetramethypiperidinoxyl (TEMPO) into the polymerisation system led to complete inhibition of the polymerisation process.[18,37] At the same time, the presence of protic compounds in the system such as water or methanol in amounts comparable with the catalyst concentration did not affect the mechanism of the process.[37] Moreover, complex **1** turned out to be very effective in catalysing the MMA suspension polymerisation in aqueous and alcoholic media.[47] These facts point to the radical mechanism of polymerisation.

As a rule, components of the initiating system, alkyl halide–ruthenium complex–Lewis acid, did not affect the stereoregularity of macromolecules formed. In the majority of cases, the probability for the formation of syndio-, iso- and atactic sequences of units in the polymers synthesised using this system is the same as in the polymers synthesised in the presence of a common radical initiator.[18]

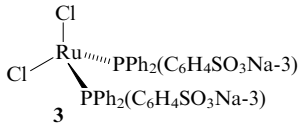
Polymerisation according to the ATRP mechanism was accompanied by the increase in the polymer molecular weight and polydispersity index and also by the increase in the degree of conversion, which pointed to the controlled nature of this process. The introduction of a fresh portion of monomer into the polymerisation system resulted in resumption of polymerisation and further increase in the molecular weight of polymers without additional portions of the catalyst.[18,36,38–41,47–51]

A distinguishing feature of the MMA controlled radical polymerisation in the presence of ruthenium compounds is that the isolated polymers purified from catalyst traces did not lose their activity and could act as macroinitiators of MMA polymerisation. Thus the addition of MMA to a solution of such a polymer led to an increase in the polymer molecular weight and narrowed its MWD.[37]

The initiating systems described above can also be used in the synthesis of di- and tri-block-co-polymers of MMA with butyl acrylate (BA) (*e.g.*, co-polymers MMA-BA, MMA-BA-MMA[36]) and other monomers. Interesting results were obtained in the initiation of MMA co-polymerisation with styrene by systems based on complex **1**.[38] It was shown that ruthenium complex **1** has no effect on the relative activities of these monomers. As the degree of conversion increased, the co-polymer molecular weight also increased, with the MWD remaining fairly narrow. The polymerisation process was resumed after each introduction of every new portion of monomers,[38] which served as convincing evidence that the process proceeded in the living chain mode.

The considered initiating systems proved to be efficient not only in the synthesis of poly(methyl methacrylate) and MMA-based co-polymers (*e.g.*, in the MMA co-polymerisation with acrylamide derivatives), but also in the synthesis of poly(*N*,*N*-dimethylacrylamide), a polymer that defied the earlier attempts of synthesising by the 'pseudoliving' mechanism in the presence of transition metal compounds.[40]

Ruthenium complexes with phosphine ligands, particularly, complex **1,** were also used in the synthesis of water-soluble poly(2-hydroxyethyl methacrylate) in methanolic solutions.[49] However, due to the low solubility of complex **1** in methanol, the polymerisation proceeded as a heterogeneous process to yield polymers with relatively wide MWD. At the same time, the use of a water-soluble analogue of phosphine complex **1**, namely, complex **3**, which contains polar sulfo groups in the phosphine ligand, imparted the required homogeneity to the system and thus allowed synthesising narrow-distribution poly(2-hydroxyethyl methacrylate) and also block-co-polymers on its basis.[50]



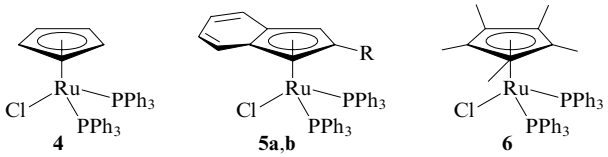
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Co-polymerisation of methyl methacrylate with styrene in the presence of aforementioned ruthenium phosphine complexes proceeded at a low rate as compared with the classical radical polymerisation. The 80%–90% conversion was reached in 80–100 h. In subsequent studies (*e.g.*, see Ref. 51), it was found that the addition of amines to the polymerisation system led to a substantial increase in the polymerisation rate; moreover, in some cases, amines (Lewis bases) proved to be more effective co-catalysts than aluminium alkoxide. Polymers formed in the presence of amines were characterised by the narrow MWD. With hydroxyl-containing amines, the degree of control over the polymerisation process was determined by both the number of substituents at the nitrogen atom and the length of a carbon chain that separates the hydroxyl and amino groups.[52] The living mechanism of the polymerisation process

in the presence of amines was confirmed by its re-initiation with the introduction of a new portion of the monomer. The specific mechanism of activation by amines is so far unknown. Probably, in the course of polymerisation, amines react with the ruthenium complex, transferring the latter in its more catalytically active form.

2. Half-metallocene ruthenium complexes

Among a wide spectrum of ligands capable of forming coordination bonds with heavy metal atoms, special place belongs to aromatic systems, particularly, benzene, cyclopentadienyl anion and its derivatives and also to their analogues. The mentioned molecules exhibit specific properties that distinguish them from other ligands, namely, they form a relatively strong, donor bond with a central metal atom.[53] To date, quite a number of studies were devoted to the catalytic activity of half-metallocene ruthenium compounds in polymerisation of vinyl monomers [50, 53–59] of which the most thoroughly studied are complexes **4**–**6** that contain the cyclopentadienyl (Cp), indenyl (Ind) and pentamethylcyclopentadienyl (Cp*) ligands.



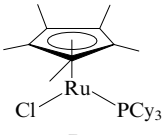
4 **5a,b** **6**

R = H (**a**), NMe_2 (**b**).

Among complexes shown above, complex **5a** with an indenyl ligand in the metal atom coordination sphere proved to be the most active catalyst in the polymerisation processes. MMA polymerisation in its presence proceeded rather actively even in the absence of aluminium alkoxides to yield samples with narrow polydispersity (M_w/M_n = 1.15). Introduction of aluminium alkoxides improved the molecular weight characteristics.[54] Compounds **5a** surpassed ruthenium triphenylphosphine complexes in their activity in polymerisation of 2-hydroxyethyl methacrylate.[50]

A comparison of results on the MMA, styrene and methyl acrylate (MA) polymerisation with the dimer $H(MMA)_2Cl$ as the initiator and $Al(OPr^i)_3$ as the activator, which were carried out in the presence of isoelectronic complexes **5a** and **6**, demonstrated that indenyl derivatives of ruthenium provided higher polymerisation rate and pentamethylcyclopentadienyl derivatives ensured the narrower MWD, especially for styrene and MA. Polydispersity indices (M_w/M_n) of polymers synthesised in the presence of complexes **5a** and **6** were 2.28 and 1.23, respectively, for MA and 1.88 and 1.07, respectively, for styrene.[55, 56]

Interesting results were obtained for the MMA polymerisation in the presence of 16-electron complex **7** containing tricyclohexylphosphine (PCy_3) as a ligand.[56]



7

Compound **7** exhibited higher catalytic activity as compared with complex **5a**. In the presence of the former, the process was much faster even at lower temperatures and the resulting poly(methyl methacrylate) was characterised by a narrow MWD (M_w/M_n = 1.11). It cannot be ruled out that such a high activity of metal complex **7** might be caused by the presence of a vacant coordination site at the ruthenium atom due to the absence of one of ligands. It should be noted that polymerisation of styrene and MA in the presence of this complex had an uncontrolled character.

