ATRP – POLARIZING / DEPOLARIZING FUNCTIONAL MECHANISM

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Abstract. The Atom Transfer Radical Polymerization (ATRP) in the conventional – copper mediated variant is the main representative case of the controlled radical polymerizations (CRP). That's why, the discussions of the new notions about the complex formation, polymer chains initiation, growth and termination are oriented to comparison with the reactions included in the conventional ATRP mechanism.

The basic postulate of this mechanism is the opinion for reversible haloid atom transfer at every chain growth elementary act. This mechanism however, can not to explain the effect of the ATRP acceleration observed at the vinyl monomers polymerization under of magnetic field influence. That's why, it is proposed a new functional mechanism named: ATRP – Polarizing / Depolarizing Functional Mechanism. The proposed theory submit that the monovalent copper complex chemical activity is a consequence from the complex brief-living molecular structure physical asymmetry. Because of this, the resulting effect is double electrostatic and electrochemical polarization of the complex molecules and following biphase depolarization at the chain grouth and the termination steps.

This mechanism throw additional light not only on the ATRP reversible equilibrium and the haloid atom transfer effects, but also on the motive forces essence at all of the cases by transition metals mediated radical polymerizations with identical complex formation.

Key words: CFM, DMP, PDFM, EMCC, SFED, IMERS.

01. Introduction

At the investigation of the external applied magnetic fields influence on the radical polymerization, it is established that permanent magnetic field (PMF) accelerates the homopolymerization (HPM) [1-5] and radical copolymerization [6] of the vinyl monomers. On the other hand, the impulsive magnetic field (IMF) accelerates the radical copolymerization in bigger degree [7,8,9], but retards the vinyl monomers HPM [5,8,9]. Extremly intriging is the fact, that 2-hydroxyethylmethacrylate (2-HEMA) HPM accomplished by ATRP in an IMF do not retards, but on contrary accelerates [10]. The attempt this phenomenon to be explained by the IMF influence on the ATRP reversible equlibrium is not convincing. This fact causes a doubt on the ATRP conventional functional mechanism (CFM) adequacy, proposed by K. Matyjaszewski and coworcers [11-14].

Convincing argument for the support of this assumption turns out to be the case described in the literature about the ATRP acceleration under of visible light influence

[15]. The autors explain the photoexcitation as consequence from inner-sphere complex formation by charge transfer (CT) between the initiator (R-Cl) and the catalyst (Cu^{I}). This supposition is proved by means of UV-spectral analysis and runs by the scheme: $R\text{-}Cl + Cu^{I} \leftrightarrow [R\text{-}Cl\text{-}Cu^{I}]^{*} \leftrightarrow R^{\cdot} + Cl\text{-}Cu^{II}$, but the precise ATRP photoexcitation mechanism is not clarifyed yet. It is obvious however, that the complex formation discussion as a consequence from CT is an important supplement to the well known from the ATRP CFM notions about complex formation by nitrogen ligands [11-14,18-25,36-53]. The autors however, remain in the CFM frames and allow that inner-sphere complex photoexcitation accelerates the haloid atom dinamix reversible transfer, by which assists the polymerization. This supposition however, does not gives answers of some important questions such as: - Why the haloid atom remains connected by reversible equilibrium with the copper ion only to a defined moment, after that interacts with the copper ion which additionaly oxydates? What are the mechanisms by which the excited complex initiates the polymerization reaction and supports the chain growth? What are the causes for the polymers specific narrow molecular-weight distribution? What are the conditions for the chain growth termination? What are the factors leading to the macro-chains good order discreditation? By what a mechanism the IMF accelerates the ATRP?

By means of o.`s own results [5,7-10] and the known from the literature data [15] analysis, it was made an attempt recently for elucidation of the excited monovalent copper complex formation and ATRP reaction initiation mechanism [16 (Sch. 1)]. As a possible model it was accepted the excitone inductive-resonance mechanism for energy transfer from excited to non-excited complexes by Förster. Subsequently however, render an account of the nature conditons at which the ATRP realises, and the literature data [15] according which the ATRP complex formation realises by CT, in the present work it is accepted a new working hypothesis. This hypothesis permits the springing up of a specific physico-chemical effect - Double Molecular Polarization (DMP) of the complex molecules, which allow that the complexes can to be native excited from the moment of its formation. Because of this, throughout of their vital cycle they initiate polymerization reactions, giving the accumulated energy to the growing polymer chains by means of any specific depolarizing mechanisms. This hypothesis stands in the basis of one new additional attempt for the above-mentioned questions clarification, for which the ATRP CFM and the excitone mechanism do not give satisfactory answers. For this purpose it is proposed a new: ATRP – Polarizing / Depolarizing Functional Mechanism (PDFM), whose main task is to be a theoretical device for assessment of the molecular structure phisical assymetry influence on the excited monovalent copper CT complexes functional activity.

According to the above-mentioned hypothesis, at the initial components mixing: initiator (In), catalyst (Cat), ligand (Lig, L) and monomer (M), in the reaction medium springs up conditions for excited monovalent copper CT complex formation (Fig. 1). Structuraly this complex is composed from electrostatic polarized (ESP) and electrochemical polarized (ECP) molecular fragments. By the o,`s own character it is one excited, unstable molecular system of the initial components transition state at its phisico-chemical transformation. This transformation runs by two consecutive stages: multiple-stage electrostatic depolarization (ESD) and mono-stage elecrochemical depolarization (ECD).

A typical peculiarity of the above mentioned phisico-chemical transformation is the fact that at monomer presence, by the ESD process springs up conditions for activation energy transfer from the excited complex to the monomer. Because of this energy transfer initiates one specific consecutive running chemical reaction, functional connected to the excited comlex. In result from the complex ECD, which finishes off with an irreversible internal molecular electron transfer from the copper to the haloid atom, the Cu^+ ion oxidates to its second positive valency (Cu^{2+}) and an inactive for the ATRP bivalent copper complex ($C\text{-}x^{II}$; Fig. 2) forms. As a consequence from this, the chain grouth in the polymerization reaction stops irreversible.

02. ATRP initiation

It is obvious, that the idea for initiation at the ATRP CFM derives from the classical mode of initiation where under influence of a defined amount activation energy (E_a), the initiator desintegrates to primary radicals. According to the PDFM theory however, the direct transfer of these ideas on the ATRP is incorrect by essence, because of the fact that the initiator – alkyl haloid with α-functional atom is only component for the excited monovalent copper CT complex synthesis. According to the PDFM theory, the ATRP realises in a system from three different by type, but functional connected chemical reactions. The first reaction is synthetic and ensures the synthesis of a double polarized (ESP and ECP) excited monovalent copper CT complex. Because of the spontaneous tendency for electrostatic depolarization (ESD) of the excited complex, at the monomer presence springs up conditions for a specific mode of activation energy transfer from the complex to the monomer, because of which a second consecutive running chemical reaction initiates. This is a polymerization reaction and it proceeds close to a third reaction starting – excited complex electrochemical depolarization (ECD). By its essence, the ECD is an oxy-reduction reaction at which takes a part an electron transfer from Cu^+ ion to the haloid atom, which reduces to its ion state (X^-). At this, the produced Cu^{2+} ion takes a place in an inactive for the ATRP bivalent copper complex ($C\text{-}x^{II}$; Fig. 2), because of which the monomer polymerization stops. As far as any cases of connected by analogus mode chemical reactions is not described in the literature, respective any similar mechanisms for activation energy transfer, in the proposed PDFM theory the ATRP initiation is discussed as biphase process.

1. Synthesis of an excited monovalent copper CT complex, which inner molecular energy because of the DMP effect is asymmetrical distributed between the different by magnitude complex molecular fragments and ensures the complex functional activity. According to the PDFM theory, the excited monovalent copper CT complex synthesis is a stage preceding the ATRP genuine initiation, because of which this stage is named formal initiation.

2. According to the PDFM theory, at the excited monovalent copper CT complex ESD in a monomer presence, springs up conditions for the stage genuine initiation realisation. By its essence, this is a quantum-mechanical mechanism for elementary amounts of activation energy ($E_a^{'}$) transfer by a three-stepe process directed from the excited CT complex to the polymerization reaction. Because of the multy-stepe character of the energy transfer, the polymerization reaction can to be stoped by expedience at any arbitrary monomer conversion, which ensures the characteristic for the ATRP technological flexibility.

02.01. Excited monovalent copper CT complex formation – formal initiation

The proposed mechanism for excited monovalent copper CT complex formation is analogus of some similar known from the literature processes [15,27,28], and represents an attempt for additional clarification of the problem essence. This type processes are defined as complex formation by partial CT, at which obtains excited (E, *) complexes (C) with bridge-like (μ) structure) where the haloid atom hase coordinative number 2 [26]. In the PDFM theory this type excited complexes are marced as: Excited, Bridge-like(μ), Monovalent Copper (MC), CT Complexes (EμMCCTC, shortly EMCC (Excited Monovalent Copper Complexes). It must to be underlined, that the classical mechanism of CT complex formation [15,27,28], is not in condition to explain the ATRP complex formation mechanism fully exhaustively. That`s way, for the additional clarification of this process in the present work are used any fundamental physical dependences.

At the ATRP CFM, the monovalent copper complex formation in general connects to the ligand structure and properties [11-14,18-25,36-53], while in the PDFM theory without this fact to be thrown off, a key role is assigned on the haloid atom (-X) in the initiator molecule R-X.

