International Journal of
Science and Engineering Investigations
vol. 7, issue 82, November 2018
ISSN: 2251-8843

Atom Transfer Radical Polymerization-Polarizing/Depolarizing Functional Mechanism-II

Stefko Borisov Iliev
Laboratory of Water-Soluble Polymers, Polyelectrolytes and Biopolymers, Department of Applied Organic and Pharmaceutical Chemistry, Faculty of Chemistry and Pharmacy, Sofia University, Bulgaria
(38stiliev12@gmail.com)

Abstract-This is an abridged version of an analogous article published at ViXra.org [56]. The same approach has been used to compare the conventional Atom Transfer Radical Polymerization (ATRP) mechanism with the proposed new theoretical mechanism called ATRP – Polarizing/Depolarizing Functional Mechanism (PDFM). It is stated that due to the similar complexation of transition metals as promoters of ATRP, the PDFM theory has been accepted as the basis of a generalized theoretical concept called Transition Metals Complexation Polarizing/Depolarizing Theory (TMCPDT).

Keywords- *CFM, DMP, PDFM, EMCC, SFED, IMERS, TMCPDT*

I. INTRODUCTION

When analyzing [1-9] the effects of permanent and impulse magnetic fields (PMF, IMF) on radical polymerization, it has been established that IMF accelerates copolymerization to a larger extent than PMF [7, 8, 9], but it retards homopolymerization (HPM) of vinyl monomers [5, 8, 9]. Surprisingly, HPM of 2-hydroxyethyl methacrylate (2-HEMA), conducted as Atom Transfer Radical Polymerization (ATRP) in an IMF, is not retarded; on the contrary, it accelerates [10]. This fact cannot be explained by an influence of IMF on the reversible ATRP equilibrium which has given rise to doubts concerning the adequacy of the conventional functional mechanism (CFM) of ATRP.

This doubt was supported by a described case of ATRP acceleration under the influence of visible light [15]. The effect is explained as a consequence of complexation through charge transfer (CT) between the initiator (R-Cl) and the catalyst (Cu^I). It is proved by means of a UV-spectrum analysis and runs by the scheme: $R\text{-}Cl + Cu^I \leftrightarrow [R\text{-}Cl\text{-}Cu^I]^* \leftrightarrow R^{\cdot} + Cl\text{-}Cu^{II}$. This fact is an important addition to the notions of complexation by nitrogen-containing ligands [11-14, 18-25, 39-55]. The authors, however, remain within the frameworks of CFM assuming that photo-excitation of the complex accelerates the dynamics of the reversible transfer of halogen atom which assists polymerization. This assumption, however, does not provide answers to many important questions related to ATRP.

Using our own results [5,7-10] and literature data [15], it was attempted to clarify the mechanisms of monovalent copper complex formation and ATRP initiation [16 (Sch. 1)]. Considering the possible CT between R-Cl and Cu^I, however, a new working hypothesis was used in this paper suggesting the occurrence of a short-term physico-chemical effect – Double Molecular Polarization (DMP) of complex molecules. DMP assumes that they are natively excited and spontaneously initiate polymerization, giving away their inner energy through a specific depolarizing mechanism. DMP offers an objective approach towards clarification of complex formation, chain growth and chain growth termination in ATRP. To this end, a new Polarizing/Depolarizing Functional Mechanism (PDFM) of ATRP was developed.

According to the DMP theory, when mixing the initiator (In), catalyst (Cat), ligand (Lig) and monomer (M), a natively excited monovalent copper CT complex is formed (Fig. 1). The complex is made of electrostatically polarized (ESP) and electrochemically polarized (ECP) molecular fragments. It is a transient excited molecule whose transformation runs in two stages – multi-stage electrostatic depolarization (ESD) and single-stage electrochemical depolarization (ECD).

In the presence of a monomer, the ESD process triggers a transfer of activation energy from the complex to the monomer. The energy transfer initiates a polymerization reaction. Because of the ECD process of the complex, which is an irreversible mono-electron transfer to the X^- atom, the Cu^+ atom is oxidized to become Cu^{2+}. In this way, an inactive ATRP complex of the Cu^{2+} atom ($C\text{-}x^{II}$; Fig. 2) is formed, and chain growth stops irreversibly.

II. ATRP INITIATION

ATRP initiation is an analog to the classical initiation – the activation energy (E_a) decomposes the initiator to radicals. According to the PDFM theory, the transfer of these notions to ATRP is incorrect. The initiator – an alkyl halide with an α-functional atom is only a component in the synthesis of a natively excited monovalent copper complex.

According to the PDFM theory, ATRP is realized in the system of three different by type, but functionally connected chemical reactions. The first one is synthetic and ensures the synthesis of double polarized (ESP and ECP) natively excited monovalent copper CT complex. The tendency towards an electrostatic depolarization (ESD) of the complex in the presence of a monomer ensures transfer of the activation energy from the complex to the monomer initiating a second reaction which is a polymerization one. It remains active until the start of the third reaction - electrochemical depolarization (ECD) of the complex which is a redox reaction. It is an electron transfer from the Cu^+ atom to the halogen atom upon which, together with the Cu^{2+} atom, they form an inactive complex of the bivalent copper ($C\text{-}x^{II}$; Fig. 2).

In the PDFM theory, the ATRP initiation is discussed as a two-stage process:

1. Synthesis of a natively excited monovalent copper CT complex whose inner energy, due to the DMP effect, is assymetrically distributed between different in size molecular fragments from the complex for a short term. This stage precedes the essential ATRP initiation and is called formal initiation.
2. The essential initiation takes place in the ESD process of the complex, in the presence of a monomer. It is a quantum-mechanical mechanism for transfer of elementary amounts of activation energy $E_a{}'$ in a three-step process directed by the natively excited monovalent copper CT complex towards the polymerization reaction.

A. Formal Initiation

The proposed mechanism for formation of a natively excited monovalent copper CT complex is similar to those already known from the literature sources [15,27,28], and was developed to further clarify the essence of the ATRP issue. These processes are defined as complexation by means of partial CT, whereupon excited ($E,^*$) complexes (C) with bridge-like (μ) structure [26] are obtained. Their halogen atom has a coordination number 2. In the PDFM theory, these complexes are abbreviated as EMCC (Excited Monovalent Copper Complexes). The classical mechanism for formation of CT complexes [15,27,28] does not exhaustively explain the ATRP complexation. Therefore, some physical laws have been used additionally.

In the CFM of the ATRP, complexation is associated with the ligand's structure and properties [11-14, 18-25, 39-55]. In the PDFM theory, a key role is assigned to the halogen atom (-X) in the molecule of the initiator R-X, taking into account its distinct electron affinity – its electronegativity. It manifests itself at the stage of exchange interaction where the initiator molecule R-X gets closer to the Cu^+ atom of the catalyst Cu-Y (cuprous halogenide) (Fig. 1).

This gives rise to tendency for the -X atom to take away an electron from the 3d-orbital of the Cu^+ atom. If the process is not hampered, the Cu^+ atom is oxidized to its second positive valency (Cu^{2+}) (Cu-XY). The process is facilitated by the fact that the energy for d-/s- transition in the Cu^+ atom is too small, and it easily gives away a second-valency electron [17].

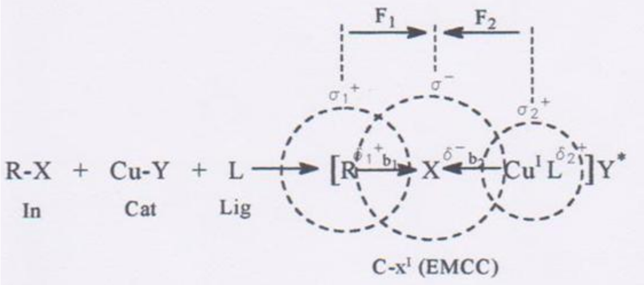

Figure 1. Scheme of excited monovalent copper CT formation according to the PDFM theory. In - initiator. Cat - catalyst. Lig - ligand. C-xI (EMCC) – excited monovalent copper complex. -Xδ- - central atom. b_1, b_2 – semipolar bonds - δ_1^+, δ_2^+ - electrostatic charges. -, σ_1^+, σ_2^+ - superficial electrical densities. F_1, F_2 – Coulomb forces.