Attention should be drawn to the results of a comparative analysis of the catalytic activities of ruthenium complexes $LRu(PPh_3)_2Cl$ containing cyclopentadienyl (**4**), indenyl (**5a**), pentamethylcyclopentadienyl (**6**), hydrotris(1-pyrazolyl)-borate (Tp) ligands and $Ru(PPh_3)_3Cl_2$ (**1**) in the MMA polymerisation and also in the exchange reaction of halogen atoms with the initiator $Me_2C(CO_2Me)CH_2C(Me)(CO_2Me)Br$ according to Scheme 5.[55]

Scheme 5

$$R{-}Br + Ru^{II}(PPh_3)_2(L)Cl \rightleftharpoons \rightleftharpoons [R^{\bullet} + BrRu^{III}(PPh_3)_2(L)Cl] \rightleftharpoons \rightleftharpoons R{-}Cl + Ru^{II}(PPh_3)_2(L)Br$$

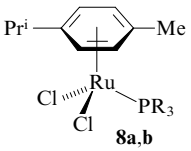
$$R = Me{-}\underset{\displaystyle CO_2Me}{\overset{\displaystyle Me}{\overset{|}{C}}}{-}CH_2{-}\underset{\displaystyle CO_2Me}{\overset{\displaystyle Me}{\overset{|}{C}}}{-} \quad ; L = Cp, Cp^*, Ind, Tp, (PPh_3)Cl.$$

The catalytic activity of ruthenium compounds **4**–**6** was found to be associated with the redox potential of the Ru(II) ⇌ Ru(III) transition the probability of which depends in turn on the electron-donor ability of ligand L. Moreover, a decrease in the redox potential accelerated the transition between the active and dormant states of the chain and, as a consequence, increased the polymer molecular weight and narrowed the MWD. However, the pronounced dependence between the electrochemical characteristics of catalysts and their activities was observed only for ruthenium complexes with the analogous structures, namely, complexes **4**–**6**. Thus the redox potentials of these complexes decreased in a series **4** > **5a** > **6** and, correspondingly, their activity in the exchange of the halogen atom with the initiator increased as **4** < **5a** < **6**.

The high activity of ruthenium complex with indenyl ligand (**5a**) can be explained by the strongly pronounced donor nature of this ligand and its ability to pass from η^5- to η^3-coordination state leaving a vacant coordination site at the ruthenium atom.[54] The rate of controlled synthesis of poly(methyl methacrylate) in the presence of complex **5a** was substantially increased by adding n-butylamine into the reaction mixture.[57]

The introduction of an electron-donor dimethylamino group also increased the catalytic activity of the ruthenium complex and enhanced its efficiency in the atom-transfer polymerisation. Thus in the presence of compound **5b**, poly(methyl methacrylate) with M_w/M_n = 1.07 was obtained, which is one of the best achievements in the controlled radical polymerisation for this monomer.[53] Electrochemical studies of ruthenium complexes with indenyl ligands have shown that the introduction of a donor substituent into the cyclopentadienyl ring of this ligand leads to a decrease in the redox potential of this complex, which confirms the existence of a correlation between the redox potentials of compounds with similar structures and their activities in the ATRP reactions.[58]

In a series of half-metallocene ruthenium complexes based on *p*-cumene, the most effective catalysts of the controlled synthesis of poly(methyl methacrylate) and polystyrene were metal complexes **8**, which contain rather bulky phosphine groups (tricyclohexylphosphine, triisopropylphosphine, *etc.*).[60, 61]



8a,**b**

R = Cy (**a**), Pr^i (**b**).

Substitution of a related tricyclohexylarsine ligand for the tricyclohexylphosphine ligand in compound **8a** produced an efficient ATRP catalyst, whereas the introduction of a tricyclohexylstibine ligand led to a complex that was devoid of catalytic activity in polymerisation reactions.[61]

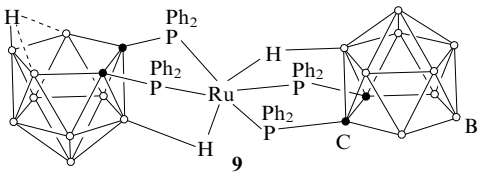
The catalytic activity of compound **8a** in the controlled atom-transfer polymerisation initiated by microwave radiation was studied.[62] A comparative analysis of the heat- and microwave radiation-induced processes suggested that microwave radiation had an accelerating effect on the polymerisation.† However, an increase in the active radical concentration increased the fraction of irreversible chain terminations as a result of disproportionation and, hence, led to the formation of polymers with broader MWD. Moreover, the effect of microwave radiation on a catalyst induced its destruction during the polymerisation resulting in cessation of the polymerisation at 60% conversion.

Although polymerisation according to the ATRP mechanism can be formally considered as the Kharasch reaction extended to the synthesis of high-molecular compounds, nonetheless, the catalytic activity of one and the same ruthenium compound in these two processes can substantially differ. As was mentioned above, among compounds with the structure analogous to that of complexes **8a**,**b**, compounds containing bulky basic phosphines proved to be highly efficient in the polymerisation of vinyl monomers. It is noteworthy that these compounds are virtually inactive in the Kharasch reaction. In contrast, compounds containing the less basic and sterically unhindered ligands were inefficient catalysts in the polymerisation processes but very actively catalysed the Kharasch-type reaction of alkene addition.[32, 60]

3. Ruthenium carborane complexes

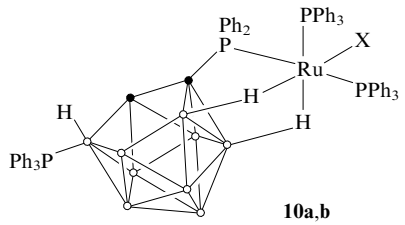
A special group of catalysts of the Kharasch reaction and ATRP processes consists of ruthenium complex compounds containing carborane ligands.

Demonceau and co-workers [64–67] were the first to propose using ruthenium compounds containing carborane ligands in the controlled synthesis of macromolecules.



9

† It should be noted that microwave radiation also accelerates the ATRP-relative Kharasch reaction catalysed by ruthenium compounds of the same structure.[63]

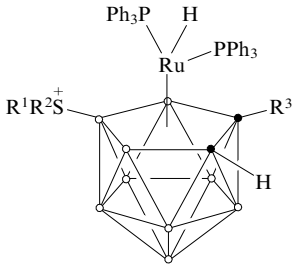


10a,**b**

X = H (**a**), Cl (**b**).

They have shown that compounds **9** and **10**, which contain single-charged *nido*-diphosphinocarborane anions as the ligands, catalyse carbon tetrachloride-initiated polymerisation of MMA and styrene. The degree of control over the polymerisation was found to depend on the complex structure and the monomer nature, *viz*., under the same conditions, it was possible to synthesise poly(methyl methacrylate) with a relatively narrow distribution (M_w/M_n = 1.25), whereas synthesised polystyrene had a wider MWD.[64] Ruthenium catalysts containing a carborane ligand exhibited high activity. In some cases, their use made it possible to carry out efficiently the controlled synthesis of macromolecules without additional introduction of Lewis acids or bases into the system.

Yet another group of ruthenacarborane catalysts is represented by compounds **11** with the *closo*-structure that include a single-charged sulfur-containing substituent. Carborane fragments in such compounds are isoelectronic to the cyclopentadienyl anion.

