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# Cationic Polymerization of Vinyl Monomers Under the Action of Metalorganic Compounds

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Additional information is available at the end of the chapter

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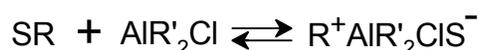
## 1. Introduction

The most part of known metalorganic compounds with Metal-carbon bond of  $\sigma$ -p type belongs to Lewis acid class. These compounds are the most effective catalysts of cationic polymerization of metalorganic monomers. Explanation of initiative action of such systems is very complicated because of their complex structure as well as contaminations in the reaction mixture.

Formation of active site is the main process in all initialization reactions (including metalorganic Lewis acid action). The process of interaction of vinyl monomers with metalorganic Lewis acid (MLA) consists of several equilibrium stages [1], such as formation of active charged particles and their counter ions and subsequent addition of the charged pair to the monomer. The initial equilibrium is usually slow process while the further attack of the monomer (initialization) is very fast and is comparable with the rate of the reaction of chain growth. Moreover, presence of the cationogenic contaminations in the reaction mixture causes a lot of confusion to chemistry of cationic processes. Now we can consider more or less confidently only two possible ways of initialization of polymerization of vinyl monomers by MLA: direct initialization and co-initialization [2-5].

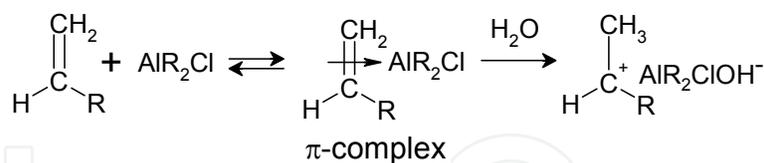
## 2. Initiators and co-initiators

During co-initialization the charged particles are formed as a result of bimolecular reaction or heterolytic decomposition of a molecule:

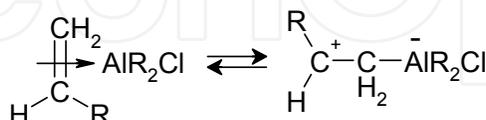


where SR – cationogen ( $H_2O$ ,  $HHal$ ,  $R-Hal$ , etc.).

After injection of cationogen into the last stage the complexing between the monomer and MLA is completing; and initialization in this case consists in the cationogen attack on the complex:



The  $\pi$ -complex can cause the initialization if it is transformed to isomeric carbenium ion:

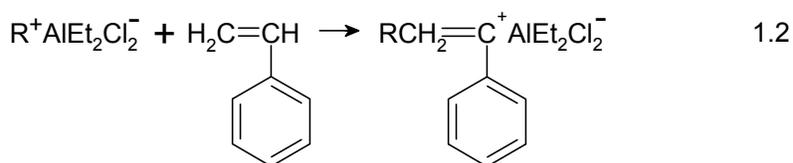
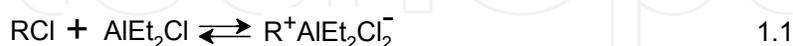


Such regrouping is possible if the electronic density of the double bond is small. Therefore, the heightened electronic density of the double bond of asymmetric substituted alkenes has to decrease significantly at interaction with MLA.

MLA can be divided into 2 types. The first type is presented by MLA of B and Al who has no d-electrons in the valence sphere of the central atom. The second one consists of compounds containing heavier atoms with d-electrons. Usage of MLA of the 2<sup>nd</sup> type makes possible formation of the  $\pi$ -complex from monomer and its further interaction due to overlapping of full d-orbitals of MLA and empty antibonding orbitals of vinyl monomer. Such interactions strengthen the complex and complicate transformation into the carbenium ions because of increasing the electron density of the double bond.

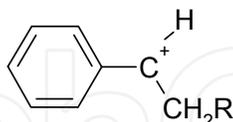
Thus, to start the initialization process it is usually necessary presence of cation donor. Role of MLA consists in assistance to cationogen to form the initiating particle by the way of complexing [6]. According to Ref. [7] MLA allows stabilizing and removing the anion; and initialization is caused by cationogen who is a principal initializer while MLA is only co-initializer.