In the PDFM theory, the excited monovalent copper CT complex formation is considered giving an account of the underlined haloid atom electron affinity, respective its electronegativity. This property displaises at the exchange interaction stage, when the initiator molecule R-X draws closer to the Cu^+ ion of the catalyst Cu-Y (cupros haloid) in the reaction medium (Fig. 1). In general, this property generates strong tendency for tacing away an electron from the Cu^+ ion d-orbital to the haloid atom. If by any reasons this process is not hampered, the Cu^+ ion oxydates to its second positive valency (Cu^{2+}). By principle, similar process facilitates from the circumstance that the Cu^+ ion d-/s- transition energy is rather small and it easy gives second valency electron [17]. Because of the fact however, that the -X atom in the initiator molecule is covalently linked to the fragment R-, and that the Cu^+ ion at the complexing agent (L) presence is fundamentaly dispo sed to complex formation, this principally possible process of the Cu^+ ion direct oxydation can not to runs spontaneously. That`s way, the Cu^+ ion direct oxydatin maces impossible, but creates conditions for an excited monovalent copper CT complex ($C\text{-}x^I$; Fig. 1) formation.

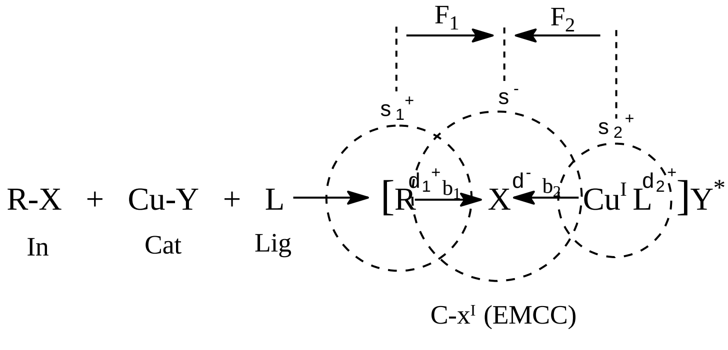

Figure 1. Scheme of the excited monovalent copper CT complex formation according to the PDFM theory. In - initiator. Cat - catalyst. Lig (L) - ligand. $C\text{-}x^I$ (EMCC) – excited monovalent copper CT complex. $-X^{\delta-}$- - central atom. b_1, b_2 – semipolar bonds. δ^-, δ_1^+, δ_2^+ - electrostatic charges. σ^-, σ_1^+, σ_2^+ - superfacial electrical densities. F_1, F_2 - Coulomb′s forces. (On the figure: s = σ; d = δ).

According to the ligand-field theory, at the transition elements compounds synthesis, the inner coordination sphere formation (connecting molecular orbital (MO)) is in result from the recover between the metal atom d-orbitals and the ligand p-orbitals. The obtained complex structure in general expresses by the form: $[Mt^{n+}L_m]X_n$ [27]. By theirs character, the chemical bonds of the coordinative compounds are covalent bonds from donor-acceptor type (semipolar), because of which they are more unstable than the normal covalent bonds [27,28].

According to the PDFM theory (Fig. 1), because of the –X atom high electronegativity in the reaction medium creates conditions that permits to the exchange interaction between d- and p-orbitals of the Cu^+ ion and the ligand electrons, to be added the exchange interaction with the covalently linked –X atom p-electron layer electrons. Because of the orbital overlap creates a generalized conecting MO of the Cu^+ ion complex in which inner coordinative sphere, by the –X atom includs together the initiator and the catalyst molecules. Under of the –X atom influence, the connecting MO is bilateral polarized from an inductive (-I) effect, because of which the molecular fragments R- and –Cu^+L valent electrons are delocalized and directed to the –X atom ($R^{\delta1+}\rightarrow X^{\delta-}\leftarrow Cu^{\delta2+}$) (Фиг. 1). As a result from this, the existing covalent bond R-X polarizes and transforms to a semipolar bond $R^{\delta1+}\rightarrow X^{\delta-}$ (b_1). In the same time, between the –X atom and the fragment -Cu^+L, because of a partial CT creates a new semipolar bond $X^{\delta-}\leftarrow Cu^{\delta2+}$ (b_2). By means of the b_2 bond, the –X atom turns out to be connected to the Cu^+ ion, but because of the b_1 bond existence an additional Cu^+ ion oxidation prevents effective. At the eventual b_1 bond breacing off however, the Cu^+ ion oxidation can not to be prevented. In this case the –X atom accepting an electron from the Cu^+ ion, and passing from atom to its ion X^- state, abandons the complex inner coordination sphere and occupies the place of a second contrary ion in a newly formed bivalent copper complex (C-x^{II}; $[Cu^{2+}L]YX$).

At the case observed (Fig. 1), by means of b_1 and b_2 semipolar bonds, on the –X atom concentrates two partial negative electrostatic charges. That`s way, its electron affinity satiates and the –X atom loads with a generalized electrostatic charge (δ^-) and transforms to a central atom (-$X^{\delta-}$-) of a brief-living EMCC (Fig. 1 – square braskets) with a coordinative number 2. Because of the EMCC structural peculiarities and the difference between b_1 and b_2 bonds origin (b_1 – polarized covalent bond and b_2 – polarized by a partial CT bond), the negative electrostatic charge δ^- must to be considered like composed from two different by magnitude components (δ_1^- and δ_2^-), respective $\delta^- = \delta_1^- + \delta_2^-$, where $\delta_1^- \neq \delta_2^-$. That`s way, at the initial moment of the bonds formation between its energies (E) and lenghts (l) exist brief-living discoordinations. They stipulates a defined amount of the complex excited state asymmetrical (unequilibrium) potential energy (E_p^*) existence, asymmetric distributed between the molecular fragments (R- and –Cu^+L). At this, E_p^* is proportional (≡) of a defined amount asymmetrical electrostatic charge (δ*) and corresponding to him asymmetrical electrostatic potential (φ*) ($E_p^* \equiv \delta^* \equiv \varphi^*$). The spontaneous tendancy that E_p^* to accept values equivalent of the stationary state potential energy (E_p) (when $\delta^* = 0$ and $\varphi^* = 0$) is the source of the EMCC functional activity. In fact its functional activity is consequence from a spontaneous tendency for the system inner energi diminition (-ΔU), which in the end is the cause for the above-mentioned quantities dropping off: E_p^* to E_p value, and δ* and φ* to zero at the end of the excited CT complex vital cycle.

Because of the valent electrons delocalization caused from the bilateral –I effect and the -$X^{\delta-}$- atom electrostatic field effect, the molecular fragments R- and -Cu^+L loads with reciprocal of the δ_1^- and δ_2^- positive electrostatic charges δ_1^+ and δ_2^+ (Fig. 1). The sum of these charges ($\delta_1^+ + \delta_2^+ = \delta^+$) by absolute value is equal of the generalized negative electrostatic charge δ^- ($\delta^+ = \delta^-$), respective $\delta_1^- = \delta_1^+$ and $\delta_2^- = \delta_2^+$.

The electrostatic charges δ_1^+ and δ_2^+ are contrary arranged towards to the charge δ^-, respective towards to the charges δ_1^- and δ_2^-. Under their influence springs up two mutually compensating on the $-X^{\delta-}-$ Coulomb`s forces of attraction: ($F_1 = \delta_1^+\delta_1^-/4\pi\varepsilon\varepsilon_o l_{b1}^2$) and ($F_2 = \delta_2^+\delta_2^-/4\pi\varepsilon\varepsilon_o l_{b2}^2$) [29]. Mechanical moment vectors direction of the forces is mutually contrary and coincides with semipolar b_1 and b_2 bonds directions. They are equivalent of the bonds strenght and compensating on the $-X^{\delta-}-$ ensures the EMCC structural stability (Fig. 1). The structural stability term wants that the equilibrium between F_1 and F_2 forces to be continuously observed from the moment of the excited CT complex formation till to its destruction. The structural stability term ensures due of the continuous quantitive conformity between the semipolar b_1 and b_2 bonds energies and lenghts throughout of the excited CT complex vital cycle duration.

According to the electrostatics, the stationary state potential energy (E_p) of the loaded with an electrostatic charge (q) system is equivalent of the work necessary for the charge shifting of a distance (r) between two points on the field. At this, E_p is proportional of the charge value square and reciprocal of the distance ($E_p = q^2/4\pi\varepsilon_o r$) [29]. In the case concrete, the δ_1^+ charge potential energy on the R- fragment, be apart of a distance l_{b1} from the central haloid atom in fact is the b_1 bond energy and posses value $E_{b1} = (\delta_1^+)^2/4\pi\varepsilon_o l_{b1}$. On o.`s own part, the δ_2^+ charge potential energy on the $-Cu^+L$ fragment, be apart of a distance l_{b2} from the central haloid atom is the b_2 bond energy and posses value $E_{b2} = (\delta_2^+)^2/4\pi\varepsilon_o l_{b2}$. But because of the fact that $\delta_1^- \neq \delta_2^-$, respective $\delta_1^+ \neq \delta_2^+$, follows that at the complex excited state the charges potential energies on the molecular fragments (R- and $-Cu^+L$), respective b_1 and b_2 semipolar bonds energies and lenghts, towards to the symetry center $-X^{\delta-}-$ are not equal too ($E_{b1} \neq E_{b2}$ and $l_{b1} \neq l_{b2}$). It is clear, that the difference between E_{b1} and E_{b2} is quantitative equal of the E_p^* ($E_p^* = E_{b1} - E_{b2}*$) and this is the energetic cause for the EMCC functional activity.