According to the ligand-field theory, at the formation of complex compounds of transition metals, the inner coordination sphere formation (connecting molecular orbital (MO)) is the result of overlapping between the metal atom d-orbital and the ligand p-orbital. The structure of the resulting complex is characterized by delocalized covalent bonds (donor/acceptor – semipolar) [27, 28] and is generally expressed as follows: $[Mt^{n+}L_m]X_n^-$ [27].

Due to the high electronegativity of the -X atom (Fig. 1), conditions are created to add to the exchange interaction between the electrons of the d- and p-orbitals of the Cu^+ atom and the ligand the exchange interaction with the electrons of the filled in p-electronic layer of the -X atom. At the overlapping of orbitals, a generalized connecting MO of the Cu^+ atom complex is obtained. Its inner coordination sphere, through the -X atom, comprises the molecules of both the initiator and the catalyst. Under the influence of the -X atom, MO is polarized by a bilateral induction effect (–I), and hence the valent electrons of the molecular fragments R- and $\text{-}Cu^+L$ are delocalized in the direction of the -X atom ($R^{\delta+}\rightarrow\text{-}X^{\delta-}\leftarrow Cu^{\delta+}$) (Fig. 1). The present covalent bond R-X is polarized to a semipolar bond $R^{\delta+}\rightarrow\text{-}X^{\delta-}$ (b_1), while between the -X atom and the $\text{-}Cu^+L$ fragment, due to CT, a new semipolar bond $\text{-}X^{\delta-}\leftarrow Cu^{\delta+}$ (b_2) is formed. By means of b_2, the -X atom remains bonded with the Cu^+ atom, but owing to the presence of b_1, the additional oxidation of the Cu^+ atom is hindered.

By means of the semipolar bonds b_1 and b_2, two partial negative electric charges concentrate on the -X atom (Fig. 1). Its electron affinity satiates, and it is loaded with a generalized electric charge (δ^-) transforming into a central atom ($\text{-}X^{\delta-}\text{-}$) of one EMCC (Fig. 1 – the square brackets), where the $\text{-}X^{\delta-}$- atom has a coordination number 2. Because of the different origin of bonds b_1 and b_2, the charge δ^- should be considered as being composed of two components of different size (δ_1^- and δ_2^-), i.e. $\delta^- = \delta_1^- + \delta_2^-$ ($\delta_1^- \neq \delta_2^-$). This is why, at the initial stage of formation of these bonds, there are short-term correlation discrepancies between their energies (E) and lengths (l). They condition the existence of a certain amount of non-equilibrium potential energy of the excited state (E_p^*) of EMCC, asymmetrically distributed between the semipolar bonds. What is more, E_p^* is proportional (≡) to a certain asymmetrical (non-equilibrium) electric charge (δ*) and its corresponding asymmetrical (non-equilibrium) electric potential (φ^*) ($E_p^* \equiv \delta^* \equiv \varphi^*$). The spontaneous tendency of the E_p^*, at the end of its life cycle, to accept values that are equivalent to the stationary state of the potential energy (E_p) (where $\delta^* = 0$ and $\varphi^* = 0$), leads to an equivalent reduction of the inner energy ($-\Delta U$) of the system, ($E_p^* - E_p = -\Delta U$), which is the source of the EMCC functional activity.

Because of the bilateral –I effect and the dislocation of the valent electrons, the R- and -Cu$^+$L fragments are loaded with positive electric charges δ_1^+ and δ_2^+ which are reciprocal to δ_1^- and δ_2^- (Fig. 1). The sum of these charges ($\delta_1^+ + \delta_2^+ = \delta^+$) in an absolute value is equal to the generalized negative electric charge δ^- ($\delta^+ = \delta^-$), i.e. $\delta_1^- = \delta_1^+$ and $\delta_2^- = \delta_2^+$.

The δ_1^+ and δ_2^+ charges are arranged opposite to the δ_1^- and δ_2^- charges which gives rise to two Coulomb attraction forces compensating each other on the -X$^{\delta-}$- atom: ($F_1 = \delta_1^+\delta_1^- / 4\pi\varepsilon\varepsilon_o l_{b1}^2$) and ($F_2 = \delta_2^+\delta_2^- / 4\pi\varepsilon\varepsilon_o l_{b2}^2$) [29]. The vectors of mechanical moments of these forces are opposite and coincide with the direction of bonds b_1 and b_2. They are proportional to the strength of these bonds and, compensating each other on the -X$^{\delta-}$- atom, they ensure the structural stability of EMCC (Fig. 1).

The potential energy of the stationary state (E_p) of a system loaded with electric charge (q) is equivalent to the work necessary to move the charge at a distance (r) between two points of the electrostatic field. Moreover, E_p is proportional to the charge value square and is reciprocal to the distance ($E_p = q^2/4\pi\varepsilon_o r$) [29]. The δ_1^+ charge potential energy on the R-fragment located at a distance l_{b1} from -X$^{\delta-}$- is actually the energy of the b_1 bond and has a value of $E_{b1} = (\delta_1^+)^2/4\pi\varepsilon\varepsilon_o l_{b1}$. The δ_2^+ charge potential energy on the –Cu$^+$L fragment located at a distance l_{b2} from -X$^{\delta-}$- is the energy of the b_2 bond and has a value of $E_{b2} = (\delta_2^+)^2/4\pi\varepsilon\varepsilon_o l_{b2}$. But since $\delta_1^- \neq \delta_2^-$, respectively $\delta_1^+ \neq \delta_2^+$, in the case of an excited state of the complex, the potential energies of the charges on R- and -Cu$^+$L, respectively the energies and lengths of the b_1 and b_2 bonds as compared to the center of symmetry (-X$^{\delta-}$-) are not equal as well ($E_{b1} \neq E_{b2}$ and $l_{b1} \neq l_{b2}$). Therefore, the difference between the E_{b1} and E_{b2} values is quantitatively equal to E_p^* ($E_{b1} - E_{b2} = E_p^*$).

B. Density of Electric Charges

Because of the dielectric nature of the complex molecule and the lack of galvanic bond between the δ_1^+, δ^- and δ_2^+ charges, they cannot neutralize each other and remain to exist as electrostatic charges distributed with different σ on the molecular fragments (R-, -X$^{\delta-}$, -Cu$^+$L).

The hypothesis of DMP discusses the effect of the superficial electrostatic density (SFED – (σ)) of electric charges on fragments R-, -X$^{\delta-}$ and -Cu$^+$L [29].

The parameter σ plays a key role for the hypothesis as it is responsible for the occurrence of E_p^*, for the degree of ESP of the EMCC as well as for its chemical activity. In this case, subject to discussion is σ of the charges δ_1^+ and δ_2^+ distributed on the different in size and surface molecular fragments (R- and -Cu$^+$L) (Fig. 1). The size of σ is proportional to the size of the charge (q) and is reciprocal to the surface (S) of the fragment on which the charge is distributed, i.e. $\sigma = q/S$ [29]. The density σ^- of the charge δ^- localized on -X$^{\delta-}$ is displayed with the expression $\sigma^- = \delta^-/S_X^{\delta-}$. But since the charge δ^- is composed of two components: δ_1^- and δ_2^-, σ^- is also composed of two components: $\sigma_1^- = \delta_1^-/S_X^{\delta-}$ and $\sigma_2^- = \delta_2^-/S_X^{\delta-}$, respectively $\sigma^- = \sigma_1^- + \sigma_2^-$.