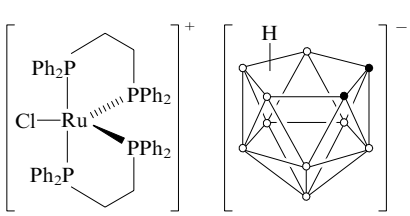


11

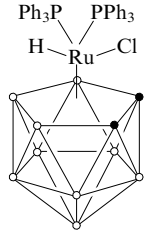
R^1	R^2	R^3
Me	Me	H
Et	Et	H
Et	Ph	H
(CH$_2$)$_4$		H
Me	Me	Me
Et	Et	Me

Compounds **11** are much more active catalysts of the styrene and BA polymerisation as compared with ruthenium cyclopentadienyl or indenyl complexes, *e.g*., the polymerisation of butyl acrylate proceeded at relatively low temperature (30 °C). A drawback of catalysts under consideration was that they provided relatively weak control over the MWD (M_w/M_n > 1.5).[65]

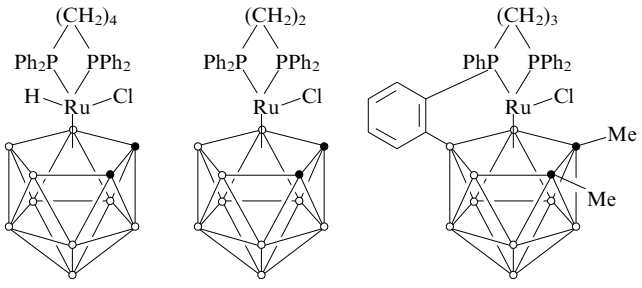
Classical ruthenium carborane complexes with the *closo*- and *exo-nido*-structures (compounds **12**–**18**) proved to be efficient catalysts of the MMA and styrene polymerisation.[68–72]



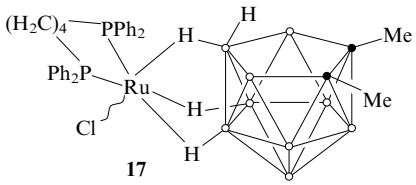
12



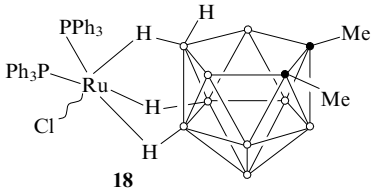
13



14 **15** **16**



17



18

The structure of ruthenium carborane complexes (*closo*- or *exo-nido*-) was shown to strongly affect the kinetic parameters of polymerisation and also the molecular weight characteristics of the synthesised polymers. In the MMA polymerisation according to the ATRP mechanism, the highest degree of conversion was observed with diamagnetic *exo-nido*-complexes **17** and **18**. The corresponding polymers synthesised were characterised by the number-average (M_n) and weight-average (M_w) molecular weight relatively high for the controlled polymerisation processes. At the same time, it should be noted that the rather high polydispersity of the polymers synthesised ($M_w/M_n > 2$) suggested the low degree of control over the polymerisation of methacrylic monomers with complexes **17** and **18**.

In the styrene polymerisation catalysed by complexes **12**–**18**, the highest molecular weights were obtained for compounds **17** and **18**, but the polydispersity indices were lower ($M_w/M_n \ll 2$) than for poly(methyl methacrylate).

The use of ruthenium complexes **13**–**16** with the *closo*-structures made it possible to synthesise polymers with much narrower MWD. For example, with compounds **14** and **15** narrow-distribution polymers were synthesised from both MMA and styrene (M_w/M_n ratios fell in the range of 1.23–1.25). At the same time, it should be noted that molecular weights of polymers synthesised using these complexes were substantially lower than those of the polymers obtained in the presence of either *exo-nido*-complexes **17** and **18** or common radical initiators such as azobis(isobutyronitrile) (AIBN) and peroxides.‡

The polymerisation of MMA in the presence of complex **14** was shown to proceed uniformly up to high degrees of conversion. The time dependence $\ln([M]_0/[M])$ was linear. This suggested the absence of processes of irreversible chain termination, which is typical of polymerisation in the living chain mode.[10] The molecular weight of the polymer also increased linearly with the conversion. The molecular-weight distribution curves were unimodal, with the mode gradually shifting to the high-molecular weight range with conversion.[70] Thus, the process demonstrated all the major signs typical of the living chain polymerisation processes.

By the example of polymerisation of styrene in the presence of ruthenium complexes **12**–**18**, it was shown that as the temperature was elevated, the process accelerated, the time of attainment of the limiting degrees of conversion shortened and the molecular weight of the synthesised polymer decreased.[70]

Polymerisation of styrene under the Reverse ATRP conditions with the above-mentioned complexes and AIBN as the initiator was less efficient as compared with the ATRP conditions. The best molecular-weight characteristics were observed for the Reverse ATRP process carried out in the presence of ruthenium carborane complexes with the *closo*-structure (compounds **14** and **15**), these being the same as in the synthesis of polystyrene according to the ATRP mechanism.

Polydispersity indices of poly(methyl methacrylate) samples synthesised under the Reverse ATRP conditions somewhat exceeded the corresponding parameters of polymers synthesised according to the ATRP mechanism. Probably, the higher polydispersity indices were due to the uncontrolled synthesis of macromolecules, which proceeded in parallel with the living process according to the conventional radical initiation mechanism as the result of the AIBN thermal decomposition.[68–70]

Addition of amines substantially accelerated the MMA polymerisation in the presence of ruthenacarboranes, shortened the time of attainment of the limiting conversion and increased the maximum yield of polymers. This fact is interesting and extremely important from the practical viewpoint. This trend was observed when both *closo*- and *exo-nido*-ruthenacarboranes were used. Particularly, the addition of *tert*-butylamine, the most efficient activating agent, to almost all ruthenium complexes resulted in the attainment of the MMA conversion close to 100% in less than 2.5 h.

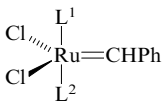
The effect of amines on the MMA polymerisation in the presence of 17-electron ruthenium complex **15** deserves special mention. Thus in the absence of amines, the limiting conversion of MMA in the presence of complex **15** did not exceed 40% even 200 h after the beginning of the polymerisation, whereas in the presence of amines, 100% conversion was reached in ~2 h with the M_w/M_n ratio not exceeding 1.3.[72]

Thus, the ruthenium carborane complexes are efficient catalysts of the controlled synthesis of macromolecules by both the ATRP and Reverse ATRP mechanisms, where the ligand environment of the metal atom in a complex had a more substantial effect on the polymerisation process than its degree of oxidation and the electronic configuration.

4. Ruthenium complexes with carbene ligands

Ruthenium compounds proved to be efficient catalysts in reactions of metathesis of alkenes and also in polymerisation of cyclic alkenes by the ring-opening mechanism.[73–77] The metathesis reactions are as a rule catalysed by metal complexes with carbene ligands. Belgian scientists have shown that ruthenium carbene complexes such as complex **19** are also efficient in the catalysis of the Kharasch reaction and atom-transfer radical polymerisation.[75–77]

‡ Molecular weights of polyacrylates synthesised under conventional conditions varied from several hundred thousands to millions and their polydispersity indices substantially exceeded 2.

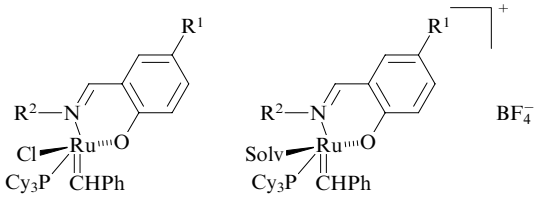


19

$L^1 = L^2 = PPh_3$, PCy_3, $P(cyclo\text{-}C_5H_9)_3$ and *etc*.

Such catalysts allowed one to synthesise poly(meth)acrylates in high yields with narrow molecular weight distributions ($M_w/M_n < 1.1$).

Ruthenium carbene complexes **20** with salicylaldimine ligands were used in the controlled radical polymerisation of MA, MMA and styrene.[78]



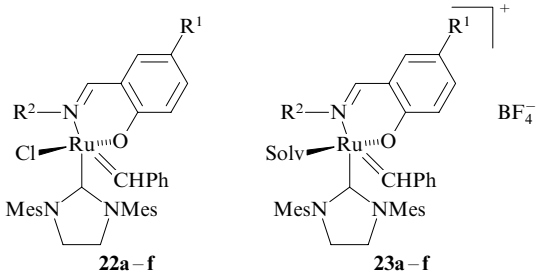
20a–f **21a–f**

Compound	R^1	R^2	Compound	R^1	R^2
a	H	Me	**d**	NO_2	2,6-Me_2-4-BrC_6H_2
b	NO_2	Me	**e**	H	2,6-$Pr^i_2C_6H_3$
c	H	2,6-Me_2-4-BrC_6H_2	**f**	NO_2	2,6-$Pr^i_2C_6H_3$

It was found that the yield of polymers and their molecular weight characteristics depend on the catalyst structure, particularly, on the nature of substituents R^1 and R^2. Complex **20d** proved to be the most efficient. The polymerisation of MA, srytene and MMA in the presence of this catalyst carried out for 17 h afforded the corresponding polymers with degrees of conversion of 26%, 88% and 28% and polydispersity indices of 1.28, 1.44 and 1.22, respectively. As the degree of conversion increased, the molecular weight of polymers increased linearly and the polydispersity indices decreased. It seemed unusual that the increase in the catalyst activity not only accelerated the process, but also increased the degree of control over the MWD.