02.02. Superficial electrical density

For explanation of the causes for the asymmetrical (unequlibrium) potential energy E_p^* distribution between the two opposite arranged EMCC molecular fragments, and that the above mentioned equation $E_p^* = E_{b1} - E_{b2}$ to be proved, the DMP hypothesis admits the presence of some effects depending on from the Superficial Electrical Density (SFED (σ)) size, of the adjoined electrostatic charges [29]. This parameter occupy a key role in the hypothesis, because of its responsibility for the E_p^* springing up, for the EMCC ESP degree, and indirectly for the EMCC molecular chemical activity. In the case concrete it is discusses the δ_1^+ and δ_2^+ charges SFED, that are distributed on the different by size and surfaces molecular fragments (R- and $-Cu^+L$) (Fig. 1). It is proved theoretical, that by value σ size is proportional of the charge (q) size and it is reciprocal of the molecular fragment surface (S) size, on which the charge is distributed, respectively $\sigma = q/S$ [29]. Consequently, the σ^- density of the localised on the central haloid atom δ^- charge, can to be presented by the expression $\sigma^- = \delta^-/S_X^{\delta-}$. But since the negative δ^- charge is composed from two components: δ_1^- and δ_2^-, it follows that σ^- consist from two components too: $\sigma_1^- = \delta_1^-/S_X^{\delta-}$ and $\sigma_2^- = \delta_2^-/S_X^{\delta-}$, respective $\sigma^- = \sigma_1^- + \sigma_2^-$.

Because of the fact, that the initiator (alcyl haloid) is low-molecular compound, in the initial moment of the EMCC formation the fragment R- possess more-little volume, respective more-little surface than the fragment $-Cu^+L$. That`s way, the density σ_1^+ of the charge δ_1^+ induced on the fragment R- ($\sigma_1^+ = \delta_1^+/S_R$), must to be bigger than the density σ_2^+ ($\sigma_2^+ = \delta_2^+/S_{Cu^+L}$) of the charge δ_2^+ induced on the fragment $-Cu^+L$, which weight, volume and surface are practically always bigger because of the ligand L contribution

($S_{Cu^{+}L} >> S_R$), respective $\sigma_1^+ > \sigma_2^+$. Consequently, the difference $\sigma_1^+ - \sigma_2^+ = \Delta\sigma^+$ between the electrical densityes σ_1^+ and σ_2^+ is proportional of the difference $\delta_1^+ - \delta_2^+ = \Delta\delta^+$, between the positive electrostatic charges δ_1^+ and δ_2^+. In fact, the $\Delta\delta^+$ charge is already defined asymmetric electrostatic charge δ^* ($\Delta\delta^+ = \delta^*$), and as it is underlined, δ^* is proportional of the asymmetrical electrostatic potential φ^* and energy E_p^*.

According to the theory [29], at an electrostatic field the potential (φ_M) of a defined point (M) on the field, be of a distance (r) from the charge (q) creating the field, is equal of the quotient of the charge size and the distance to the point, respective $\varphi_M = q/4\pi\varepsilon_o r$. In the case concrete (Fig. 1), the charges δ_1^+ and δ_2^+ (corresponding to the potentials φ_1^+ and φ_2^+) on the molecular fragments R- and -Cu$^+$L determination is executed towards the potential φ^- of the charge δ^- concentrated on the -$X^{\delta-}$- atom. If it is possible that the potential φ^- to be accepted as a base (conventional zero), the energetic asymmetry (in electric equivalent) of the semipolar b_1 and b_2 bonds can to be reported by him, i. e. towards to the central haloid atom observed as the EMCC molecular structure symmetry center.

By an analogy with δ^- and σ^-, φ^- is two-components composed too ($\varphi^- = \varphi_1^- + \varphi_2^-$), where φ_1^- is the δ_1^- charge potential at σ_1^- electric density, and φ_2^- is the δ_2^- charge potential at σ_2^- electric density. Since by the absolute value $\sigma_1^+ = \sigma_1^-$, and $\sigma_2^+ = \sigma_2^-$, at the l_{b1} and l_{b2} bonds lenghts, the potential φ_1^+ can to be presented as $\varphi_1^+ = \varphi_1^-/4\pi\varepsilon_o l_{b1}$, and the potential φ_2^+ as $\varphi_2^+ = \varphi_2^-/4\pi\varepsilon_o l_{b2}$. Because of the fact that φ^-, respective φ_1^- and φ_2^- are accepted as basic values ($\varphi_1^- = 0$ and $\varphi_2^- = 0$) towards which φ_1^+ and φ_2^+ are accounted, than the differences $\varphi_1^+ - \varphi_1^- = \varphi_1^+$ and $\varphi_2^+ - \varphi_2^- = \varphi_2^+$ by essence are the potential differences on the semipolar b_1 and b_2 bond ends, i. e. φ_1^+ on the b_1 bond ends and φ_2^+ on the b_2 bond ends. But after that $\sigma_1^+ > \sigma_2^+$, it follows that $\varphi_1^+ > \varphi_2^+$. The deduction show, that towards to the electric symmetry center (-$X^{\delta-}$-), the b_1 bond is polarized in a bigger degree than the b_2 bond with the asymmetrical electrostatic potential (φ^*) value ($\varphi_1^+ - \varphi_2^+ = \varphi^*$). That`s way, the EMCC chemical activity as an E_p^* function can to be quantitive estimated by the φ^* value on the b_1 bond ends, by which value this bond is polarised in a bigger degree towards to the b_2 bond.

By principle, the potential energy E_p and the potential φ are not equivalent quantities, but between them exist the functional dependence $E_p = q\varphi$ [29]. This dependence permits that the potential equation $\varphi_1^+ - \varphi_2^+ = \varphi^*$ can to be transformed to an energy equation, which permits that E_p^* can to be estimated by means of the b_1 and b_2 bonds energies. So that of the φ_1^+, φ_2^+ and φ^* potentials corresponds proportional electrostatic charges: of the $\varphi_1^+ \rightarrow \delta_1^+$, of the $\varphi_2^+ \rightarrow \delta_2^+$ and of the $\varphi^* \rightarrow \delta^*$, than $\delta_1^+\varphi_1^+ = E_{b1}$, $\delta_2^+\varphi_2^+ = E_{b2}$ and $\delta^*\varphi^* = E_p^*$. From the potential equation analogy follows thet $E_{b1} - E_{b2} = E_p^*$, respective $E_{b1} > E_{b2}$. This conclusion confirms the affirmation from paragraph 02.01., where $E_p^* = E_{b1} - E_{b2}$. Consequently, the b_1 bond energy is bigger than b_2 bond energy with the asymmetrical potential energy E_p^* value of the excited CT complex.

03. ATRP chain growth

03.01. Monomolecular chain growth

At real conditions, EMCC formation realises in a monomer presence, because of which the process is depending on from the electrostaic coordination efficiency between the semipolar b_1 bond active centers -$C^{\delta 1+} \rightarrow X^{\delta-}$- (potential φ^* on the b_1 bond ends) and δ^- and δ^+ charge potentials on the polar monomer molecules (polar factor (*e*); Q-*e* scheme [30]). In fact, this is a natural mechanism for the two-centred electrostatic coordination of the monomer molecules to the complex, and their electoral join to the growth polymer chain, as it is shown (Fig. 2).

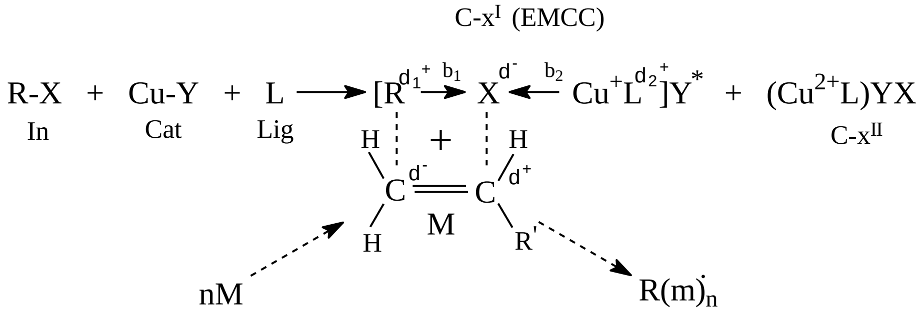

Figure 2. Scheme of the two-centred electrostatic monomer molecule (M) coordination to the excited monovalent copper CT complex (C-x^I; EMCC). In - initiator, Cat - catalyst, Lig - ligand, C-x^{II} – bivalent copper complex. nM – n in number monomer molecules. $R(m)\cdot_n$ – growing macroradical. (On the fig. d =δ).

At successful two-centred electrostatic coordination and chain growth process development, at every elementary act of monomer join the fragment R- (Figs. 1, 2) by every one monomer link, consecutively increases o.`s own molecular weight and surface. Consequently, the electrical density σ_1^+ of the charge δ_1^+ on the fragment R- still more decreases and in a defined moment maces level by value of the density σ_2^+ of the charge δ_2^+ on the fragment -Cu$^+$L ($\sigma_1^+ = \sigma_2^+$). In parallel, with the tendency for the charges δ_1^+ and δ_2^+ electrical densities macing level, runs process of the E_p^* value and b_1 bond electrostatic polarization degree diminition ($E_p^* \rightarrow E_p$, and $\varphi^* \rightarrow 0$). That`s way, at the moment when δ_1^+ and δ_2^+ charges electrical densities maces level the φ^* value happens equal of zero ($\varphi^* = 0$, and $E_p^* = E_p$), the polarity of the b_1 bond equalizes with this of the b_2 bond ($\varphi_1^+ = \varphi_2^+$) and the EMCC structural stability violates because of its passing to an electrical neutral state. This state is unstable and in the following moment, with the consecutive monomer molecule join comes an electrical balance dramatic violation, i. e. the φ_1^+ value becomes more-litle than the φ_2^+ value. Than the semipolar b_1 bond breaks off, the brief-living mechanical balance between the F_1 and F_2 Coulomb`s forces violates and the EMCC molecule destrois. At this moment, because of an inactive for the ATRP bivalent copper complex (C-x^{II}) formation the polymer chain growth reaction stops. Obviously, the moment when σ_1^+ and σ_2^+ densities of the δ_1^+ and δ_2^+ charges maces level ($\varphi^* = 0$), marcs the end of the chain growth because of the fact that the E_p^* exhauts to E_p value. This event depends on from the fakt that in the moment of these values (σ_1^+ and σ_2^+) equalization the process hase quantitative character and runs irreverseby by high accuracy.