Due to the fact that the initiator (alkyl halide) is a low-molecular compound, on formation of EMCC, the fragment R- has a smaller volume and a smaller surface than the fragment -Cu$^+$L. This is why the density of σ_1^+ of the charge δ_1^+ induced on R- ($\sigma_1^+ = \delta_1^+/S_R$) is greater than σ_2^+ ($\sigma_2^+ = \delta_2^+/S_{Cu^+L}$) of the charge δ_2^+ induced on -Cu$^+$L whose surface, due to the contribution of L, is bigger ($S_{Cu^+L} >> S_R$), i.e. $\sigma_1^+ > \sigma_2^+$. Therefore, the difference $\sigma_1^+ - \sigma_2^+ = \Delta\sigma^+$ between the σ_1^+ and σ_2^+ densities is proportional to the difference $\delta_1^+ - \delta_2^+ = \Delta\delta^+$ between the electric charges δ_1^+ and δ_2^+. The charge $\Delta\delta^+$ is the already defined asymmetrical charge δ^* ($\Delta\delta^+ = \delta^*$) and is proportional to the asymmetrical potential φ^* and energy E_p^*.

In an electrostatic field, the potential (φ_M) in a given point (M) of the field located at a distance (r) from the field-creating charge (q) is equal to the quotient of the charge size and the distance to the point, i.e. $\varphi_M = q/4\pi\varepsilon_o r$ [29]. In this particular case (Fig. 1), the potentials (φ_1^+ and φ_2^+) of charges δ_1^+ and δ_2^+ induced on R- and -Cu$^+$L have been determined against the potential φ^- of charge δ^- on the -X$^{\delta-}$ atom. If the potential φ^- is accepted as a base (conventional zero), the degree of energy (in electric equivalent) asymmetry of semipolar bonds b_1 and b_2 may be reported according to it, i.e. according to -X$^{\delta-}$ which has been accepted as an electric symmetry center of EMCC.

Analogously to δ^- and σ^-, φ^- is also made up of two components: ($\varphi^- = \varphi_1^- + \varphi_2^-$), where φ_1^- is the potential of charge δ_1^- with density σ_1^-, whilst φ_2^- is the potential of charge δ_2^- with density σ_2^-. Since, by absolute value, $\sigma_1^+ = \sigma_1^-$, and $\sigma_2^+ = \sigma_2^-$, in bond lengths l_{b1} and l_{b2}, potential φ_1^+ may be presented as: $\varphi_1^+ = \varphi_1^-/4\pi\varepsilon_o l_{b1}$, and potential φ_2^+ may be presented as: $\varphi_2^+ = \varphi_2^-/4\pi\varepsilon_o l_{b2}$. Because of the fact that φ^-, respectively, φ_1^- and φ_2^-, have been accepted as base values ($\varphi_1^- = 0$ and $\varphi_2^- = 0$) used to report φ_1^+ and φ_2^+, the differences $\varphi_1^+ - \varphi_1^- = \varphi_1^+$ and $\varphi_2^+ - \varphi_2^- = \varphi_2^+$ are in essence the potential differences at the ends of the bonds b_1 and b_2, i.e φ_1^+ at the ends of bond b_1 and φ_2^+ at the ends of bond b_2. But since $\sigma_1^+ > \sigma_2^+$, it follows that $\varphi_1^+ > \varphi_2^+$. Obviously, as compared to the electric symmetry center (-X$^{\delta-}$-), the b_1 bond is polarized to a greater extent than the b_2 bond with the value of the asymmetrical electric potential (φ^*) ($\varphi_1^+ - \varphi_2^+ = \varphi^*$).

The potential energy E_p and potential φ are not equivalent; however, they are dependent on each other: $E_p = q\varphi$ [29]. Thus, the equation of potentials: $\varphi_1^+ - \varphi_2^+ = \varphi^*$, may transform into equation of energies, and E_p^* will be assessed by means of the energy of bonds b_1 and b_2. Since the following charges correspond to potentials φ_1^+, φ_2^+ and φ^*: to $\varphi_1^+ \rightarrow \delta_1^+$, to $\varphi_2^+ \rightarrow \delta_2^+$ and to $\varphi^* \rightarrow \delta^*$, hence $\delta_1^+\varphi_1^+ = E_{b1}$, $\delta_2^+\varphi_2^+ = E_{b2}$ and $\delta^*\varphi^* = E_p^*$, from the analogy of potentials follows that $E_{b1} - E_{b2} = E_p^*$ or $E_{b1} > E_{b2}$. Therefore, the energy of bond b_1 is greater than the energy of bond b_2 with the size of E_p^*.

III. ATRP CHAIN GROWTH

A. Monomolecular Chain Growth

Complexation of monovalent copper occurs in the presence of a monomer, therefore the process is dependent on the efficiency of a “two-centered electrostatic coordination” between the active centers of semipolar bond b_1 ($-C^{\delta 1+}\rightarrow -X^{\delta -}$-, i.e. the potential φ* at the ends of bond b_1) and the potentials of charges δ^- and δ^+ on polar monomer molecules (polar factor (*e*); Q-*e* scheme [30]) (Fig. 2).

In the event of successful two-centered electrostatic coordination and joining of a monomer (Fig. 1, 2), R- grows sequentially in weight and volume by one monomer unit and increases its surface. Thus, σ_1^+ of charge δ_1^+ on R- reduces and, at some point, becomes equal to σ_2^+ of charge δ_2^+ on $-Cu^+L$. At the same time, the degree of asymmetrical polarization of b_1 decreases ($\varphi^* \rightarrow 0$). When σ_1^+ and σ_2^+ equalize, the value of φ* becomes equal to zero ($\varphi^* = 0$), the polarities of bonds b_1 and b_2 equalize ($\varphi_1^+ = \varphi_2^+$) and the structural stability of EMCC is broken because it becomes electrically neutral. This state is unstable and at a certain successive point the electric balance is broken ($\varphi_1^+ \leq \varphi_2^+$). Bond b_1 breaks, the balance between forces F_1 and F_2 ceases to exist and EMCC is destroyed. Meanwhile, due to the formation of a negative complex ($C\text{-}x^{II}$), the growth reaction stops. Obviously, the moment of equalization of the values of σ_1^+ and σ_2^+ ($\varphi^* = 0$) marks the end of the chain growth reaction.

B. ATRP Genuine Initiation

The driving forces of the two-centered electrostatic coordination and joining of a monomer to EMCC are potential φ* on bond b_1 and polar factor (*e*) of the monomer [30]. It is obvious that the intensity of electrostatic fields of charges δ_1^+ and δ_1^- on b_1 and charges δ^- and δ^+ on the double bond of the monomer are responsible for such coordination (Fig. 2).

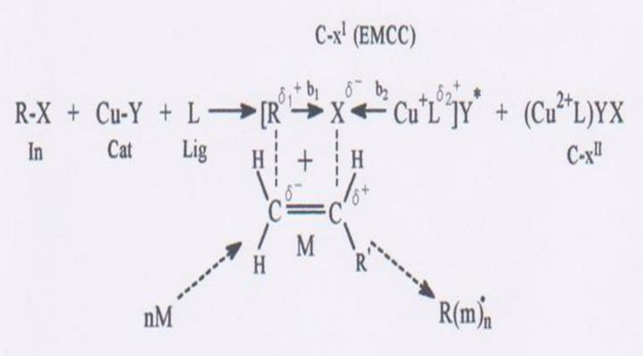

Figure 2. Scheme of two-centered electrostatic coordination of a monomer molecule (M) to an excited monovalent copper CT complex (C-xI; EMCC). In - initiator, Cat - catalyst, Lig - ligand, C-xII – bivalent copper complex. nM – n number of monomer molecules. R(m)·n – growing macroradical

According to the PDFM theory, ATRP is realized in a system of three different by type yet functionally related reactions. The bond between them occurs in the stage of two-centred electrostatic coordination and joining of a monomer in the zone of b_1. This ensures transfer of activating energy $E_a^{\prime}$ from EMCC to the polymerization reaction in three consecutive steps.