A mechanism of initialization by alkylhalogenides is the most studied now. Role of R-Hal was cleared on the example of styrene polymerization because intermediate carbenium ion of styrene is rather stable [8]:



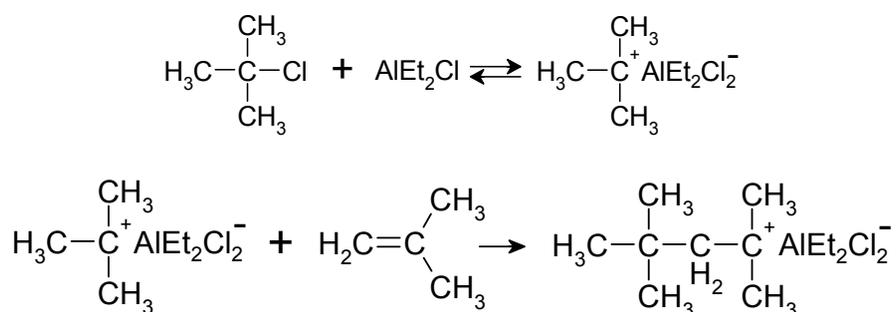
Efficiency of the initialization reaction (1.2) depends on stability of the carbenium ion and its availability. According to equation (1.1) the initialization has to be favored by R-Hal (or Ar-Hal) having low bond dissociation energies and low ionization potentials of alkyl groups

[9,10] as well as by solvation of the formed ions [11]. In the case of R-Hal producing primary or secondary carbonium ions (e.g., n-butylchloride or isopropylchloride) the direct reaction is not observed. If such very active ions can be formed they have to initiate styrene polymerization and produce comparatively stable styrene cations:



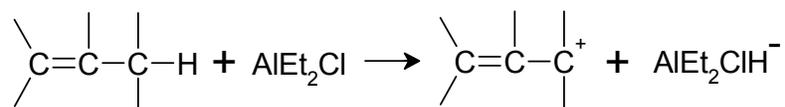
Tert-butylchloride forms rather stable tertiary carbonium cation. However, it is less stable as compared with styrene cation; that is why fast initialization takes place. In contrast, triphenylchloromethane forms very stable tert-cation which cannot cause styrene polymerization [9]. Thus, carbonium ion has to be less stable as compared with styrene cation, but not very unstable to exclude its formation from R-Hal and MLA.

Application of suitable R-Hal and Ar-Hal (together with MLA co-initiators) gives opportunity to control the initialization process [12,13]. In this case a type of alkylhalogenide influences structure of head group of the polymer:



Now it is known a great number of cationogens which can efficiently initiate cationic polymerization of vinyl monomers and ensure production of polymers with certain head group.

In the case of absence of cation donors (e.g., at high pure conditions) other mechanisms of initialization of polymerization of vinyl monomers may be realized under the action of MLA. For example, if the monomer contains allyl hydrogen tearing off hydride-ion from the monomer may be one of possible ways of initialization [14]:

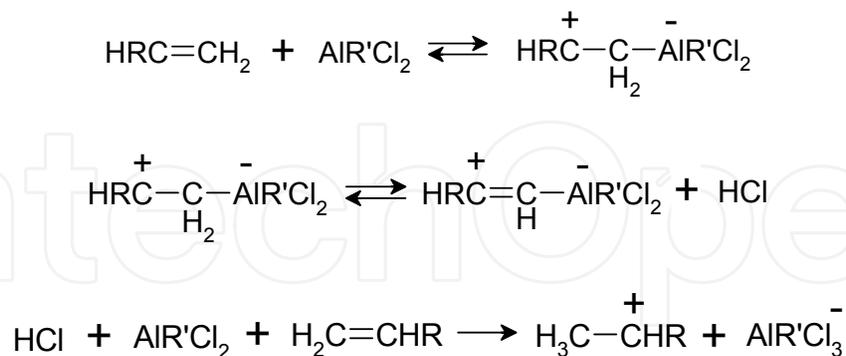


In this case the monomer is a donor of cations that is one of self-initialization mechanisms.