03.02. ATRP genuine initiation

It is obvious, that the moving forces for the processes two-centred electrostatic coordination and polar monomer molecules join to the EMCC, are the asymmetrical electrostatic potential φ^* on the semipolar b_1 bond ends, and the polar factor (*e*) of the joining monomer molecules [30]. In fact, the successful two-centred electrostatic coordination depends on from the charges δ_1^+ and δ_1^- electrostatic fields intensity on the b_1 bond ends, and the charges δ^- and δ^+ electrostatic fields intensity on the double-bonded monomer molecule (Fig. 2).

It is underlined that according to the PDFM theory, the ATRP realises in a system from three different by type but functional connected chemical reactions. Structural and functional the connection between them realizes at the electrostatic coordination and monomer join stage on the semipolar b_1 bond zone. This stage ensures activation energy $E_a^{\prime}$ transfer from the EMCC to the polymerization reaction, at every elementary act of the polymer chain growth by three consecutive steps.

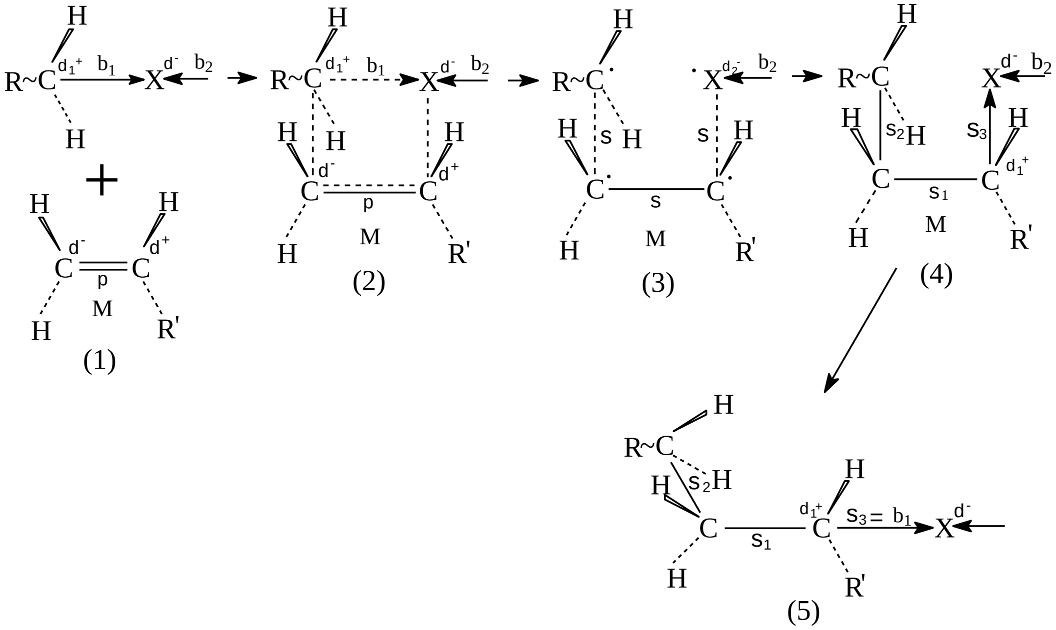

Figure 3. Scheme of the two-centred electrostatic coordination and monomer (M) insertion to the EMCC polar centers ($R\sim C^{\delta 1+}\rightarrow X^{\delta -}$-) - initial act of the interaction and the consecutive chain growth. δ^- and δ^+ - induced electrostatic charges on the R' carbo atoms of the monomer molecule. (On the figure: d = δ; s = σ; p = π).

1. The first step of the energy transfer from the EMCC to the polymerization reaction ensures an elementary portion activation energy for the two-centred electrostatic coordination ($E_{ec}^{\prime}$) between the polar monomer molecule (M) and the b_1 bond polar centers (-$C^{\delta 1+}\rightarrow X^{\delta -}$-) (Fig. 3, (1)). The energy exchange runs likely interaction between electrostatic fields and it is proportional of the work necessary for the reciprocal electrostatic charges moving each to other, up to the moment of an effective quantum-mechanical exchange interaction begining.
2. The second step of the energy transfer depends on from quantum-mechanical causes. At sufficient drawing together between the b_1 bond σ-electrons and the double-bonded monomer π-electrons, the electrostatic interraction between the electrostatic charges drops off, but begins exchange interaction at which starts the genuine initiation of the polymerization reaction (Fig. 3 (2)). The genuine initiation is a consequence from the energy transfer at the valent electrons spin evolution. It runs as transformation of the characteristic for the monomer carbon atoms sp^2 hybridization of the π-bonds, up to the typical for the satureted compounds sp^3 hybridization of the σ-bonds. At the transformation process forms one transitional – Inter-Molecular Electron-Resonance Structure (IMERS), which possess four-membered ring-shaped configuration (Fig. 3 (2)). The IMERS obtained is a brief-living inter-molecular structure, which because of the

unsufficient π-electrons number and the heteroatom ($-X^{\delta-}-$) presence, do not possess aromatic stability and it is exceptionally unstable [27]. Throughout of the IMERS brief-living vital cycle however, because of the aforesited electron-resonance ensures conditions for effective valent electrons spin evolution and energy exshange.

Under of the exchange interaction influence and $-X^{\delta-}-$ atom bilateral –I effect in the IMERS system induces S→T / T→S electron transitions, which violates its stability. Because of the S→T transitions the monomer molecule π-bond and the semipolar b_1 bond breaks off, which leads to three radical pair(s) (RP, RPs) formation. The first RP originates from the monomer molecule and it is a covalently linked RP (biradical $>C^{\bullet}—C^{\bullet}<$) (Fig. 3, (3)). The second RP is uncoalently (||) linked ($R\sim C^{\bullet}H_2 \parallel >C^{\bullet}-$) and forms between growing macroradical $R\sim C^{\bullet}H_2$ and the left biradical carbon atom ($>C^{\bullet}-$). The third RP is uncovalently linked too ($-C^{\bullet}< \parallel {}^{\bullet}X^{\delta 2-}-$) and forms between the $-X^{\delta 2-}-$ atom and the right biradical carbon atom ($-C^{\bullet}<$) (Fig. 3, (3). Because of the temporarily preservation of the b_2 bond covalent character, the component $-X^{\delta 2-}-$ possess partial negative charge δ_2^- and displays as a brief-living ion-radical (${}^{\bullet}X^{\delta 2-}-$). In a result from the T→S transitions and the recombination between the uncovalently linked RPs singlet electrons, except presenting in the biradical ($>C^{\bullet}—C^{\bullet}<$) σ_1 bond, forms two new σ bonds - σ_2 and σ_3 (Fig. 3, (4)). The σ_1 and σ_2 bonds are normal covalent bonds, while the third - σ_3, finding itselfs under of the central haloid atom influence is strongly polarized, and by essence restores the breaked off in the previous stage semipolar b_1 bond ($\sigma_{3\,=}\,b_1$) (Fig. 3 (5)). Because of the b_1 bond breaking off and its consecutive reconstruction with one monomer link more forward, the monomer molecule join resembles an insertion process between the EMCC polar centers ($-C^{\delta 1+}\rightarrow X^{\delta-}-$). Without the insertion, the prolonged with a monomer link (m) fragment $-C^{\delta 1+}$, by the restored b_1 bond remains connected to the haloid atom ($-Cm^{\delta 1+}\rightarrow X^{\delta-}-$).

According to the PDFM theory, the ATRP chain growth is consequence from a quantum-mechanical process of IMERS formation and degradation to radicals, because of the exchange interaction and the induced by the $-X^{\delta-}-$ atom S→T / T→S transitions. The IMERS role as connecting link for energy transfer to the polymerization reaction at the valent electrons spin evolution is analogous of the ideas generalized in the non-adiabatic reactions theory [31]. In the case concrete, the IMERS role well coordinates with the quantum-mechanical process of an energy transfer between near arranged potential surfaces at S→T / T→S electron transitions, attended the valent electrons spin evolution. This conclusion confirms the comprehension, that the ATRP genuine initiation derives from the quantum-mechanical transport of a portion activation energy ($E_{gi}{}'$) in a non-adiabatic transition process to the polymerization reaction. The transport repeats repeatedly at every elementary act of the chain growth, and because of this can to be stoped or restored at any arbitrary for the ATRP development stage.

3. The third step of an energy transfer from the EMCC to the polymerization reaction is connected with a portion of activation energy consumption for the primary conformational adaptation ($E_{pa}{}'$) at the consecutive elementary link integration to the growth chain. This energy posses quantum-mechanical character and it is function of the IMERS brief-living electron-resonance stability, because of which at this energy exhaust the four-membered ring-shaped IMERS planar configuration desintegrates. This event depends on from the energetic disadvantageous at the σ_2 and σ_3 bonds overshadowed conformation after their formation. Under of the carbo atoms valent angles influence (109^{o}, $28'$) springs up a tension, which by a partial rotation around the σ_1 bond ensures

thermodinamic more-advantageous gauche conformation between the bonds. The eliminated at the rotation energy utilizes under of a heat form in the reaction medium. According to the PDFM theory this process is the necassary quantum-mechanical condition for the primary conformational adaptation of the last monomer link to the chain (Fig. 3, (4,5)).