1. The first step of energy transfer from EMCC to the polymerization reaction ensures an elementary portion of activating energy ($E_{ec}^{\prime}$) for two-centered electrostatic coordination between the polar monomer molecule (M) and the polar centers ($-C^{\delta 1+}\rightarrow -X^{\delta -}$-) of bond b_1 (Fig. 3, (1)).

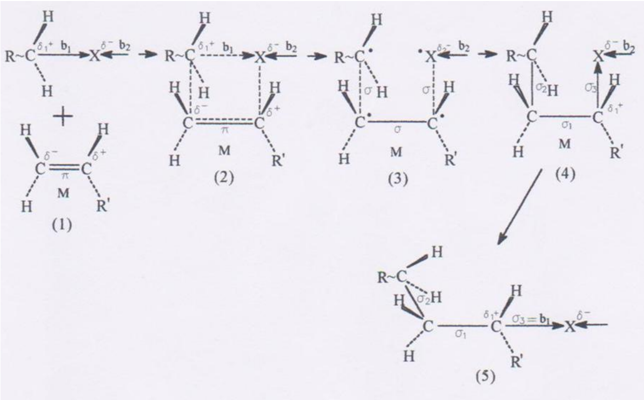

Figure 3. Scheme of two-centered electrostatic coordination and joining of a monomer molecule (M) to polar centers $-C^{\delta 1+}\rightarrow -X\delta$--. Initial interaction, and subsequently, at each elementary act of monomolecular chain growth. δ^- and δ^+ - partial electrostatic charges on carbon atoms of the monomer molecule.

2. The second step of energy exchange is of quantum-mechanical nature. Upon approximation of the σ-electrons of bond b_1 and the π-electrons of the double monomer bond, the electrostatic interaction between the charges ceases to exist. An exchange interaction occurs which initiates the second step of energy exchange – genuine initiation (Fig. 3, (2)). This is an effect of energy exchange in the spin evolution of valent electrons. It runs with transformation of the sp^2 hybridization of carbo-atoms which is typical of the π-bonds of the monomer, up to the sp^3 hybridization which is typical of the σ-bonds of saturated compounds. During the transformation process, a transition Intermolecular Electron-Resonance Structure (IMERS) is formed which possesses a four-member configuration (Fig. 3 (2)). IMERS is a short-lived structure which, due to an insufficient number of π-electrons and the presence of a heteroatom ($-X^{\delta -}$-) has no aromatic stability and is unstable [27]. During the short life cycle of IMERS, the electronic resonance causes the occurrence of spin evolution of valent electrons and energy exchange between them.

The exchange interaction and the bilateral –I effect of the -$X^{\delta -}$ atom induce S→T/T→S electronic transitions in IMERS and its stability is violated. In the S→T transitions, the monomer π-bond and bond b_1 break off and three radical pairs are formed (RPs, RP). The first RP originates from the monomer molecule and is covalently linked to the radical pair (biradical $>C^{\bullet}—C^{\bullet}<$) (Fig. 3, (3)). The second one is non-covalently (‖) linked and is formed between the growing macroradical $R\sim C^{\bullet}H_2$ and the left carbon atom of the biradical ($>C^{\bullet}$-) ($R\sim C^{\bullet}H_2$ ‖ $>C^{\bullet}$-). The third one is also non-covalently linked and is formed between the $-X^{\delta 2-}-$ atom and the right carbon atom of the biradical $(-C^{\bullet}<)$ $(-C^{\bullet}< \parallel {}^{\bullet}X^{\delta 2-})$ (Fig. 3, (3)). Because of the temporary preservation of the covalent nature of bond b_2, the component ${}^{\bullet}X^{\delta 2-}$ has a partially negative charge δ_2^- and manifests as a short-lived ion-radical $({}^{\bullet}X^{\delta 2-})$. As a result of the T→S transitions and the recombination between the singlet electrons of the non-covalently linked radical pairs, with the exception of the σ_1 bond which is present in the biradical, two new σ bonds are formed - σ_2 and σ_3 (Fig. 3, (4)). Bonds σ_1 and σ_2 are normal covalent bonds, but the third one – σ_3, which is under the influence of the $-X^{\delta -}-$ atom, is polarized and in fact repairs an already broken off b_1 bond $(\sigma_3 = b_1)$ (Fig. 3. (5)). Due to the b_1 breakoff and its repair with one monomer unit forward, the monomer joining resembles a process of “insertion” between polar centers $-C^{\delta 1+} \rightarrow -X^{\delta -}-$ of EMCC. Irrespectively of the insertion, fragment $-C^{\delta 1+}$, which is elongated by one monomer unit (m) through the repaired bond b_1 remains linked to a halogen atom $(-Cm^{\delta 1+} \rightarrow X^{\delta -}-)$.

According to the PDFM theory, the ATRP chain growth is the result of a quantum-mechanical process. The IMERS role corresponds to the theory of non-adiabatic chemical reactions [31] and tunes well with the mechanisms of quantum-mechanical energy transfer between closely situated potential surfaces in the S→T/T→S electronic transitions.

3. The third step of energy transfer to a polymerization reaction ensures the activating energy for primary conformational adaptation $(E_{pa}^{\prime})$ of yet another elementary unit to be joined to the macrochain. The energy is of a quantum-mechanical nature and is due to the short-term electron-resonance stability of IMERS. Upon its exhaustion, the four-membered ring-shaped configuration of IMERS breaks off owing to the energetically disadvantageous overshadowed conformation between bonds σ_2 and σ_3. Under the influence of valent angles of carbon atoms, tension and partial rotation arise around bond σ_1 up to the more advantageous gauche conformation between bonds σ_2 and σ_3.

The functional dependency between the three related reactions requires, upon each act of monomer joining, an elementary amount of activating energy $E_a^{\prime}$, which is used up in three steps: (a) for two-centered electrostatic coordination - $E_{ec}^{\prime}$; (b) for genuine initiation - $E_{gi}^{\prime}$; and (c) for primary conformational adaptation of the monomer unit to the macrochain – $E_{pa}^{\prime}$, i.e. $E_a^{\prime} = E_{ec}^{\prime} + E_{gi}^{\prime} + E_{pa}^{\prime}$.

C. Paramagnetic Properties of Radical Pairs

Because of the presence of uncoupled electrons in IMERS, the biradical and the non-covalently linked RPs possess paramagnetic properties as a result of which the ATRP velocity increases in IMF [10,16].

Under the influence of conclusions drawn by N. Turro [1,2,32,33], the effects of PMF and IMF, as described in the works [5,7-10,16], have been explained to be the consequence of the triplet nature of RPs, obtained from thermally degradable initiators.

The binding of ATRP’s magnetic sensitivity with the triplet nature of RPs is, however, unjustified. According to the PDFM theory, the acceleration of ATRP [10,16] results from the polarization paramagnetism of the Cu^+ atom induced in the magnetic field. It manifests itself under the influence of an external magnetic field applied on diamagnetic molecules containing atoms of transition elements, where the symmetry of the electron shell of the atom of the transition element has been violated [34]. Bond b_2 in the molecule of EMCC is due to a deformation of the d-orbital of the Cu^+ atom caused by the –I effect of the halogen atom. Under the influence of an externally applied magnetic field, the broken symmetry creates a measurable paramagnetic receptivity (χ_p) of the Cu^+ atom, which induces its polarization paramagnetism. In the Larmor precession, the Cu^+ atom electrons precess on parallel surfaces situated perpendicularly to the externally applied magnetic vector. This is why the spin magnetic moments of electrons are oriented according to this vector and hence the electronic shells of the Cu^+ atom acquire an anisotropic magnetic polarization. Therefore, the energy barrier for d-/s- transitions in the electronic shell of the Cu^+ atom increases, the complex becomes more stable and the Cu^+ atom oxidation to a state of Cu^{2+} is hampered. As a result, the life cycle of EMCC is prolonged and the velocity of ATRP is increased [10,16].