Treatment of compounds **20a–f** with silver tetrafluoroborate produced ruthenium complexes with the ionic structure (compounds **21a–f**). These compounds proved to be efficient catalysts of the controlled synthesis of polymers in a water–toluene emulsion.[78] Emulsion polymerisation in the presence of ionic compounds made it possible to increase the degree of control over the polymerisation and enhance the efficiency of initiation as compared with polymerisation in solutions; however, this involved deceleration of the process. Thus polymerisation of MA, styrene and MMA in a water–toluene emulsion for 17 h led to the corresponding polymers with polydispersity indices of 1.37, 1.48 and 1.34. In toluene, both the degree of conversion and the polydispersity indices were higher (1.66, 1.71 and 1.46, respectively).

Further studies in the area of development of new effective catalysts of controlled radical polymerisation based on ruthenium complexes have shown that the replacement of the tricyclophosphine ligand in compounds **20** and **21** by a 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (N-heterocyclic carbene, NHC) ligand (compounds **22**, **23**) favoured the increase in the degree of control over the processes of polymerisation of MA, styrene and MMA.[79] Thus in the polymerisation of these monomers with complex **22d** used in place of complex **20d**, the yields of poly(methyl acrylate), polystyrene and poly(methyl methacrylate) somewhat decreased (24%, 75% and 27%, respectively), but the polydispersity indices decreased (1.21, 1.25 and 1.18, respectively).

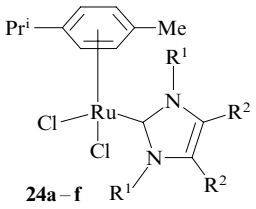


22a–f **23a–f**

Mes = 2,4,6-$Me_3C_6H_2$; R^1, R^2 are the same as in compounds **20** and **21**.

Compounds **22** were converted into ionic complexes **23**, which also proved to be the more efficient catalysts of the polymerisation of styrene, MA and MMA in water–toluene emulsions as compared with their tricyclohexylphosphine analogues.

Ruthenium complexes **19** and **24a–f** containing imidazol-2-ylidene carbene ligands pertain to a different group of ruthenium compounds capable of efficient catalysis of the metathesis reactions and the atom-transfer radical polymerisation.[80–84]



24a–f

Compound	R^1	R^2
a	Mes	Me
b	Mes	H
c	Mes	Cl
d	Cy	Me
e	Cy	H
f	Cy	Cl

The fact that the polymerisation of MMA and styrene in the presence of these metal complexes demonstrated the linear increase in the polymer molecular weight with the degree of conversion and a linear dependence of $\ln([M_0]/[M])$ on time indirectly confirmed the controlled§ nature of this process. However, the parallel reaction of metathesis to yield stilbene was a negative factor in view of the controlled synthesis of macromolecules. Moreover, MWD of polymers synthesised using complexes **24** was broader ($M_w/M_n > 1.4$) than that of polymers synthesised in the presence of aforementioned ruthenium complexes with benzylidene carbene ligands.

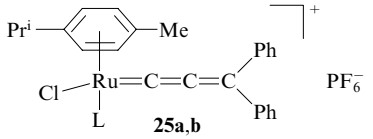
The steric and electronic properties of catalysts **24a–f** that determine their activity in the atom-transfer polymerisation strongly depended on the structure of their heterocyclic carbene ligand and the number of substituents in it, which largely determined the mechanism of observed reactions.[83] Compounds **24a–c** containing mesityl substituents at the nitrogen atoms proved to be the most efficient catalysts in the MMA polymerisation; however, polymerisation of styrene was accompanied by a side reaction of metathesis to form stilbene; hence in the polymerisation of styrene, complexes **24d–f** with

§ It should be noted that the polymerisation of vinyl acetate and BA in the presence of catalysts **19** containing imidazol-2-ylidene ligands followed the uncontrolled mechanism to yield polymers with relatively wide MWD ($M_w/M_n > 2$).[82]

cyclohexyl substituents at the nitrogen atoms were preferred. It is of note that substitution of bromine atoms for chlorine atoms in complex **19** ($L^1 = L^2$ is 1,3-diisopropylimidazol-2-ylidene) led to a substantial reduction of the catalyst efficiency.[82]

Cyclic voltammetry studies have shown that the nature of substituents at the nitrogen atoms affects not only the redox potential of the complex, but also the reversibility of addition of a halogen atom to the ruthenium atom. The absence of reversibility led to conventional (uncontrolled) radical polymerisation initiated by a redox reaction that could occur in the system under study.

Among other catalysts that had been developed for the metathesis reaction and proved to be efficient in the atom-transfer radical polymerisation, mention should be made of cationic structures **25** containing allene carbene ligands.[85]

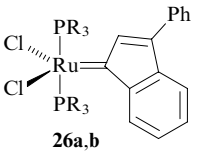


25a,**b**

L is PCy_3 (**a**), 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene (NHC) (**b**).

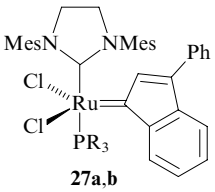
Compounds **25** demonstrated high activity in the synthesis of a wide spectrum of polymers, namely, poly(methyl methacrylate), poly(methyl acrylate), polystyrene, poly(butyl acrylate) and poly(isobutyl methacrylate). Polymerisation of styrene in a toluene solution catalysed by complexes **25** led to polymers with a very low polydispersity index ($M_w/M_n = 1.14$). Due to their ionic structure, the systems under consideration proved to be efficient in emulsion polymerisation as well. Although the rate of emulsion polymerisation in the presence of complexes **25** increased, the MWD of the polymers became broader and the efficiency of initiation dropped. The fact that the polymerisation process in the presence of compounds **25** can be controlled was confirmed by the linear form of dependences of the molecular weight and $\ln([M_0]/[M])$ on time and also by the possibility of performing post-polymerisation. However, during the post-polymerisation, a slight broadening of MWD curves was observed.

Yet another class of ruthenium coordination compounds with carbene ligands employed as the catalysts of the Kharasch reaction and the controlled radical polymerisation according to the ATRP mechanism are complexes **26**–**28** with indenylidene ligands.[86, 87]



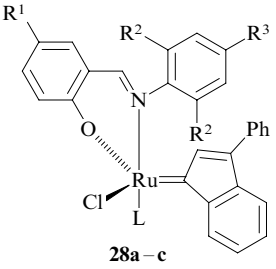
26a,**b**

R = Ph (**a**), Cy (**b**).



27a,**b**

R = Ph (**a**), Cy (**b**).



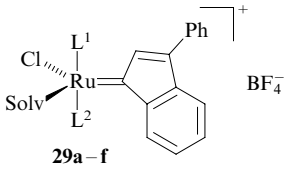
28a–**c**

Compound **28**	L	R^1	R^2	R^3
a	PCy_3	NO_2	Me	Br
b	NHC	NO_2	Me	Br
c	PCy_3	H	Pr^i	H

Thus in the presence of catalyst **28a**, polystyrene and poly(methyl methacrylate) were synthesised with polydispersity indices of 1.12 and 1.19, respectively. Complex **28b**, which simultaneously contains the N,O-chelate (salicylaldimine) and N-heterocyclic carbene ligands, also proved to be effective in the synthesis of narrow-distribution polymers.