In general, the analysis of the functional dependences between the above-mentioned three connected reactions show that for every act of monomer join it is necessary an elementary amount of activation energy $E_a{}'$, which uses up by three steps: a/ at the electrostatic coordination - $E_{ec}{}'$, b/ at the genuine initiation - $E_{gi}{}'$ and c/ at the primary conformational monomer links adaptation – $E_{pa}{}'$, respective $E_a{}' = E_{ec}{}' + E_{gi}{}' + E_{pa}{}'$.

03.03. Radical pairs paramagnetic properties

Because of uncoupled electrons presence in the IMERS both, the biradicals and the uncovalently linked RPs possess paramagnetic properties. That`s way the RPs can to interact with external applied magnetic fields (PMF or IMF), which permits its existence to be experimental proved. At the ATRP accomplished in an IMF this property is practical presented, and it is proved that under of a magnetic field influence, the polymerization velosity and productivity increase at least two-fold [10,16].

The affirmation for the RPs paramagnetic properties existence derives from the results described in the quoted works [5,7-10,16] and it can to be correctly well founded by the mechanisms known from the N. Turro`s works [1,2,32,33]. According to this autor, the polymerization reactions magnetic sensitivity depends on of the RPs triplet character, formed at the thermo-destructive initiators homolytic cleavage. The RPs triplet character promotes theirs more long vital cycle, and in general the significant polymerization reactions acceleration.

Under influence of this classical setting, the PMF and the IMF effects on the results in the quoted works [5,7-10,16] was discussed as consequence from the RPs triplet character obtained at the thermo-destructive initiators degradation. It turns out however, that such an approach is inapplicable regarding to the ATRP. According to the PDFM theory, the ATRP initiation depends on of a quantum-mechanical energy transfer from the EMCC to the monomer. That`s why, the ATRP magnetic sensitivity binding to the RPs triplet character is groundless. In case opposite, because of the RPs triplet character the $T \rightarrow S$ transitions in the IMERS system will be embarrased, which shall prolong the time for the σ_2 and the σ_3 bonds formation (Fig. 3 (2,3,4)). Because of this cause in a corresponding degree to the magnetic field character, the ATRP velosity and productivity will be decreased.

Acoording to the PDFM theory, the ATRP acceleration under of a magnetic field influence [10,16] is more well-grounded to be discussed as consequence from quantum-meschanical causes and more-especially, as a consequence from the Cu^+ ion polarizing paramagnetism induced by magnetic field. This property displays under of an external applied magnetic field influence on the diamagnetic molecules containing transition element atom when its electron cover symmetry is violated [34]. In fact, the semipolar b_2 bond existence in the EMCC molecule depends on namely of the Cu^+ ion d-orbital deformation provoced from the haloid atom –I effect. Under of an external applied magnetic field influence, the violated symmetry creates measurable paramagnetic receptivity (χ_p) and arouse the Cu^+ ion polarizing paramagnetism. At the Larmor`s precession all of the electrons precessed upon parallel surfaces, perpendicularly situated towards to the external applied magnetic vector. That`s way, the electron spin-magnetic moments are oriented to this vector direction, because of which the Cu$^+$ ion electron cover obtains an anisotropic magnetic polarization. At these conditions the energy barier for d-/s-transitions in the Cu$^+$ ion electron cover increases above on the normal value, because of which the complex becomes more stable and the Cu$^+$ ion oxydation to its Cu^{2+} ion state embarrasses. As a result from this the EMCC vital cycle becomes longer, the coordinated and the joined monomer molecules number increase, respective ATRP velosity and productivity increase too [10,16].

Because of the triplet RPs partitipation thrown-off as unacceptable in relation to the ATRP acceleration, the observed phenomenon about the IMF extremal effects on the ATRP [10,16] can to be explained as a consequence from an frequency beating effect springing up at the interference between the IMF impulsive component frequency and the S→T / T→S elektron transitions frequency. It is logical to expect that the frequency beating maximal amplitude shall be correspond to the most effective energy exchange between the EMCC and the monomer at the S→T / T→S transitions, which can to be decisive factor for the more faultlesly σ_2 and σ_3 bonds formation. That`s way, at the defined magnetic induction (B) and pulsatile coefficient (P) values, the ATRP velosity and productivity increase considerably [10,16].

03.04. Bimolecular chain growth

By its mechanism, the Atom Transfer Radical Coupling process (ATRC), known from the ATRP CFM and practice [22,38], logical confirms the proposed PDFM theory. In fact, the ATRC meaning for the ATRP reduces to an uncomon for this method example for bimolecular chain grouth finishing. Towards to the PDFM theory however, this fact has a big meaning because of that it proves the DMP effect existrnce. According to the PDFM theory, the DMP effect creates conditions for a two-centred electrostatic interaction and coordination between the polarized complex molecules obtained in the reaction medium, which is prerequisite for bimolecular chain grouth and termination (Fig. 4).

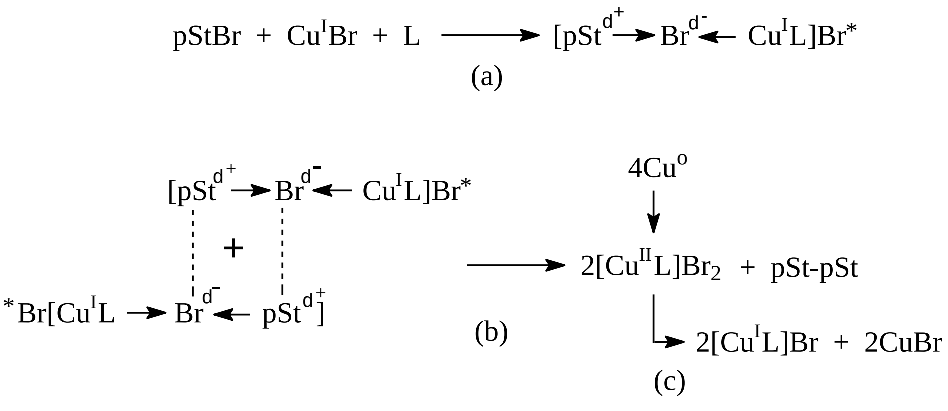

Figure 4. Scheme of the bimolecular ATRC chain grouth according to the PDFM theory. (a) – excited pSt-complex formation before the coupling reaction begining. (b) – excited pSt-complexes two-centred electrostatic coordination, pSt-dymer formation by coupling reaction, respective bimolecular chain grouth termination. (c) – deactivator reduction to the initial components by nanodispersed Cu^o. (On the fig. d = δ).

By the ATRP CFM, the ATRC principle is to force the macroradicals recombination formed in the active reaction phase by drastic reduction of the deactivator concentration in the system. It is accepted, that by the ATRP activity suppression the ATRP eqilibrium can to be so affected, that it shall be reached more big macroradicals concentration in the system and by this maner to be favorised the bimolecular termination [22,38].

According to the PDFM theory however, the pStBr-macroinitiators at the catalyst and the ligand presence forms excited electrostatic polarized polystyrene complexes (a), that coordinates mutualy at the coupling reaction (b). By the bringing of a big amount of high-active reductor (nanodispersed Cu^o) (c), it is do not influences any equlibrium, but prevents deactivator obtain at the synthetic reaction phase, because of which the polystyrene complexes remains in ESP state. According to the PDFM theory, this state creates possibilities for an effective electrostatic coordinaton between the neighbouring excited complex molecules and macroradicals recombination, respective for a bimolecular chain grouth stimulation, i. e. for a bimolecular chain grouth termination (Fig. 4).

04. ATRP chain grouth termination

04.01. Electrochemical polarization and depolarization

Except the EMCC ESP effect, the DMP hypothesis admits any other effects existence, which are consequence from the excited complex electrochemical polarization (ECP). These effects are consequence from the specific for the excited complex inner molecular grouping $-X^{\delta-}\leftarrow Cu^{+}L$ existence, which conteins the components of one oxy-reduction pair ($X^{\delta-}/Cu^{+}$) (Фиг. 1). Under of the b_1 bond unequilibrium electrostatic potential φ^* influence, in the initial moment of the EMCC formation, this pair is in inactive state (by structure blocked). Depending on from the haloid atom type (Cl, Br, J), this pair posses specifc oxy-reduction potential ($\varphi_{o/r}$). This potantial can to appears on the semipolar b_2 bond ends only when the $X^{\delta-}/Cu^{+}$ pair can to be by structure unblocked, i. e. when because of an electrostatic depolarizing process the potential φ^* drops of to zero and b_1 bond is breaked off. In fact, this electrochemical potential is already described potential φ_2^{+} ($\varphi_{o/r} = \varphi_2^{+}$). It is charecteristic, that this potential latently exist on the b_2 bond ends while the chain growth reaction is active, i. e. while the EMCC electrostatic depolarization (ESD) is not finished and the semipolar b_1 bond is not breaked off.

It is explained that with the b_1 bond breaking off creates conditions for an electron transfer from $-Cu^{+}L$ to $-X^{\delta-}-$, at which the haloid atom reduces to its ion X^{-} state. This is a key event for the EMCC following destiny. With him drops off the structural limitations for the oxi-reduction pair $X^{\delta-}/Cu^{+}$ activation, and this gives possibility for potential $\varphi_{o/r}$ phisical transformation. By its essence, the electron transfer from $-Cu^{+}L$ to $-X^{\delta-}-$ is the basic mechanism for the oxy-reduction pair $X^{\delta-}/Cu^{+}$ ECD, respective of the EMCC transformation. In result from this electron transfer the b_1 bond breaks off, the semipolar b_2 bond potential φ_2^{+} drops off to zero ($\varphi_2^{+} = 0$, respective $\varphi_{o/r} = 0$), the EMCC destroys and the chain growut reaction instantly and irreversible stops. The moment when the potential $\varphi_{o/r}$ drops off to zero, Cu^{+} ion oxydates to its Cu^{2+} ion state and a bivalent copper complex ($C\text{-}x^{II}$) obtains sets in so characteristic, that it can to be established visual – the reaction medium color changes from broun-redish to blue-green.