According to the PDFM theory, the extreme effects of IMF on ATRP are due to the frequency beat occurring in the interference between the frequency of the impulse component of IMF and the frequency of the S→T/T→S electronic transitions. The maximum frequency beat amplitude corresponds to a most efficient energy exchange between EMCC and the monomer and is the main factor for the formation of bonds σ_2 and σ_3. This is why, at a value of the efficient magnetic induction of IMF {B [0.15 T]} and pulsation frequency of the impulse component of IMF {f [150 Hz]}, the ATRP velocity is increased multiple times [10,16].

D. Bimolecular Chain Growth

By its mechanism, the Atom Transfer Radical Coupling (ATRC) process [22, 38] indirectly confirms the PDFM theory (Fig. 4).

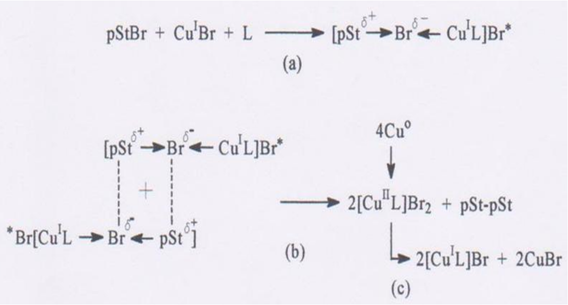

Figure 4. Scheme of bimolecular chain growth in ATRC, according to the PDFM theory. (a) formation of excited pSt complexes before the onset of the coupling reaction. (b) two-centered electrostatic coordination between pSt complexes, formation of pSt dimer in the coupling reaction, bimolecular completion of the chain growth, respectively. (c) deactivator reduction to its initial components by means of nanodispersed copper.

According to the PDFM theory, the pStBr macroinitiators, in the presence of a catalyst and ligand, form polarized polystyrene complexes (a) which coordinate in the “coupling” reaction (b). The large quantity of reductor does not affect any ATRP balance, yet it hampers the obtaining of a deactivator, therefore the complexes remain in an ESP state. This gives an opportunity for a two-centered electrostatic coordination and bimolecular chain growth.

IV. ATRP CHAIN GROWTH TERMINATION

A. *Electromechanical Polarization and Depolarization*

The DMP hypothesis provides for the occurrence of an electromechanical complex polarization (ECP). It is due to the inner molecular grouping $-X^{\delta-} \leftarrow Cu^{+}L$ which contains the components of the redox couple $X^{\delta-}/Cu^{+}$ (Fig. 1). Under the influence of potential φ^* on b_1, this couple is structurally blocked. Depending on the atom type (Cl, Br, J), it possesses a specific redox potential ($\varphi_{o/r}$). It occurs on b_2 only when the couple $X^{\delta-}/Cu^{+}$ is structurally deblocked, i.e. when because of ECD, φ^* drops to zero and b_1 breaks off. In fact, the electrochemical potential of this couple is the previously described potential φ_2^{+} ($\varphi_{o/r} = \varphi_2^{+}$).

The break-off of b_1 triggers the transfer of an electron from $-Cu^{+}L$ to $-X^{\delta-}$-, whereupon it reduces to a state of an ion (X^{-}). Thus, the redox couple $X^{\delta-}/Cu^{+}$ is activated, the potential φ_2^{+} on b_2 drops off ($\varphi_2^{+} = 0$, $\varphi_{o/r} = 0$), EMCC is violated and the chain growth is irreversibly terminated. The moment is so typical that it can be established even visually – the staining of the reaction medium changes from red-brown to green-blue.

Because of the fact that the $-X^{\delta-}$- atom is functionally valid both for EMCC and for the $X^{\delta-}/Cu^{+}$ couple (Fig. 1), the processes in the two systems are connected and run in a consecutive manner. Therefore, the direct oxidation of the Cu^{+} atom to a Cu^{2+} state cannot run spontaneously before the ESD of EMCC has ended.

B. *Macrochain Formation*

When discussing radical chain growth, we introduced the term insertion. It is possible to occur due to the covalent link between the active centers ($-C^{\delta1+} \rightarrow -X^{\delta-}$-) of EMCC, however, by mechanism, it is materially different from the growth observed in the free-radical polymerization (Fig. 2, 3).

The joining of monomer molecules to the EMCC active centers runs by a radical mechanism. Moreover, the creation of the new σ bonds in the framework of the short-lived IMERS (Fig. 2, 3, 4) runs only through electron coupling. This is why the unbalanced amount of inner energy of the asymmetric electrostatic polarization (ΔU_{esp}), proportional to E_p^* ($\Delta U_{esp} \equiv E_p^*$), is not utilized as neutralization of electrostatic charges, but in the energy transfer processes. The inner energy ΔU_{esp} of EMCC is equal to the inner energy reduction due to electrostatic depolarization ($-\Delta U_{esd}$) ($\Delta U_{esp} = -\Delta U_{esd}$). This energy reduction is realized by means of n in number elementary quantities $-\Delta U_{esd}'$, proportional to the elementary quantity of activating energy E_a which is needed for the realization of each act of monomer joining. In this way, because of the ESD of EMCC, at the end of chain growth, a total reduction of the system’s inner energy is ensured at a value of $-\Delta U_{esd}$ ($-\Delta U_{esd} = n.-\Delta U_{esd}'$).

V. GENERALIZED ATRP FUNCTIONAL SCHEME

The link between the functionally connected chemical reactions is presented in a generalized ATRP functional scheme (Fig. 5). The main reaction (a) is synthetic. In the presence of a monomer (Fig. 2,5), due to the two-centered electrostatic coordination of monomer molecules with EMCC, a quantum-mechanical transfer of activating energy occurs, thus initiating a specific polymerization reaction (b).

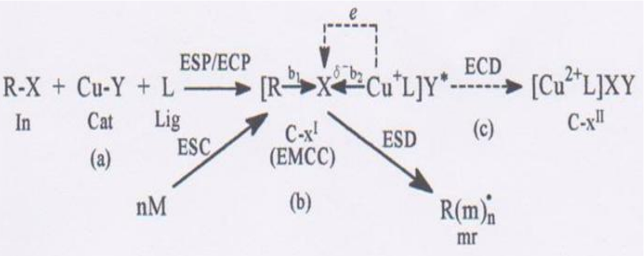

Figure 5. Generalized ATRP functional scheme. In – initiator. Cat – catalyst. Lig – ligand. C-xI (EMCC) – excited Cu^{+} complex. nM – n in number monomer molecules. ESC – two-centered electrostatic coordination process. ESP/ECP – electrostatic and electromechanical polarization of EMCC. ESD – electrostatic depolarization. ECD – electrochemical depolarization. mr – macroradical. e – electron. C-xII – inactive $Cu2^{+}$ complex.

The initiation is the result of a trend towards EMCC inner energy decrease and runs as an irreversible multi-stage ESD. With the end of ESD, a polymer product (mr) is obtained, and a single-stage process ECD of EMCC is started (c). It is an irreversible one-off electron (*e*) transfer from Cu^{+} to $-X^{\delta-}$-, whereupon Cu^{+} is oxidized to Cu^{2+}, while $-X^{\delta-}$- is reduced to an ion (X^{-}). Then the bond of the macroradical with $-X^{\delta-}$ breaks off, and the X^{-} ion passes to the external coordination sphere of a newly-formed complex of the bivalent copper $C\text{-}x^{II}$ (c) (Fig. 5). As a result, EMCC is destroyed and the chain growth reaction discontinues.