For all proposed catalysts, the behaviour of polymerisation processes obeyed first-order kinetics and showed a linear increase in the polymer molecular weight with the degree of conversion, which confirmed the controlled nature of the process.

The activity of catalytic systems **26**–**28** was shown to increase with their conversion into the cationic forms (complexes **29**) upon treatment with silver tetrafluoroborate.



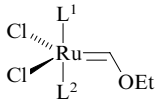
29a–**f**

Compound **29**	L^1	L^2
a	PPh_3	PPh_3
b	PCy_3	PCy_3
c	NHC	PPh_3
d	NHC	PCy_3
e	N,O-ligand [a]	PCy_3
f	N,O-ligand [a]	NHC

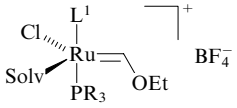
[a] *o*-$OC_6H_3O(R^1)CH{=}N-C_6H_2R^2_2R^3$.

The ionic nature makes it possible to use the *in situ* synthesised complexes for polymerisation in both toluene solutions and water–toluene emulsions. Substitution of a water–toluene emulsion for the toluene solution substantially accelerated the polymerisation, but reduced the degree of control over the process.

It was shown that the nature of the vinylidene fragment substantially affects the catalyst efficiency. Thus substitution of the ethoxymethylidene ligand (complexes **30**) for the indenylidene ligand in complexes **26**–**28** accelerated the ATRP process. Ionic complexes **31** derived from complexes **30** make it possible to carry out polymerisation of MMA in water-organic media with high rate and degree of control.



30



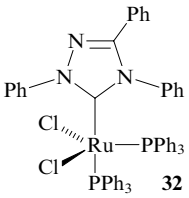
31

L^1 = PPh_3, PCy_3, NHC; L^2 = PPh_3, PCy_3, N,O-chelating ligand; R = Ph, Cy.

It deserves mention that in some cases macromolecules synthesised by the emulsion polymerisation had more narrow MWD ($M_w/M_n = 1.11$)[86] as compared with the polymers synthesised in solutions.

As mentioned above, the activity of ruthenium catalysts with carborane ligands in the ATRP processes can be substantially enhanced by adding amines to the polymerisation medium. A similar situation was observed for catalysts with vinylidene and allene fragments.[85–88] Polymerisation of MMA in the presence of complexes **25**–**27** and di(n-butyl)amine was faster, but was accompanied by a certain broadening of the MWD.[85, 86]

The effect of the structure of amines added on polymerisation of MMA catalysed by complex **32** containing a triazole carbene ligand was studied.[89]



32

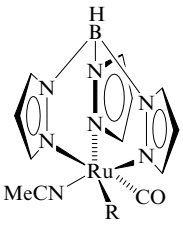
It should be noted that compound **32** exhibited low catalytic activity, which substantially increased upon addition of amines. *N*-Butylamine proved to be the most efficient additive, which allowed the synthesis of narrow-distribution polymers. An increase in its concentration relative to the ruthenium complex concentration increased the polydispersity indices of synthesised polymers (from 1.08 to 1.40). Addition of di(n-butyl)amine to complex **32** was less efficient, whereas triethylamine had no accelerating effect on the polymerisation of vinyl monomers in the presence of the aforementioned ruthenium complexes.[89] Thus, primary amines were more efficient activating additives to metal complexes with carbene ligands than the secondary or tertiary amines.

On the whole, the reason of the observed acceleration of polymerisation of MMA and styrene catalysed by ruthenium complexes in the presence of amines is still unclear. It cannot be ruled out that the acceleration was associated with the *in situ* formation of new, more active catalysts as a result of insertion of an amine into the ruthenium coordination sphere. Moreover, the increase in the catalytic activity of ruthenium complexes in the course of polymerisation in the presence of amines could be caused by a chain transfer reaction due to the presence of mobile hydrogen atoms at the nitrogen atom. However, the low concentration of amines and the concomitant broadening of the MWD of polymers with the increase in the concentration [89] do not completely agree with this assumption.

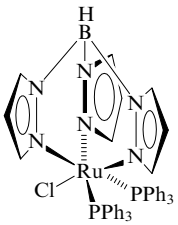
5. Miscellaneous ruthenium complexes in the catalysis of polymerisation processes

a. Tris(pyrazolyl)borate complexes of ruthenium

As has been noted above, the ligand environment of a ruthenium atom is the key factor that determines the activity of ruthenium complexes in the catalysis of polymerisation processes. In connection with this, special attention should be drawn to the results of synthesis of polystyrene and poly(-methyl methacrylate) in the presence of a ruthenium complex with a hydrotris(1-pyrazolyl)borate anion (compounds **33a**,**b**), the latter anion being isoelectronic with cyclopentadienyl.[90] Polymerisation of styrene and MMA in the presence of complexes **33** proceeded even in the absence of alkyl halides, which suggests that these complexes themselves act as the polymerisation initiators. However, the synthesised polymers were characterised by a relatively broad MWD ($M_w/M_n > 1.5$). Moreover, as should be expected, no linear increase in the number-average molecular weight with the degree of conversion was observed, which suggests the low degree of control over the polymerisation. In was assumed [90] that in the presence of ruthenium complexes **33a**,**b**, two parallel processes occur, namely, the radical and the coordination polymerisation.



33a,**b**



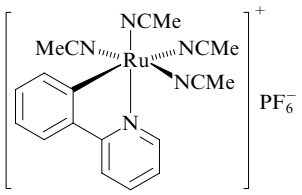
34

R = CO (**a**), Me (**b**).

In contrast to complexes **33**, complex **34** containing the same hydrotris(pyrazolyl)borate ligand turned out to be efficient catalyst of the atom-transfer polymerisation. In the presence of this catalyst, narrow-distribution poly(methyl methacrylate) ($M_w/M_n = 1.13$) was synthesised. The reaction rate was higher than in the presence of ruthenium cyclopentadienyl derivatives **4**–**6** described above.[55]

b. Ruthenium complexes with acetonitrile ligands

A group of Mexican scientists [91] proposed that cationic ruthenium complex **35** in which Ru is involved in a five-membered ring can be used as the catalyst of polymerisation of MMA, styrene and BA.

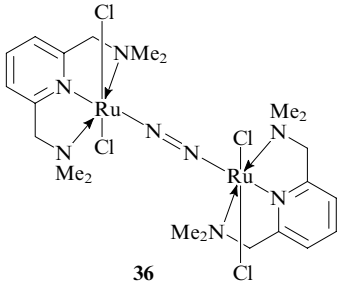


35

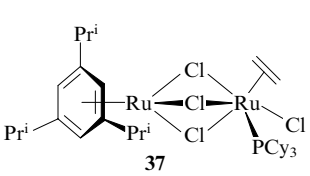
Compound **35** exhibited sufficiently high catalytic activity only in the presence of aluminium alkoxides. Although the process proceeded according to the radical mechanism (this was inhibited upon introduction of TEMPO), nonetheless, this was of the 'living' nature, as evidenced by a sufficiently broad MWD. However, the introduction of the third component, tin chloride, into this system made it possible to switch this process to atom-transfer living polymerisation. It should be noted that in this case, too, the polymer yield did not exceed 70% and relatively low polydispersity indices ($M_w/M_n < 2$) could be observed only for samples isolated in the initial stages of the reaction.

c. Binuclear ruthenium complexes

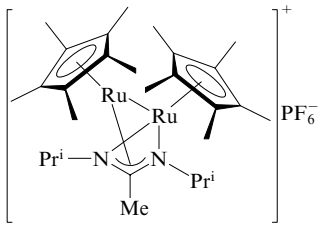
Binuclear ruthenium complexes **36**–**38** proved to be interesting systems that catalyse the polymerisation of vinyl monomers according to the ATRP mechanism.