Because of the fact, that the central haloid atom $-X^{\delta-}-$ is common possession both, the electrostatic polarized EMCC molecule, and the electochemical polarized oxy-reduction pair $X^{\delta-}/Cu^{+}$ (Fig. 1), the processes in the two systems runs consecutively. That`s way, the direct Cu^{+} ion oxydation to Cu^{2+} ion state do not runs spontaneously before the EMCC ESD finishing. By phisical stipulated causes however - higher polar components concentration in the reaction medium and because of this facilitated electrostatic interactions, the ESD alwais runs before ECD. As it is shown, the ESD process can to runs both, in the presene or at the monomer absence. In the first case as ESD between the excited complexes and the monomer molecules (Fig. 2) and in the second as mutual ESD between the neighbouring excited complex molecules (Fig. 4).

04.02. Macrochain formation

At the radical chain growth discussion it is used the term insertion process. The purpose is to be achieved bigger clearnes about the mode of the monomer molecules join to the chain. At the free-radical polymerization theory the growth by monomer join has a simple meaning. This is a process of monomer join of the last to the before-last molecule, by two-valent electrons gemination.

At the ATRP however, because of the semipolar bond existence between the EMCC active centers ($-C^{\delta 1+} \rightarrow X^{\delta -}-$), the monomer join is more complicated and looks like as monomer insertion into the excited complex molecule (Figs. 2,3). At this case the monomer join pass throughout preliminary two-centered electrostatic coordination, breaking off the existing chemical bond and creation of two new σ bonds (σ_2 and σ_3), by four valent electrons gemination. Obviously, the number (n) of the consecutive monomer molecules insertion in the EMCC molecule is an important parameter for the polimerization process assesment, as it has important attitude to the chain growth at the EMCC ESD process.

The monomer molecules insertion and join to the EMCC active centers pass by radical mechanism. At this both, the existing b_1 bond breaking off, and the new σ bonds creation in the frames of the brief-living IMERS (Фиг. 3 (2,3,4)), pass without any electron transfer: in the first case by keeping of the o.`s own atomic electrons, and in the second by these electrons gemination. This means that the uneqilibrium amount of the EMCC electrostatic polarizing inner energy (ΔU_{esp}) proportional of the E_p^* ($\Delta U_{esp} \equiv E_p^*$), do not utilizes in direct electrostatc charges neutralization, but at any others energetic transition processes about the two-centred electrostatic coordination, genuine initiation and the phase transformations attendant the monomer aggregate state change.

The chain growth progress to the terminal product with middle-numbered molecular weight M_n is a sequence from the consequtive join of n in number monomer molecules to the growth radical and leads to change of the aggregate state from liquid of the monomer to solid of the polymer. From thermodynamix point of view this is a typical case of phase transition process connected with the particals number and the system degree of freedom diminition, respective with entropy diminition, because of which for its realisation it is necessary energy expense. At the case concrete, this is the mentioned above EMCC electrostatic polarizing inner energy ΔU_{esp} which diminition at the ESD is identical by absolute value of the amount electrostatic depolarizing inner energy ($-\Delta U_{esd}$) diminition ($\Delta U_{esp} = -\Delta U_{esd}$). This energy diminition realises by n in number elementary amounts inner energy ($-\Delta U_{esd}'$), proportional of the elementary amount activation energy E_a', necessary for every act of monomer join realisation. By this way, because of the EMCC ESD at the end of the chain growth ensures general system inner energy diminition by the electrostatic depolarization with a value $-\Delta U_{esd}$ ($-\Delta U_{esd} = n.-\Delta U_{esd}'$). Throughout of the chain growth process, of every consequtive monomer link join and proportional inner energy diminition with the value $-\Delta U_{esd}'$, corresponds a material chain conformational optimization process, and more advantageous for the concrete conditions molecular structure.

05. Generalized ATRP functional scheme

The PDFM theory proposed a new generalized ATRP functional scheme (Fig. 5), which show the conections between the different by type, but functional connected chemical reactions characterising this method. The basic reaction is synthetic (a), which if realises by macroinitiators in monomer absence (bimolecular chain growth – Fig. 4), because of the pSt-complexes mutual ESD, leads to the transition metal bivalent complex (C-x^{II}) and polystyrene dimer (pSt-pSt) formation. In a monomer presence however (Figs. 2, 5), because of the EMCC formation, the polar monomer molecules two-centred electrostatic coordination and by the IMERS participation creates conditions for quantum-machanical activation energy transfer, by which initiates a specific polymerization reaction (b).

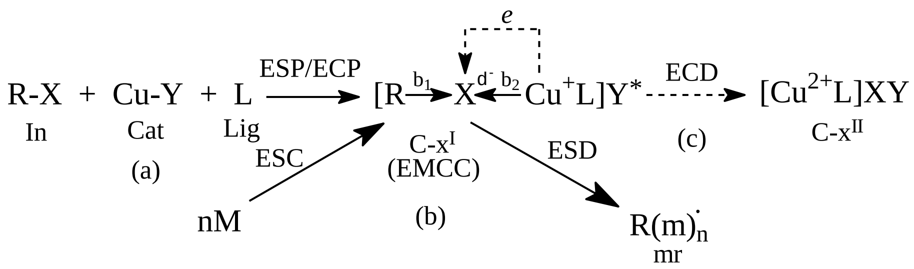

Figure 5. Generalized ATRP functional scheme. In – initiator. Cat – catalyst. Lig – ligand. C-x^{I} (EMCC) – excited Cu^{+} complex. nM – n in number monomer molecules. ESC – electrostatic coordination process. ESP/ECP – electrostatic and electrochemic polarization. ESD – electrostatic depolarization. ECD – electrochemic depolarization. m – monomer links. mr – macroradical. *e* – electron. C-x^{II} – Cu^{2+} complex. (On the figure; d = δ).

Tthe polymerization reaction (b) initiation is consequence from the EMCC spontaneous inner energy diminition, which realizes as an irreversible ESD process. At monomer presence the ESD, respective E_p^* exhauting till to E_p value is multy-stage process. In result from the chain growth arizes up a moment, when the EMCC ESD finishes and a polymer product (macroradical - mr) obtains. At this moment starts by the structure blocked till now mono-stage EMCC ECD process (c). The ECD is process of an irreversible single time electron (*e*) transfer from the monovalent copper ion to the haloid atom, at which the copper ion additionaly oxydates and the haloid atom reduces to its ion state. In the same time the conection between the macroradical and the haloid ion breaks off and the haloid ion pass to the external coordination sphere of one new-formed bivalent copper complex C-x^{II} (c) (Fig. 5). In result from this the EMCC destroys and the chain growth reaction stops. In a next stepe, the macroradicals (mr) being in condition to finish its growth bimolecularly, can to form double by weight but halogen-uncaped polymer molecules. At real conditions however, when the aim is to be obtained well defined polymers the polymerization reaction stops at a more-early stage, and do not permits that the bimolecularly terminated macrochains number to exceed several per-cents [14,18,20,37].

06. ATRP energetic balance

It is established that the polymerization process thermodinamix determines in general by the chain growth reaction, because of that the stages of initiation and chain growth termination are unrepeated acts [35]. Independently from this, the initiation stage requests a defined amount of activation energy E_a expense, for the initiator degradation to primary radicals. At the free-radical polymerization the activation energy penetrates from an external for the system source. According to the PDFM theory, at the ATRP conditions this source is the accumulated at the EMCC formation unequilibrium potential energy E_p^* of the excited state, which is proportional of a part from the EMCC inner energy. This part is asymmetric distributed on the EMCC molecular fragments, and it is marced as electrostatic polarizing inner energy (ΔU_{esp}), respective $E_p^* \equiv \Delta U_{esp}$. But an inner energy asymmetric distribution is cause for unstability, which compensates by one spontaneous process of the energetic diferences equalization between the EMCC molecular fragments (R- and $–Cu^+L$).

In the case concrete, this act achieves by the unequilibrium part of the electrostatic polarizing inner energy ΔU_{esp} exhaust, under form of n in number elementary amounts inner energy of the electrostatic depolarization ($-\Delta U_{esd}'$). These amounts are proportional of the mentioned above elementary amounts activation energy E_a', necessary for the two-centred electrostatic coordination, genuine initiation and the macrochains primary conformational organization at every act of monomer insertion ($E_a' \equiv \Delta U_{esp}/n = -\Delta U_{esd}'$). The consequtive ΔU_{esp} diminition (consumption) by n in number elementary amounts of $–\Delta U_{esd}'$ values outlines the borders of the EMCC active state. They extends between the EMCC and monomer two-centred electrostatic coordination beginning and the EMCC ESD conclusion. From energetic point of view this means, that after EMCC ESD finishing and ΔU_{esp} exhaust, the excited till now complex molecule pass to an unexcited state. This state corresponds to the general EMCC inner energy diminition ($–\Delta U_{esd}$), because of an electrostatic depolarization by n in number times by $–\Delta U_{esd}'$ values ($–\Delta U_{esd} = n.–\Delta U_{esd}'$). As it is mentioned above, at the polymerization advance comes equalization of the charges δ_1^+ and δ_2^+ densities distributed on the molecular fragments (R- and $–Cu^+L$), and EMCC passage in an unexcited state. The EMCC staying in this state is brief-living and after b_1 bond breking off, for the $X^{\delta-}/Cu^+$ oxy-reduction pair unlocks an ECD mechanism (Fig. 5). This process is irreversible single act of an electron (*e*) transfer, because of which the oxy-reduction potential $\varphi_{o/r}$ instantaneously exhausts to zero value ($\varphi_{o/r} = 0$). By its esence, this is one additional by electrochemical depolarization inner energy ($-\Delta U_{ecd}$) diminition. It must to be outlined however, that the energy $-\Delta U_{ecd}$, eliminated at the EMCC ECD is fully wasted for the polymerizatin process. At this oxy-reduction reaction, the potential $\varphi_{o/r}$ physical transformation can not to be realised for the polymer obtain and it utilizes under of a heat form. In fact, this is the heat of the bivalent copper complex $C\text{-}x^{II}$ formation. Consequently, at full EMCC depolarization, the general inner energy diminition ($-\Delta U$) must to be equal of the sum from the two consecutive depolarizing processes: electrostatic ($-\Delta U_{esd}$) and electrochemical ($-\Delta U_{ecd}$), i. e. $-\Delta U = -\Delta U_{esd} + (-\Delta U_{ecd})$.