VI. ATRP ENERGY BALANCE

Thermodynamics of polymerization processes is mainly determined by the chain growth reaction [35]. The initiation stage requires an outlay of activating energy (E_a) to obtain primary radicals. In the ATRP, the source of energy is the unbalanced potential energy E_p^* - proportional to ΔU_{esp} of EMCC – which is asymmetrically distributed over the EMCC fragments. The asymmetrical distribution of ΔU_{esp} is the reason for instability which is compensated by means of an equalization process of the energy differences between the R- and $-Cu^{+}L$ fragments.

The equalization is achieved through the exhaustion of ΔU_{esp} by n in number equivalent elementary quantities of inner energy of the electrostatic depolarization ($-\Delta U_{esd}'$), proportional to the amount of activating energy E_a' which is necessary for two-centered coordination, genuine initiation and macrochain structuring ($E_a' \equiv \Delta U_{esp}/n = -\Delta U_{esd}'$). After the completion of ESD of EMCC and the exhaustion of ΔU_{esp}, the complex molecule passes into an unexcited state. Moreover, the total reduction of the inner energy of EMCC due to ESD ($-\Delta U_{esd}$) is by n in number quantities of $\Delta U_{esd}'$ ($-\Delta U_{esd} = n. -\Delta U_{esd}'$).

The unexcited state of EMCC is short-lived and, after the b_1 breakage, it triggers a mechanism for ECD of the $X^{\delta 2-}/Cu^+$ couple (Fig. 5). This is an irreversible one-off electron transfer, whereupon $\varphi_{o/r}$ immediately acquires a zero value ($\varphi_{o/r} = 0$). This leads to an additional decrease of the complex inner energy by the size of the inner energy of electrochemical depolarization ($-\Delta U_{ecd}$). The energy $-\Delta U_{ecd}$, released in ECD of EMCC, is fully wasted for polymerization, because $\varphi_{o/r}$ is utilized as heat during formation of the $C\text{-}x^{II}$ complex. Obviously, in the case of complete depolarization of EMCC, the total reduction of the inner energy ($-\Delta U$) will be: $-\Delta U = -\Delta U_{esd} + (-\Delta U_{ecd})$.

VII. Properties of polymers obtained using the ATRP method

A. Molecular Weight Distribution

According to the PDFM theory, M_n, M_w/M_n and MWD are a function of the development of ESD of EMCC. The equalized values of σ_1^+ and σ_2^+ and the drop of φ^* on b_1 to zero mark the end of the chain growth. The equalization or the exhaustion of these values occurs quantitatively at high precision. This determines the reproductivity of M_n, M_w/M_n and MWD of polymers obtained, which is typical of ATRP. This is why, to a certain degree of polymerization, M_n grows in a straight-line dependence on conversion (q).

B. Macrochains Regularity

The conclusion that tacticity and stereoregularity of polymers obtained through ATRP are not much different than those in the free-radical polymerization [12, 14] has become a reason to reject the coordination mechanism of joining as possible. According to the PDFM theory, this conclusion is unjustified. The resemblance is explained by the fact that EMCC molecules have bridge-like (μ) (linear) structure, and the b_1 bond is single (Fig. 1). These are factors which, due to the presence of translation, rotary and vibration degrees of freedom of movement between fragments in real complex molecules, allow a great number of temporary conformation states.

Because of the inevitable rotation of the growing $R{\sim}C{\cdot}H_2$ fragment around the b_1 bond, the insertion of the last monomer molecule between the centers of EMCC ($-C^{\delta 1+} \rightarrow - X^{\delta -}-$) may run at an angle of rotation of the macrochain different than that at which the joining of the last molecule but one has taken place. This compromises the advantage of the two-centered electrostatic coordination in the joining because the regularity of obtained polymers is drastically violated. The opportunity for free rotation of the growing radical along the molecule axis to a random angle around b_1 makes it possible to obtain random atactic or syndiotactic successions with a different degree of probability and, as a result, the free-radical chain growth can be convincingly imitated.

VIII. ATRP peculiarities

A. Reversible Equilibrium and Reversible Atom Transfer

An analogy with the Kharash reaction [11] has spread the opinion that ATRP is reversible (equilibrium) method [12, 14, 21, 22, 39, 40]. In chemical kinetics [36],

eversible equilibrium is related to reversible reactions in specific thermodynamic conditions. In the case of equal velocities of the straight-line and opposite reaction, the moment state is defined by a particular equilibrium constant.

According to the PDFM theory, ATRP is an irreversible process. This is evident from the fact that the chain growth reaction and the polymer weight increase, as material processes, are irreversible. According to Berthollet [37], reactions in which one of the products is water, gas or an insoluble matter, are irreversible and run till the end. Therefore, the depolymerization reaction in ATRP is impossible, and the moment state of polymerization reactions is in principle assessed according to conversion.

B. Polymerization Reaction Control

According to the PDFM theory, the methods for control [14, 20, 22, 35, 39, 40] over the polymerization process are not related to any ATRP equilibrium. The described methods are experimental techniques for controlled slowdown or termination of the growth reaction at a certain stage, where the growing end is still linked to the $-X^{\delta -}-$ atom ($R{\sim}C^{\bullet}H_2 \rightarrow -X^{\delta -}-$) (Fig. 3, pos. (5)). It is impossible to control the chemistry of growing in such a way as to prevent the occurrence of exchange and termination effects [14]. This is why two-stage technological methods have been developed and used to obtain block-copolymers [13, 14, 18, 52-55].

1) Use of Reductors

According to [13, 14, 18-22, 39, 40], the equilibrium state and velocity of ATRP can be controlled through reduction of the oxidized metal form in the $C\text{-}x^{II}$ complex. According to the PDFM theory, the Cu^+ atoms obtained during the reduction in the presence of an excess of initiator, ligand and free monomer, take part in a new complex formation. The newly synthesized EMCC initiate new polymerization reactions whose products are added to the first reaction thus increasing the polymer output.

2) Use of Deactivator or Halogen Salts

It has been established [20, 22, 39] that, by adding a complex $C\text{-}x^{II}$ (deactivator) to a reaction medium, we can combat the deterioration of polymer MWD.

According to the PDFM theory, by introducing a deactivator (a complex which is external for the system or halogen salt) in the system [20, 22, 39], a superstoichiometric amount of X^- ions is introduced. Because of their negative electric charge, they interact electrostatically with the Cu^+ atoms from the catalyst (Cu^+Y) and screen them. Thus, the normal electrostatic interaction which is needed to form the b_2

bond in EMCC (Fig. 1) is compromised and the concentration of complex molecules decreases and so does the efficiency of ATRP initiation and velocity.

Literature sources reveal that the experience gained in the use of reductors, deactivators and halogen salts, as well as the statement that "ATRP equilibrium is accessible from both sides" [20,22] have become a reason to develop several technologically modified ATRP processes, such as reversible ATRP [12,20,22,49-51], SR&NI [20,52-55], AGET [22,41,42], ARGET [22,46-48], ICAR [22] and ATRC [22,39].

IX. SUMMARY OF PDFM THEORETICAL ASPECTS

A main postulate in the PDFM theory is the statement of irreversibility and non-equilibrium of the processes which are typical of ATRP, as well as that of the one-off nature and irreversibility of halogen atom transfer. It has been clarified that the postulated effect of a reversible halogen atom transfer in CFM of ATRP [11-14, 25, 43-55] can actually be realized only once and irreversibly, whereupon the chain growth ends. This is why the abbreviation ATRP does not reflect the actual essence of processes and it would be normal to replace it with ATTRP (Atom Transfer Terminated Radical Polymerization).