36



37



38

Activation of the carbon—halogen bond in alkyl halides under the action of compound **36** was studied.[92] It was shown that under the reaction conditions, complex **36** underwent decomposition with the elimination of a nitrogen molecule to yield two species that could add a halogen atom due to the formation of vacant coordination sites at the metal atom. The addition of MMA to the reaction system led to the formation of poly(methyl methacrylate) with $M_n/M_w \geqslant 1.5$.

Yet another example of a binuclear ruthenium complex that allows controlled synthesis of polymers is compound **37** (Ref. 93). This catalyst exhibited higher catalytic activity as compared with complex **36**. In the presence of the former, polymerisation of MMA initiated by ethyl α-bromoisobutyrate proceeded at temperatures as low as 35 °C to yield polymers with an extremely narrow MWD ($M_w/M_n < 1.15$). It should be noted that when the polymerisation was continued to the high degrees of conversion (above 70%), the second peak appeared in the high-molecular-weight range of the MWD curves. Complex **37** also proved to be efficient in the polymerisation of different esters of methacrylic acid, namely, ethyl, *tert*-butyl and isobornyl methacrylates.

A group of Japanese scientists[94] have proposed a cationic binuclear ruthenium complex **38** as a catalyst for the radical polymerisation according to the living chain mechanism. They have studied the catalytic activity of a series of mono- and binuclear ruthenium complexes with pentamethylcyclopentadienyl ligands in the reactions of atom-transfer radical addition and polymerisation. Complex **38** proved to be the most active in the polymerisation reaction. Complex **38** has a vacant coordination site suitable for the addition of a halogen atom from the initiator, which renders it active in the ATRP process. In the presence of this complex, polymerisation of MMA initiated by ethyl α-bromoisobutyrate proceeded even at 25 °C to yield polymers with a narrow MWD ($M_w/M_n = 1.2$). The controlled nature of this process was confirmed by carrying out post-polymerisation with poly(methyl methacrylate) as the macroinitiator. However, the unsaturated coordination state of this complex, which determined its high catalytic activity, had a negative effect on its stability. In the course of reaction, catalyst **38** quickly decomposed and lost its activity, which made impossible attainment of the degree of conversion above 50%.

6. Immobilised ruthenium complexes

One of drawbacks of the ATRP processes that limits to a certain extent their practical application is the necessity of separating the catalyst from the polymers when the polymerisation is over. Therefore, the use of ruthenium catalysts immobilised on a solid support seems promising. On the one hand, this allows one to simplify the procedure of polymer isolation and, on the other hand, opens up wide possibilities for the catalyst recovery. It was shown[95] that ruthenium catalysts $[RuCl_2(p\text{-}Pr^iC_6H_4Me)]_2$ bound to silica gel or to MCM-41 modified with $PPh_2[CH_2CH_2Si(OEt)_3]$ are effective in polymerisation of various acrylates, methacrylates and styrene. In certain cases, the use of heterogeneous catalysts was shown to provide higher degrees of monomer conversion under comparable conditions. However, polymers synthesised with the use of immobilised catalysts were characterised by rather broad MWD [$M_w/M_n = 1.7$ (silica gel) and 2.8 (MCM-41) for polystyrene and 1.8 (silica gel) and 2.3 (MCM-41) for poly(methyl methacrylate)].

Another interesting example was polymerisation of MMA-catalysed by compound **1** deposited on amine-modified silica gel.[96] It is noteworthy that as under the action of free amines,[51] the effect of polymerisation acceleration was observed.

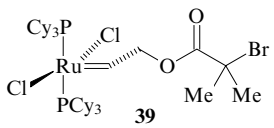
7. *In situ* syntheses of ruthenium catalysts

An important drawback of the catalysts used in the Kharasch reaction and ATRP processes and based on divalent ruthenium compounds is their low stability. It is known[97] that with the addition of carbon tetrachloride to styrene, due to side reactions of recombination of radicals $^{\bullet}CCl_3$, catalytically inert adducts Ru(III)—Cl are accumulated in the system, which leads to termination of the polymerisation process. The addition of a radical initiator (AIBN) made it possible to substantially increase efficiency of ruthenium catalysts. A radical initiator is the source of free radicals that react with the ruthenium(III) complex to reduce it into the divalent state. Carrying out an ATRP reaction in the presence of a radical initiator makes it possible to use more accessible and air-stable compounds of trivalent ruthenium as the pre-catalysts. The latter react with the radical generating *in situ* the active Ru(II) catalysts.

8. Tandem catalysis

The possibility of 'tandem catalysis', *i.e.*, the use of one and the same catalyst for carrying out two or more reactions, advantageously distinguishes ruthenium compounds from the known systems based on other transition metals. Sawamoto and co-workers[98] demonstrated the prospects of using ruthenium complex $RuCl_2(PPh_3)_3$ (**1**) in the production of poly(methyl methacrylate) by the atom-transfer polymerisation followed by *in situ* substitution of hydrogen atom for the terminal halogen atom. A significant and practically important merit of tandem catalysis lies in the fact that the polymer does not require cleaning from the catalyst, the new portions of catalysts need not be added and the catalyst is transformed from the 'polymerisation' to 'hydrogenation' form just in the reaction medium (*in situ*).

Yet another extremely interesting ruthenium catalyst is compound **39** that contains in its structure a fragment of a radical initiator and can simultaneously catalyse both the polymerisation according to the mechanism of metathesis with ring opening and the atom-transfer radical polymerisation.[99,100]



39

The use of catalyst **39** made it possible to carry out the radical polymerisation of cyclooctadiene according to the metathesis mechanism with ring opening, polymerisation of MMA according to the ATRP mechanism and co-polymerisation of MMA with cyclooctadiene in one reaction vessel.[99] The co-polymer can be hydrogenated in the presence of the

same ruthenium catalyst to yield its saturated analogue.[99] Block co-polymers based on caprolactone and styrene were synthesised in a similar way.[101]

* * *

Japanese scientists [102, 103] carried out the synthesis of stereogradient polymers based on 2-hydroxyethyl methacrylate in the presence of ruthenium complex **6**. The structure of these polymers features stereoregularity that varies along the polymer chain. Such water-soluble polymeric materials with the controllable macromolecular architecture are of special interest for medicine, *e.g.*, they can be used in the development of macromolecular biologically active drugs or in the directed transport of drugs to injured tissues and organs.[104]

At present, several studies [105–109] are known in which ruthenium compounds did not act as the catalysts as above but played a somewhat unusual role of multifunctional initiators of polymerisation to be used in combination with compounds of other metals, *e.g.*, copper, nickel, zinc, *etc*. As a rule, in such complexes the ruthenium atom is bound with several chelate nitrogen-containing ligands (*e.g.*, with bipyridine and its derivatives) to form a chromophore group which is involved in the polymer and imparts special optical properties, particularly, induces luminescence.[106]

IV. Conclusion

The analysis of literature data summarised in Tables 1–3 suggests that to date ruthenium complexes are among the most efficient catalysts of polymerisation of a wide range of monomers according to the living chain mechanism. They allow one to obtain polymers with narrow molecular weight distributions and also new materials based on the gradient and block co-polymers. Among essential advantages of ruthenium compounds over other radical polymerisation catalysts are their multifunctional nature and the ability of acting as effective catalysts of several reactions at once (which may proceed simultaneously). This opens up wide prospects for their use in the synthesis of new classes of polymer materials with unique combinations of properties.