07. Polymer properties

07.01. Molecular weight distribution

The polymer products obtained by an ATRP process have controlled properties and categoryzes as well defined polymers. According to the PDFM theory, the middle-numbered molecular weight (M_n), the parameter of polydispersity (M_w/M_n), respective molecular-weight distribution (MWD) are function of the EMCC ESD development in general. It is explained that the moment when the electrical densities σ_1^+ and σ_2^+ of the δ_1^+ and δ_2^+ charges makes level by value, and the potential φ^* on the semipolar b_1 bond ends eliminates exactly marks the chain growth end. These values have concrete phisical essence and because of this, its making level by value comes by high accuracy and hase quantitative character. The quantitative conection between them defined characteristic for the ATRP method both, the middle-numbered molecular weight M_n, and the parameter of polydispersity M_w/M_n, respective molecular-weight distribution MWD of the polymers obtained. Because of this cause, up to a defined degree of polymerization, M_n grow in liniar dependence from the conversion (q) magnitude, respective from the number n of the joined monomer molecules, and M_w from the number of the integrated monomer molecules with defined molecular weight magnitude.

Any factors exist however, that impedes the normal EMCC ESD runing and leads to the polymers MWD worsen. The PDFM theoretic analysis show, that at the chain growth reaction progress, the two-centered electrostatic coordination and the monomer molecules join to the semipolar b_1 bond polar centers ($-C^{\delta 1+}\rightarrow X^{\delta -}-$) (Fig. 2), gradually worsens. This effect is consequence from the inevitable φ^* potential tendency of movement to zero, and electrostatic attraction intensity between the monomer molecules and the polar centers $-C^{\delta 1+}\rightarrow X^{\delta -}-$ diminition. So it is reaches to a state similar of a completed ESD, when macroradicals ($R\sim C^{\bullet}H_2$) in the monomer presence, can continue to grow by the free-radical polymerization laws. Similar uncontroled ATRP development is described in the literature [12,14,18,20]. It favorises from the polymerizable system viscosity increase, because of which the bimolecular chain growuth facilitates. By this cause, the high macrochains regularity and suitable polymers MWD reaches at the polymerization velosity lowering and comparative litle values of the conversion [14,20,22,36-39]. In the case opposite the chains reguliarity and MWD violates to such degree that happens equal of the free-radical polymerization [12,14].

07.02. Macrochains reguliarity

The conclusion, that the reguliarity and the tacticity of the polymers by ATRP obtained are not distinguishable from these obtained at the free-radical polymerization [12,14] is the reason that the coordination mechanism of the monomer join to be thrown off as possible. From the PDFM theory point of view however, this conclusion is not well grounded theoretically, independent from the likeness with the free radical polymerization. This likeness can to be plausable explained by the circumstance that the EMCC molecules have bridge like (μ) (linear) structure, and that the semipolar b_1 bond is single bond (Fig. 1). These factors are prepositions, which because of the translational, rotational and vibrational degries of free motion between the separated fragments of the real complex molecules, allow to be occupied big amounts of temporarily existing conformational states. A part from these states are connected with a bending of the molecular longitudinal axis in the zone around the central haloid atom and arising from this of different steric difficultyes at the monomer two-centred electrostatic coordination (Fig. 2, 3).

On the other hand, because of the inevitable molecular fragment $R\sim C^{\bullet}H_2$ rotaion around the single semipolar b_1 bond (Fig. 1), the last monomer molecule insertion between the EMCC active centers ($-C^{\delta 1+}\rightarrow X^{\delta -}-$) can to runs at the macrochain rotative angle different from this, at which was runs the before-last monomer molecule join. All of this is sufficient that the two-centered electrostatic coordination mechanism advantages of join to be discredited and the polymers obtained reguliarity to be drastic violated.

Obviously, the possibility of the growing molecular fragments for free rotation around the longitudinal molecular axis up to an arbitrary angle around the b_1 bond, is in state to ensures conditions for random atactic or sindiotactic consecutives obtain at different degree of probability. This fact allows that to be imitated free-radical chain grouth at the polymerization. That`s way all of this however, can not to be cause for the categorical thrown off the coordinative mechanism of join, which by the PDFM theory obviously is fully possible as a mechanism.

08. ATRP peculiarities

08.01. Reversible equlibrium and reversible atom transfer

According to the CFM, the ATRP is a development of ATRA process [11,12,14,19,20,22], respective of the well known copper-mediated Kharash reaction [11] and it is in the basis of the all CRP methods realisation. The close analogy gives occasion that the ATRP to be conected with the notions about the reversible equilibrium and reversible haloid atom transfer at the chain growth [11-14,25,40-53], which is the basic postulat of the ATRP CFM. By this way, it is dominated the attitude that the ATRP is a method with reversible (equilibrium) character [12,14,21,22,36,37], which afterwards is utilized till now as a theoretical basis for all experimental results explanation. It mast to be underlined however, that at the chemical kinetics notions, the reversible equilibrium connects in general with the reversible runing ractions in homogeneous medium, which moment state can to be defined by an equlibrium constant.

According to the PDFM theory however, the ATRP equalization to the reversible runing reactions is indelicate, because of the obviously irreversible character of the EMCC formation and destruction processes, the polymerization process development and the macrochains formation too. By the PDFM theory, the phisico-chemical processes leading to the EMCC formation and characterising its vital cicle are categorical irreversible. The complex syntheses in one step and by similar way degradates at the bimolecular chain growth (Fig. 4). More complicated ESD mode at the monomolecular chain growth (Fig. 2, 3) only confirms the fact, that this by meaning phisical process of electrostatic discharege is irreversible. This is so, because of that at one runing ESD the spontaneous restore of one electrostatic charge to the initial value is impossible after already achieved one more-low level of discharge. Tacing on account its phisical essence, the electrostatic discharge processes run by one-way mode and can not to be directed on oposit direction. That`s way, the EMCC synthezis and destruction can not to be discussed as processes that can to be conected with one dinamic reversible equilibrium.

According to the PDFM theory, the essential for the monomer polymerization EMCC ESD runs as an irreversible process dependent on from the difference between the electrical σ_1^+ and σ_2^+ densities distributed on the molecular fragments (Figs. 2,3). At the σ_1^+ and σ_2^+ equalization by value, the potential φ^* drops off to zero and the b_1 bond breaks off because of the monofold irreversible haloid atom transfer. This is a key moment for the future complex destany, which by the PDFM realises as an irreversible desintegration. In suport of the affirmation that the ATRP processes are irreversible stand the facts, that the chain growth reaction and the amounts of polymers obtained increases by weight in an inhomogeneous reaction medium and as material processes are irreversible. This follows from the fact, that one depolymerization reaction at the ATRP process practical is impossible. That`s why, the moment state of the real polymerization reactions estimates in general by the initial components degree of conversion or by the weight of the terminal products obtained. All of this show that the notions for reversible equilibrium and reversible haloid atom transfer included in the ATRP CFM [11-14,25,39-52] are groundless.

08.02. Polymerization process development control

According to the PDFM theory, the described in the literature [14,20,22,35,37,38] methods for the polymerization process development control, and the magnitude of the molecular-weight and the molecular-weight distribution of the polymers obtained do not have any attitude towards the ATRP equilibrium. These methods are experimental developed technics for controled retaining or stopping of the chain growth reaction on the stage, when the EMCC ESD is not finished and the monomer in the reaction medium is not exhausted. At such a state, by the semipolar b_1 bond the macroradicals growth ends remain connected to the complex central haloid atom ($R{\sim}C^{\bullet}H_2{\rightarrow}X^{\delta-}$-) (Fig. 3, (5)), because of which suits of the notions about “sleeping” macroradicals, which growth can to be restored.

Theoretical exist a possibility that the chain growth process can to be retained at any expedience before the EMCC ESD finishing, if the monomer amount bear into the raction medium is insufficient for the reaction finishing. It can to be expected, that because of the quick monomer exhaust, in a defined moment the potentials φ_1^+ and φ_2^+ will remain not leveled by value ($\varphi_1^+ > \varphi_2^+$). Because of which, there shall be a possibility that after adding of new monomer amount, the chain growth to be restored. By this way, it can to be observed effects connected to the notions for “awaken” of “sleeping” polymer chains and even of possibility for block-copolymers obtain, after other kind of monomer adding. In fact, at similar state the chain growth reaction in time stops because of that the monomer deficit is dificult to be realised.