The PDFM theory is in all cases applicable to ATRP promoted by complexes of transition metals (Ti, Mo, Re, Ru, Fe, Rh, Ni, Pd, Co, Os and Cu [12, 22]). It has been developed mainly for Cu as an ATRP promoter, but the results obtained [56] lie in the basis of a more general theoretical concept defined as: Transition Metals Complexation Polarizing/Depolarizing Theory (TMCPDT). This theory proves that the mechanisms of conventional ATRP [11-14, 18-25, 39, 42-45], the reversible ATRP, SR&NI, AGET, ARGET, ICAR and ATRC processes are in fact only isolated cases of ATRP. Summarizing the transition metals complexation theory, TMCPDT is a necessary addition to the theoretical aspects of the chemistry of complex compounds and catalytic chemistry.

X. CONCLUSION

This is an abridged version of an analogous article published at ViXra.org. [56]. The same approach of analytical interpretation of the CFM of ATRP has been used, accompanied by an objective discussion which is typical of the PDFM theory. The mechanisms of EMCC formation, of the monomolecular, bimolecular growth, and the chain growth termination have been discussed in detail.

The PDFM theory lies in the basis of a generalized theoretical concept of transition metals complexation which is defined as Transition Metals Complexation Polarizing/Depolarizing Theory (TMCPDT).

REFERENCES

[1] N. J. Turro, M-F. Chow., C-J. Chung., C-H. Tung, "Magnetic Field Effects on Polymerization Efficiency and Polymer Molecular Weight," *J. Am. Chem. Soc*., 102, pp. 7391-7393, 1980.

[2] N. J. Turro, M-F. Chow., C-J. Chung., C-H. Tung, "Magnetic Field and Magnetic Isotope Effects on Photoinduced Emulsion Polymerization," *J. Am. Chem. Soc.*, 105, pp. 1572-1577, 1982.

[3] C. I. Simionesku, A. P. Chiriac., M. V. Chiriac, "Polymerization in a Magnetic Field: 1. Influence of Esteric Chain Length on the Synthesis of Various Poly(methacrylate)s," *Polymer.*, 34(18), pp. 3917-3920, 1993.

[4] A. P. Chiriac, C. I. Simionesku, "Polymerization in a Magnetic Field. X. Solvent Effect in Poly(methylmethacrylate) Synthesis," *J. Polym. Sci. Part A. Polym. Chem.*, 34, pp. 567-573, 1996.

[5] S. B. Iliev, G. S. Georgiev, "Inversion of the Magnetic Field Effect on the Radical Methylmethacrylate Homopolymerizationin in Bulk at a Transition from a Constant to a Pulsatile Magnetic Field," *Ann. Univ. Sofia. Fac. Chem*., 104-105, pp. 109-124, 2013.

[6] C. I. Simionesku, A. Chiriac., I. Neamtu., V. Rusan, "Influence of a Magnetic Field on the Emulsion Copolymerization of Vinyl Acetate with Methyl Methacrylate and Acrylamide," *Macromol. Chem. Rapid. Commun*., 10, pp. 601-607, 1998.

[7] S. B. Iliev, V. Toncheva., G. S. Georgiev, "Effects on the Magnetic Field and Visible Light on the Initiated by 10-1-3 Iodanes Alternating Maleic Anhydride Copolymerization with Vinyl Ester of 2,2,4-trimethylheptane Acid," *Ann. Univ. Sofia. Fac. Chem*., 104-105, pp. 81-92, 2013.

[8] S. B. Iliev, G. S. Georgiev, "Dependence of the Acceleration of Donor-Acceptor Bulk and Emulsion Copolymerization on Magnetic Field Pulsations," *Bulg. Chem. and Ind*. 74(4), pp. 91-94, 2003.

[9] S. B. Iliev, G. S. Georgiev, "Magnetochemical Effect on the Donor-Acceptor Radical Copolymerization," *Ann. Univ. Sofia. Fac. Chem*. 96, pp. 193-206, 2004.

[10] S. B. Iliev, G. S. Georgiev, "Effects of a Pulsatile Magnetic Field on the Atom Transfer Radical Polymerization of 2-hydroxyethyl Methacrylate in Methanol," *e-Polymers*. 048, pp. 1-7, 2004.

[11] J. S. Wang, K. Matyjaszewski, "Controlled/Living Radical Polymerization Promoted by a Cu(I)/Cu(II) Redox Process," *Macromolecules.* 28, pp. 7901-7903, 1995.

[12] K. Ed. Matyjaszewski, "Controlled Radical Polymerization," *ACS Symposium Series 685,* Carnegie Mellon University, San Francisco, CA, 1997, 1, pp. 2-30.

[13] K. Ed. Matyjaszewski, "Controlled Radical Polymerization," *ACS Symposium Series 685,* Carnegie Mellon University, San Francisco, CA, 1997, 24, pp. 396-417.

[14] T. E. Patten, K. Matyjaszewski, "Copper (I)-Catalyzed Atom Transfer Radical Polymerization," *Acc. Chem. Res*. 32, pp. 985-903, 1999.

[15] Z. Guan, B. Smart, "A Remarkable Visible Light Effect on Atom Transfer Radical Polymerization," *Macromolecules.* 33, pp. 6904-6906, 2000.

[16] S. B. Iliev, V. Toncheva., G. S. Georgiev, "Spin Polarization Effect on the 2-hhydroxyethyl Methacrylate Atom Transfer Radical Polymerization in Methyl Alcohol," *Ann. Univ. Sofia. Fac. Chem*. 104-105, pp. 71-79, 2013.

[17] W. A. Roiter, *Substances Catalytic Properties Manual,* Kiev: ,Ed. Ukr. Acad. Sci., 1968.

[18] J. S. Wang, K. Matyjaszewski, "Controlled (Living) Radical Polymerization. Atom Transfer Radical Polymerization in the Presence of Transition-Metal Complexes," *J. Am. Chem. Soc*. 117, pp. 5614-5615, 1995.

[19] S. Coca, K. Matyjaszewski, "Polymerization of Acrylates by Atom Transfer Radical Polymerization. Homopolymerization of 2-hydroxyethyl-, Glycidyl, Vinyl and Allyl Acrylate," *Am. Chem. Soc. Polym. Preprints,* 37, pp. 573-577, 1996.

[20] K. Matyjaszewski, "Controlled Radical Polymerization," *ACS Sympozium. Series 685,* Carnegie Mellon University, San Francisco, CA, 1997, 16, pp. 258-283.

[21] T. Pintauer, W. Braunecker., E. Collange., R. Poli., K. Matyjaszewski, "Determination of Rate Constants for the Activation Step in Atom Transfer Radical Polymerization Using the Stopped-Flow Technique," *Macromolecules*, 37, pp. 2679-2682, 2004.

[22] N. V. Tsarevsky, K. Matyjaszewski, "(Green) Atom Transfer Radical Polymerization: From Process Design to Preparation of Well-Defined Environmentally Friendly Polymeric Materials," *Chem. Rev.* 107, pp. 2270-2299, 2007.

[23] T. E. Patten, J. H. Xia., T. Abernathy., K. Matyjaszewski, "Copper(1)-Catalyzed Atom Transfer Radical Polymerization," *Acc. Chem. Res*. 32, pp. 885-903, 1999.

[24] J. Xia, K. Matyjaszewski, "Controlled/(Living) Polymerization. Homogenous Reverse Atom Transfer Radical Polymerization Using AIBN as Initiator," *Macromolecules,* 30(25), pp. 7692-7696, 1997.