Despite the abundance of experimental results on the use of ruthenium compounds as polymerisation catalysts, it is difficult to draw a clear and unambiguous correlation between their structure and catalytic activity. The analysis of experimental material shows that the efficiency of a metal complex catalyst in the atom-transfer radical polymerisation and the degree of control over the polymerisation process in the presence of these catalysts are related to the redox potental of the complex, namely, the easily oxidisable complexes exhibit the higher activity in the synthesis of macromolecules. Indeed, to date the most efficient catalytic systems are half-metallocene complexes with indenyl and carborane ligands that exhibit the high electron-donor ability. On the other hand, this relationship is ambiguous and in certain cases fulfilled only for compounds with similar structures. The electronic environment of the metal atom and its degree of oxidation have a weaker effect on the efficiency of ruthenium complexes in polymerisation processes.

An interesting and practically important effect observed in the polymerisation in the presence of ruthenium complexes is the noticeable acceleration of this process upon the addition of amines into the polymerisation system. This trend was observed for virtually all types of ruthenium complexes, namely, cyclopentadienyl, carborane, carbene, *etc*. The mechanism of action of amines is so far unclear. Further studies should be carried out in this field including those using modern experimental techniques and quantum chemical simulation methods and also in the field of the quest for new promising ligands for ruthenium catalysts.

The other no less important factors that affect the activity of catalysts under consideration are the sterical factors manifested most clearly by the example of polymerisation of (meth)acrylic monomers in the presence of ruthenium carborane complexes.

Table 1. Data on the methyl methacrylate polymerisation catalysed by ruthenium complexes.

Catalyst (ruthenium complex)[a]	Initiator	Activator (co-catalyst)	Medium	T/°C	t/h	Main characteristics of the polymer			Ref.
						conversion (%)	M_n	M_w/M_n	
1	CCl_3Br	without activator	water	80	—	83	9600	1.42	47
	$Me_2C(CO_2Et)Br$	$Al(OPr^i)_3$	toluene	80	23	> 90	9100	1.34	35
	CCl_3COMe	$Al(OPr^i)_3$	"	80	45	93	9400	1.17	35
	CCl_4	$MeAl(ODBP)_2$	"	60	4	88	5200	1.32	18
		$Al(OPr^i)_3$	"	80	60	> 90	6000	1.24	41
		$Ti(OPr^i)_4$	"	80	45	> 90	5200	1.19	41
		$Sn(OPr^i)_4$	"	80	10	> 90	5500	1.34	41
	$CHCl_2COPh$	without activator	toluene – water	80	48	89	112500	1.16	47
		$Al(OPr^i)_3$	toluene	80	30	> 90	10400	1.15	35
	$H(MMA)_2Cl$	$HO(CH_2)_2NH_2$	"	60	23	91	15400	1.43	52
		$HO(CH_2)_3NH_2$	"	60	47	93	13100	1.35	52
		$HO(CH_2)_4NH_2$	"	60	34	96	10300	1.15	52
		$HO(CH_2)_6NH_2$	"	60	34	92	9400	1.16	52
		Et_3N	"	60	120	94	12900	1.14	52
		$HO(CH_2)_2NEt_2$	"	60	23	91	10800	1.23	52
		Bu^nNH_2	"	80	8	> 90	14300	1.75	51
		Bu^n_2NH	"	80	20	> 90	13500	1.19	51
		Bu^n_3N	"	80	50	> 90	10900	1.15	51
		aniline	"	80	481	85	8800	1.34	51

Table 1 (continued).

Catalyst (ruthenium complex)[a]	Initiator	Activator (co-catalyst)	Medium	T/°C	t/h	Main characteristics of the polymer			Ref.
						conversion (%)	M_n	M_w/M_n	
2	$CHCl_2COPh$	without activator	toluene	30	306	95	14300	1.17	39
		the same	"	60	54	90	14100	1.17	39
		"	"	80	47	80	11300	1.21	39
		$Al(OPr^i)_3$	"	60	40	90	14800	1.18	39
6	$Me_2C(CO_2Et)Br$	$Al(OPr^i)_3$	"	80	388	82	10300	1.45	56
	$Me_2C(CO_2Et)I$	$Al(OPr^i)_3$	"	80	290	51	8200	1.52	56
	$H(MMA)_2Cl$	$Al(OPr^i)_3$	"	80	365	94	10700	1.10	56
5a	$CHCl_2COPh$	without activator	"	100	35	92	10500	1.16	54
		$Al(OPr^i)_3$	"	100	18	90	10500	1.14	54
	$H(MMA)_2Cl$	$Al(OPr^i)_3$	"	80	51	90	9800	1.09	54
		Bu^n_2NH	"	100	5	93	10800	1.17	57
		Bu^n_3N	"	100	~10	>90	10200	1.12	57
5b	$H(MMA)_2Cl$	$Al(OPr^i)_3$	"	80	16	91	11600	1.07	53
9	CCl_4	without activator	"	85	16	8	4700	2.30	64
10a	CCl_4	the same	"	85	16	84	28000	1.25	64
12	CCl_4	"	monomer	80	110	71	29800	1.50	70
13	CCl_4	"	"	80	45	88	36200	1.63	70
14	CCl_4	"	"	80	110	83	26800	1.25	70
15	CCl_4	"	"	80	200	39	17600	1.23	70
16	CCl_4	"	"	80	114	70	41900	1.37	70
17	CCl_4	"	"	80	9	74	104900	2.67	70
18	CCl_4	"	"	80	80	98	51900	1.93	70
19 ($L^1 = L^2 = PCy_3$)	$Me_2C(CO_2Et)Br$	"	toluene	85	16	95	66000	1.28	82
19 ($L^1 = PCy_3$, $L^2 = NHC$)	$Me_2C(CO_2Et)Br$	"	"	85	16	85	58000	1.35	82
20d	$Me_2C(CO_2Et)Br$	"	"	85	16	28	13000	1.22	78
22d	$Me_2C(CO_2Et)Br$	"	"	85	16	27	13300	1.18	79
23d	$Me_2C(CO_2Et)Br$	"	"	85	16	84	52000	1.52	79
			toluene – water	85	16	97	53000	1.33	79
24c	CCl_4	"	toluene	85	16	44	6000	1.40	80
25a	$Me_2C(CO_2Et)Br$	"	"	85	17	14	10000	1.35	85
		Bu^n_2NH	"	85	17	90	51900	1.45	85
		H_2O	"	85	17	27	92700	1.78	85
26a	$Me_2C(CO_2Et)Br$	without activator	"	85	17	40	17000	1.23	86
27b	$Me_2C(CO_2Et)Br$	the same	"	85	17	73	29400	1.21	86
28b	$Me_2C(CO_2Et)Br$	"	"	85	17	54	23500	1.19	86
29d	$Me_2C(CO_2Et)Br$	"	"	85	17	70	34300	1.21	86
			toluene – water	85	17	80	39300	1.45	86
30 ($L^1 = L^2 = PPh_3$)	$Me_2C(CO_2Et)Br$	"	toluene	85	17	54	25900	1.20	86
31 ($L^1 = L^2 = PPh_3$)	$Me_2C(CO_2Et)Br$	"	"	85	17	46	29400	1.25	86
			toluene – water	85	17	96	46900	1.11	86
32	$Me_2C(CO_2Et)Br$	Pr^nNH_2	toluene	85	5	27	28330	1.08	89
		Bu^n_2NH	"	85	5	35	33700	1.46	89
34	$H(MMA)_2Cl$	without activator	"	80	100	>90	10800	1.13	55
8	$Me_2C(CO_2Et)Br$	the same	"	85	16	90	60500	1.10	77
35	$Me_2C(CO_2Et)Br$	$Al(OPr^i)_3 - SnCl_2$	monomer	80	4.5	23	58800	1.16	91
37	$Me_2C(CO_2Et)Br$	without activator	toluene	35	96	95	38500	1.68	93
38	$Me_2C(CO_2Et)Br$	the same	monomer	40	10	32	29000	1.30	94
			1,2-dichloroethane	40	10	56	31000	2.20	94
			toluene	40	10	26	47000	1.30	94
			ethyl acetate	40	10	45	40000	1.80	94

[a] The structures of ruthenium complexes are given in the text.