In fact, it is very dificult to control the polymer chains chemical mechanism of growth, in such a way that the effects of change and termination could not to be set in [14]. According to the PDFM theory, this is owe of the unfavorable phisical conditions in the reaction medium: low dielectric constant in genaral and facilitated tendency for the potentials φ_1^+ and φ_2^+ leveling. Because of this, the reacting system is extremly unstable and the EMCC number diminishes because of spontaneous ESD uncontroled demolition for a short time. Thats`s way, for the polymers with narrow MWD obtain the polymerization stops by a suitable mode at low conversion values. By analogus considerations, for block-copolymers obtain do not use direct other sort monomer adding, but there are developed and uses biphase technological methods [13,14,18,50-53]. They realise indirectly – by any mode preliminary synthesed macroinitiators, which after this superbuild by an ATRP method.

08.02.01. Reductors usage

There are literarure data [13,14,18-22,37,38], from which is seen that by one oxy-reduction process directed to the oxydated metal form reduction of the inactive complex ($C\text{-}x^{II}$), it can to be controlled the equilibrium state and the ATRP productivity. This achieves by adding in the reaction medium different reductors: zero-valent metals (Cu^o, Fe^o), ascorbic acid or phenols. By its phisico-chemical essence however, the effects observed are not owe of control on the equilibrium or on the polymerization process reversibility, i. e. of the growing reaction retardation in “sleeping” state according to the ATRP CFM meaning.

According to the PDFM theory, at the inactive complex reduction, the Cu^+ ions obtained at an initiator excess, ligand and free monomer presence (which is normal at the ATRP), taces participation a new complex formation. By the additional synthesed EMCC initiates new additional parralel runing polymerization reactions, which products adds to the first synthetic reaction products because of which observes polymer getting increasing. Obviously, this fact is not due of the “sleeping” macrochains “awaken” because of the equilibrium moving to the right, but of the new-synthesed polymer chains.

08.02.02. Deactivator or haloid salts usage

It is established [20,22,37], that an effective device for caunteraction towards to the MWD deteriorate of the polymers obtained can to be the control on the ATRP equilibrium, by the adding in the reaction medium of an external for the system bivalent copper complex ($C\text{-}x^{II}$) in the capacity of deactivator.

Acording to the PDFM theory, by deactivator adding to the reacting system, i. e. of an external for the system bivalent copper complex or of an other haloid containing salt [20,22,37], adds super-stoichiometric amounts haloid ions X^-. Because of these ions negative electrostatic charge, they electrostatic interact with the catalist (Cu-Y) molecules positive loaded Cu^+ ions. By this manner, the catalist Cu^+ ions renders electrostatic shielded towards to the normal presented in the medium initiator haloid ions. That`s way, the electrostatic interaction which is necessary for the b_2 bond creation and the EMCC existing (Fig. 1) discredites and the complex molecules concentration decreases. So initiation effectivity diminishes and in general – the ATRP velosity and productivity. It is establishes a state, that simulates the notion for the equilibrium shifting to the left, when the system drops of from active in a “sleeping” state. It is understood, that the amount of the shielded Cu^+ ions, respective the control on the ATRP velosity and MWD of the polymers obtained, can to be regulated by the supplemented amount of the deactivator or the haloid salt. As it is seen, this possibility for control do not owe of influence on the polymerization reaction equilibrium, but of the supplemantary introduced haloid ions, which shilding effect can to be used as device for direct control on the EMCC synthesis and indirectly on the polymerization reaction parameters.

The literature data analysis show, that the attempt acquired at the reductors, deactivators and haloid salts usage, also the fact that the ATRP equilibrium is attainable from “two sides” [20,22], is cause for the several technological modified ATRP processes development, as the reverse ATRP [12,20,22,47-49], SR&NI [20,50-53], AGET [22,39,40], ARGET [22,44-46], ICAR [22] and ATRC [22,37].

09. PDFM theoretical aspects generalization

The basic postulate in the PDFM theory is the affirmation for the haloid atom transfer irreversebility and the processes characterising ATRP unequilibrity. This affirmation is proved by series fundamental phisical regularities. This fact allow that to be made realistic phisico-chemical processes interpretation of the EMCC synthesis in the synthetic reaction, and of the methods for control on the functional dependent polymerization reaction. It is categorical elucidated that the postulated in the ATRP CFM [11-14,25,41-53] reversible haloid atom transfer effect attendend the chain growth reaction, can to be realised only one-fold and only as an irreversible process, which marks the chain growth end. That’s way, the combination ATRP do not reflects the processes real meaning, and it is more-correct to be changed of ATTRP (Atom Transfer Terminated Radical Polymerization).

It must to be underlined, that the PDFM theory is applicable at all of the ATRP cases promoted by transition matals complexes (Ti, Mo, Re, Ru, Fe, Rh, Ni, Pd, Co, Os and Cu [22]) at analogus mechanism of excited complexes formation. At this meaning, the PDFM theory stands in the basis of one more-general theoretical conception, which can to be defined as: Transition Metals Complexation Polarizing / Depolarizing Theory (TMCPDT), at which the conventional ATRP [11-14,18-25,38,40-43], reverse ATRP, SR&NI, AGET, ARGET, ICAR and ATRC processes in fact are particular cases only.

According to TMCPDT, the interaction of the organic-haliods having mobile haloid atom with the transition metal haloids in the presence of some nitrogen-derivatives, pass throughout a transition stage of excited CT complex formation of the metal in low oxydated state. At the excited state, the mobile haloid atom occupies the position of a central atom of one CT complex (Fig. 1). The complex forming process is accompanied with double molecular polarization (DMP) effect of the excited complex molecule, which because of its bridge-like structure and the SFED effect springing up polarizes electrostatic (ESP) and electrochemical (ECP). At the DMP state, the excited complex is unstable and because of a tendecy for the assymetrical distributed molecular inner energy diminition, springs up irreversible processes of electrostatic (ESD) and electrochemical (ECD) depolarizations. In result from the electrochemical depolarization comes an irreversible for the central haloid atom transfer, metal oxydation to the higher oxidated state, and fol away no matter of possibility for the complexformation standing in a dinamic reversible equilibrium regime. At a monomer presence and IMERS existence however, the functional connected synthetic and polymerization reactions pass throughout a transition stage at which the polymerization process asquires high technological flexibility. This fact allow that the polymerization rection moment state to be controled indirectly, by control on the velosity of the synthesis and the amount of the EMCC obtained by the synthetic reaction. Utilize these possibilities, all of the described methods for well-defined polymers synthesis realizes by external reagents addition for indirect control on the EMCC yield, by two empirical established technological schemes:

1. Control by adding in the reaction medium of one super-stoichiometric amount of haloid ions under deactivator or haloid salt form. So because of the catalyst Cu^+ ions electrostatic shielding by the additional added haloid ions, the EMCC synthesis in the synthetic reaction controlled suppreses. By this way realises technological control on the functional connected polymerization reaction at the cases of the conventional ATRP.

2. Controlled EMCC synthesis by the synthtetic reaction modification. For this purpose at the reverse ATRP or SR&NI processes, by adding of zero-valent copper (Cu^o), the deactivator bivalent copper ion reduces to a monovalent form. By such a way creates conditions for additional complex formation in the reaction medium, respectively for a significant ATRP acceleration by adding of the new formed polymer chains to the first products. At AGET or ARGET ATRP processes, deactivator reduction realises in an additional (ERA) reaction [22], using high-effective reductors (Sn^{II}, ascorbic acid or phenols). One exception from this regulation is ICAR ATRP, at which reduces the catalyst (bivalent copper haloid salt). According to the PDFM theory however, reductors usage independently from the technological approach is only a variety of the EMCC synthesis control in the synthetic reaction.

10. Conclusion

The worcing hypothesis at this elaboration used, defined as Double Molecular Polarization (DMP) allows one specific SFED erffect springing up at the excited monovalent copper CT complex formation. This fact permits to be developed a new theoretical conception for the ATRP functional mechanism named: ATRP – Polarizing / Depolarizing Functional Mechanism (PDFM). This mechanism not only gives plausible theoretical explanation of the ATRP peculiarities, but also permits theoretical foreseen of the polymerization process development. For example: the proposed mechanism allows theoretocal determination of the transition moment ($\varphi^* = 0$) between the manners of the macrochain growth exchange from electrostatic two-centre coordinative to a free radical. Render an account of the possibility for the macroradicals free rotation around the b_1 bond, discloses the causes for the coordinative macrochain growth discreditation.

The ATRP initiation is presented as biphase process: formal initiation connected to an excited bridge-like phisical asymmetric monovalent copper CT complex (EMCC) formation, and genuine initiation depending on in general from energy transfer. According to the PDFM theory, this is one quantum-mechanical process of activation energy transfer from the EMCC to the functional connected polymerization reaction. Because of the stepe-like chain growth the energy transfer hase interrupted character and repeats manyfold at each elementary act of monomer coordination and join. This characteristic peculiarity of the genuine initiation gives possibility that the chain growth to be controled retarded or stoped at prefered monomer conversion, which guarantee the significant ATRP technoligical flexibility and the polymers obtained narrow MWD.

The chain growth termination is presented as result from an irreversible internal molecular electron transfer and haloid atom elimination in an oxy-reduction reaction leading to the EMCC desintegration and bivalent copper complex formation. It is explained why 2-HEMA homopolymerization accelerates when it is realised by impulsive magnetic field applied [10,16]. It is proved that the phisico-chemical processes defining ATRP functionality are irreversible by principle, and this throw a new light on the conventional ATRP, reverse ATRP, SR&NI, AGET, ARGET, ICAR and ATRC processes meaning, and the mode for control on the properties of the polymers obtained. It is proposed a new ATRP generalized functional scheme and energetic balabce. It is outlined the opinion, that the PDFM theory is in position to generalize all of the ATRP cases promoted by transition metals CT complexes at identical conditions, because of which the PDFM theory can to be named: Transition Metals Complexation Polarizing / Depolarizing Theory (TMCPDT).

11. References

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