[25] J. Queffeles, S. G. Gainor., K. Matyjaszewski, "Emulsion Polymerization on n-Butyl Methacrylate by Reverse Atom Transfer Radical Polymerization," *Macromolecules*, 32(9), pp. 2872-2875, 1999.

[26] H. Petrov, S. Iordanova., M. Entcheva. *Chemistry*, Sofia: Ed. Technika. pp. 84-85, 1983.

[27] Z. Hauptmann, J. Draefe., H. Remane. *Lehrbuch der Organischen Chemie*, *VEB Deutscher Verlag,* Leipzig, 1980.

[28] N. Tyutyulkov, Yu. Mardashov, *Atom and Molecular Building,* Sofia: Narodna Prosveta, 1987.

[29] N. N. Mansurov, V. S. Popov, *Theoretical Electricity*, Moskva: Energia, 1965.

[30] G. E. Ham, *Copolymerization*, Moskva: Ed. Himia. 1971.

[31] C. Cramer, Essentials of Computational Chemistry. Theories and Models, Chichester: J. Wiley & Sons Ltd, 2002.

[32] N. J. Turro, B. Kraeutler, "Magnetic Field and Magnetic Isotope Effects in organic Photochemical Reactions. A Novel Probe of Reaction Mechanisms and a Method for Enrichment of Magnetic Isotopes," *Acc. Chem. Res.* 13, pp. 369-377, 1980.

[33] N. Turro, "Miceles, Magnets and Molecular Mechanisms. Application to Cage Effects and Isotope Separation," J. Pure & Appl. Chem. 53, pp. 259-286, 1981.

[34] Ya. G. Dorfman, *Diamagnetism and chemical binding*, Moscow: State Ed., 1961.

[35] G. Odian, *Principles of Polymerization,* New York: McGraw-Hill Book, 1970.

[36] R. Brdicka, *Grundlagen der Phisicalischen Chemie,* VEB Deutscher Verlag der Wissenschaften. Berlin, 1962, pp. 434-450.

[37] N. P. Penchev, B. N. Zagorchev. *Course of Analytical Chemistry,* Sofia: D. I. Technica, p. 81, 82, 1961.

[38] K. L. Beers, S. Boo., S. G. Gainor., K. Matyjaszewski, "Atom Transfer Radical Polymerization of 2-hydroxyethyl Methacrylate," *Macromolecules*, 32, pp. 6772-6776, 1999.

[39] K. Matyjaszewski, S. M. Jo., H. J. Paik., D. A. Shipp,."An Investigation into the CuX/2,2'-Bipiridine (X=Br or Cl) Mediated Atom Transfer Radical Polymerization of Acrylonitrile," *Macromolecules,* 32, pp. 6431-6438, 1999.

[40] T. Sarbu, K. Y. Lin., J. Ell., D. J. Siegwart., J. Spanswick., K. Matyjaszewski, "Polystyrene with Designed Molecular Weight Distribution by Atom Transfer Radical Coupling," *Macromolecules,* 37, pp. 3120-3127, 2004.

[41] K. Matyjaszewski, S. Coca., S. G. Gainor., M. L. Wei., B. E. Woodworth. (1999). "The Effects of Ligands on Atom Transfer Raqdical Polymerization in Water-born Systems," *Polim. Prepr. ACS, Div. Polym. Chem*. 40(2). 418-419.

[42] W. Jakubowski, K. Matyjaszewski, "Activator Generated by Electron Transfer for Atom Transfer Radical Polymerization," *Macromolecules*, 38, 4139, 2005.

[43] K. Min, H. Gao., K. Matyjaszewski, "Preparation of Homopolymers and Block Copolymers in Miniemulsion by ATRP Using (AGET)," *J. Am. Chem. Soc*., 127, p. 3825, 2005.

[44] V. Coessens, K. Matyjaszewski, "Atom Transfer Radical Polymerization and Synthesis of Polymer Materials," *Adw. Mater.* 10, pp. 901-915, 1988.

[45] N. V. Tsarevdky, K. Matyjaszewski. "Reversible Redox Cleavage/ Coupling of Polystyrene with Disulfide or Thiol Groups Prepared by ATRP," *Macromolecules*, 35, pp. 9009-9014, 2002.

[46] V. Coessens, T. Pintauer., K. Matyjaszewski, "Controlled/Living Radical Polymerization in Aqueous Media," *Prog. Polym. Scy.* 26, p. 337, 2001.

[47] W. Jakubowski, K. Min., K. Matyjaszewski, Activators Regenerated by Electron Transfer for ATRP of Styrene". *Macromolecules.* 39, p. 39, 2006.

[48] W. Jakubowski, K. Matyjaszewski, "Zerovalent Metals in Controlled/Living Radical Polymerization," *Angew. Chem. Int. Ed.*, 45, p. 4482, 2006.

[49] J. Pietrasik, H. Dong., K. Matyjaszewski "Synthesis of High Molecular Weight Poly(styrene-co-acrylonitrile). Copolymers with Controlled Architecture," *Macromolecules,* 39, pp. 6384-6390, 2006.

[50] J. S. Wang, K. Matyjaszewski, "Controlled (Living) Radical polymerization. Halogen Atom Transfer Radical Polymerization by a $Cu^{(I)}/Cu^{(II)}$ Redox Process," *Macromolecules,* 28, pp. 7901-7903, 1995.

[51] J. Xia, K. Matyjaszewski, "Controlled/Living Radical Polymerization. Reverse Atom Transfer Radical Polymerization Using AIBN as Initiator," *Macromolecules*, 30, p. 7692, 1997.

[52] J. Xia, K. Matyjaszewski, "Homogeneous Reverse Atom Transfer Radical Polymerization of Styrene Initiated by Peroxydes," *Macromolecules*, 32, p. 5199, 1999.

[53] J. Gromada, K. Matyjaszewski, "Simultaneous Reverse and Normal Initiation in Atom Transfer Radical Polymerization," *Macromolecules*, 34, p. 7664, 2001.

[54] M. Li, K. Min., K. Matyjaszewski, "ATRP in Waterborne Miniemulsion via a Simultaneous Reverse and Normal Initiation Process," *Macromolecules*, 37, p. 2106, 2004.

[55] M. Li, N. M. Jahed., K. Matyjaszewski. (2004). "Preparation of Linear and Star-Shaped Block Copolymers by ATRP Using Simultaneous Reverse and Normal Process in Bulk and Miniemulsion," *Macromolecules*, 37, pp. 2434-2441, 2004.

[56] S. B. Iliev, "ATR Polarizing/Depolarizing Functional Mechanism," *ViXra.org.open e-print archive. Chemistry,* 1702(2), 0146. 1-24. 2017.

Stefko B. Iliev was born in Pleven, Bulgaria, on December 2nd, 1938. In 1966, he completed his studies at the Higher Medical Institute in Sofia where he obtained the qualification of pharmacist. In 1977, he was awarded the qualification of chemist engineer from the Higher Institute of Chemical Technologies in Burgas, Bulgaria. In 2009, he defended his dissertation titled "Comparative Analysis of the Effects of Continuously and Impulse Magnetic Fields on Radical Polymerization" in Sofia University, Bulgaria, and was awarded a doctoral degree.

In the autumn of 1960, he was demobilized from the army with the qualification of Radio Location Station Operator. He is currently retired. He has been a General Director of the chemical enterprise "Himik" in the Bulgarian town of Razgrad for 22 years. He has published 25 scientific articles and holds 6 patents. Among his articles are "Spin Polarization Effect on the Hydroxyethyl Methacrylate Atom Transfer Radical Polymerization in Methyl Alcohol", Annuaire de L'Universite de Sofia "St. Kliment Ohridski", 2013 and "ATRP – Polarizing/Depolarizing Functional Mechanism" available online at ViXra.org, e-print archive, Chemistry, 1702(2), 2017.