Table 2. Data on the styrene polymerisation catalysed by ruthenium complexes.

Catalyst (ruthenium complex) [a]	Initiator	Activator (co-catalyst)	Medium	T/°C	t/h	Main characteristics of the polymer			Ref.
						conversion (%)	M_n	M_w/M_n	
6	$Me_2C(CO_2Et)Br$	$Al(OPr^i)_3$	toluene	100	163	90	10000	1.10	56
	$Me_2C(CO_2Et)I$	$Al(OPr^i)_3$	"	100	553	39	1400	1.56	56
	$H(MMA)_2Cl$	$Al(OPr^i)_3$	"	100	123	93	8900	1.09	56
5a	$Me_2C(CO_2Et)Br$	$Al(OPr^i)_3$	"	100	96	91	9800	1.15	54
	$H(MMA)_2Cl$	$Al(OPr^i)_3$	"	100	99	91	11000	1.88	53
5b	$Me_2C(CO_2Et)Br$	$Al(OPr^i)_3$	"	100	38	91	9000	1.22	53
	$H(MMA)_2Cl$	$Al(OPr^i)_3$	"	100	33	91	9600	1.26	53
9	CCl_4	without activator	"	110	16	52	30000	1.75	64
10a	CCl_4	the same	"	110	16	61	28000	2.25	64
11	$PhCH_2CH_2Br$	"	"	110	16	40	3900	1.80	65
12	CCl_4	"	monomer	90	106	96	40000	1.39	70
13	CCl_4	"	"	90	106	89	31900	1.52	70
14	CCl_4	"	"	90	75	89	20700	1.62	70
15	CCl_4	"	"	90	70	91	19600	1.57	70
16	CCl_4	"	"	90	200	68	17100	1.37	70
17	CCl_4	"	"	90	119	99	31400	1.44	70
18	CCl_4	"	"	90	106	88	44300	1.74	70
19 ($L^1 = L^2 = PCy_3$)	$PhCH_2CH_2Br$	"	toluene	110	16	61	29000	1.38	82
19 ($L^1 = PCy_3$, $L^2 = NHC$)	$PhCH_2CH_2Br$	"	"	110	16	48	22000	1.60	82
20d	$PhCH_2CH_2Br$	"	"	110	16	88	41000	1.44	78
22d	$PhCH_2CH_2Br$	"	"	110	16	75	37000	1.25	79
23d	$PhCH_2CH_2Br$	"	"	110	16	92	58000	1.60	79
			toluene – water	110	16	99	54000	1.36	79
24c	CCl_4	"	toluene	110	16	34	12000	1.25	80
25a	$PhCH_2CH_2Br$	"	"	110	17	27	15600	1.40	85
		Bu^n_2NH	"	110	17	35	40400	1.53	85
		H_2O	"	110	17	61	63600	1.60	85
8	$PhCH_2CH_2Br$	without activator	"	110	–	48	19500	1.45	61
35	$PhCH_2CH_2Br$	$Al(OPr^i)_3 - SnCl_2$	–	100	4	12	15400	1.18	91

[a] The structures of the complexes are given in the text.

Table 3. Data on the polymerisation of certain acrylic and methacrylic monomers in toluene in the presence of ruthenium complexes.

Monomer [a]	Initiator	Catalyst (ruthenium complex) [b]	Activator (co-catalyst)	T/°C	t/t	Main characteristics of the polymer			Ref.
						conversion (%)	M_n	M_w/M_n	
BA	$Me_2C(CO_2Et)Br$	**11**	without activator	85	16	97	22800	1.70	65
		25a	the same	85	17	33	24900	1.39	85
		36	$Al(OPr^i)_3 - SnCl_2$	80	4	69	59200	1.56	91
BMA	CCl_4	**1**	$MeAl(ODBP)_2$	60	5	> 85	6900	1.54	36
		1	$Al(OPr^i)_3$	80	40	> 85	9600	1.25	36
HEMA [c]	$CHCl_2COPh$	**3**	without activator	80	8	90	22000	1.43	50
		1	the same	80	8	84	23700	1.69	50
		5a	"	80	17	82	18100	1.58	50
	$H(MMA)_2Cl$	**3**	"	60	–	92	24600	1.70	50
		3	Bu^n_3N	60	–	90	28300	1.51	50
DMAA	CCl_3Br	**1**	$Al(OPr^i)_3$	60	17	92	11500	1.80	40
		1	$Al(OPr^i)_3$	80	6	91	12000	1.58	40
	$MeCH(CONMe_2)_2Br$	**1**	$Al(OPr^i)_3$	80	10	91	9300	1.65	40
	$MeCH(CONMe_2)_2Cl$	**1**	$Al(OPr^i)_3$	80	10	96	11400	2.68	40
DEAA	CCl_3Br	**1**	$Al(OPr^i)_3$	80	8	93	5500	1.59	40
iPAA	$Me_2C(CO_2Et)Br$	**1**	$Al(OPr^i)_3$	100	551	89	8100	2.60	40
iBMA	$Me_2C(CO_2Et)Br$	**25a**	without activator	85	17	17	13400	1.33	85

Table 3 (continued).

Monomer [a]	Initiator	Catalyst (ruthenium complex) [b]	Activator (co-catalyst)	T/°C	t/t	Main characteristics of the polymer			Ref.
						conversion (%)	M_n	M_w/M_n	
iBRMA	$Me_2C(CO_2Et)Br$	**37**	without activator	35	96	89	40000	2.46	93
MA	$Me_2C(CO_2Et)Br$	**6**	$Al(OPr^i)_3$	80	27	97	13600	1.17	56
		5b	$Al(OPr^i)_3$	80	38	92	7700	1.47	53
	$Me_2C(CO_2Et)I$	**6**	$Al(OPr^i)_3$	80	10	95	9900	1.17	56
		5b	$Al(OPr^i)_3$	80	61	95	9400	1.32	53
	$H(MMA)_2Cl$	**6**	$Al(OPr^i)_3$	80	166	96	10400	1.27	56
		5b	$Al(OPr^i)_3$	80	64	94	9600	2.33	53
	$MeCH(CO_2Et)Br$	**20d**	without activator	85	16	26	9500	1.28	78
		22d	the same	85	16	24	9400	1.21	79
		23d	"	85	16	33	18300	1.55	79
				85 [d]	16 [d]	42 [d]	18800 [d]	1.32 [d]	79
		25a	"	85	17	40	19800	1.37	85
tBMA	$Me_2C(CO_2Et)Br$	**37**	"	35	96	88	47000	1.14	93
EMA	$Me_2C(CO_2Et)Br$	**37**	"	35	96	93	40500	1.15	93
	CCl_4	**1**	$MeAl(ODBP)_2$	60	5	> 95	7000	1.44	36
			$Al(OPr^i)_3$	80	40	> 95	7500	1.24	36

[a] The following abbreviations are used: BMA is butyl methacrylate, iBMA is isobutyl methacrylate, tBMA is *tert*-butyl methacrylate, HEMA is 2-hydroxyethyl methacrylate, iBRMA is isobornyl methacrylate, DMAA is dimethylacrylamide, DEAA is diethylacrylamide, iPAA is isopropylacrylamide, EMA is ethyl methacrylate. [b] The structures of ruthenium complexes are given in the text. [c] Polymerisation was carried out in methanol. [d] Polymerisation in a water – toluene emulsion.

Thus, elucidation of relationships between the structure and the redox potential of a metal complex, on the one hand, and its catalyic activity, on the other hand, is an important problem, which being solved would provide a clue to the targeted quest for metal complex catalysts and to the choice of optimal conditions for the synthesis of new polymer materials including nanosized polymeric structures.[5, 110]

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