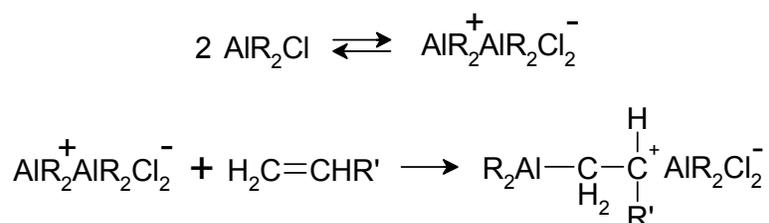
### 3. Direct initiation

The formation of the metal-carbon bonds in the polymer can occur in various ways:

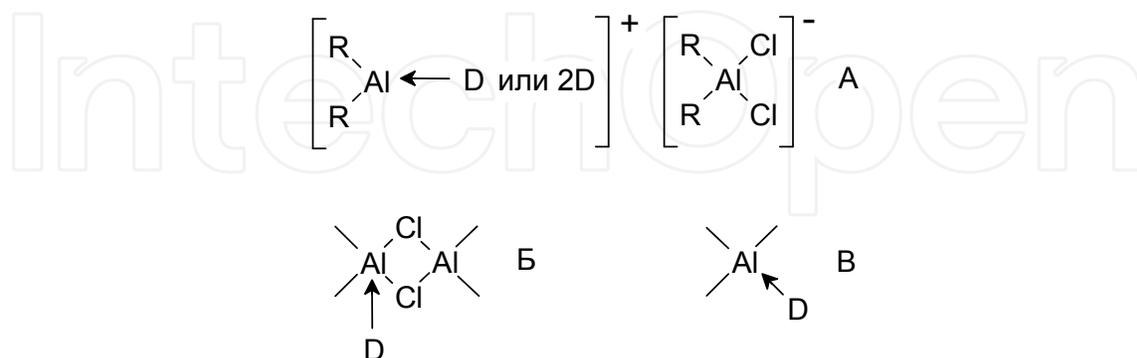
1. Direct conjunction of MLA to the double bond of monomer followed ejection of cationogen and the formation of complex counter ion [15]



2. Electrophilic addition to the monomer cation, formed as a result of MLA ionization itself [16–18]



The requirement of initiation according to the scheme 1 is a possibility of formation of cationogen at zwitterionic decay; according to scheme 2 – the presence of a polar solvent or electron-donating compounds such as ethers, thioethers, tertiary amines, etc. MLA easily adds such compounds forming a rather stable complexes [19]. Such complexes usually have a composition of 1:1. The NMR study of complexation of organoaluminum compounds with methylpyridine (D) in solutions of 1,2-dichloroethane and dichloromethane showed, that the solution may contain the following complex compounds [20]:



The presence in the solution structures of type A is also confirmed by determination of electrical conductivity.

By Wittig [21], one of the possible states of the MCL in the solutions are structures of  $\text{MeR}_{n-1}^+ \text{MeR}_{n+1}^-$ . Hypothesis about the possibility of ionization of the MLA to form complex

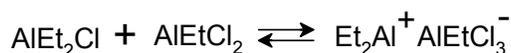
ions, including metal atom, is consistent with a number of electrochemical studies. The corresponding ionization schemes are proposed, for example, magnesium-organic compounds [22]:



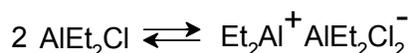
or



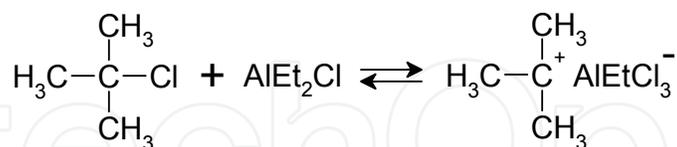
Such MLA ionization is characteristic not only for the individual MLA, but also for their mixtures. It was found that polymerization of butadiene in the presence of alkylaluminum-cobalt initiators is the most effective only in the presence of ion-pair  $\text{Et}_2\text{Al}^+\text{EtCl}_3\text{Al}^-$ . This ion pair is formed by mixing either  $\text{AlEt}_2\text{Cl}$  with  $\text{AlEtCl}_2$ , or  $\text{AlEt}_3$  with  $\text{AlCl}_3$  [6]:



At present, the mechanism of the formation of MCL self-ionization ion pair is widespread [4, 23]. However, the equilibrium constant for the reaction



is much lower than in the case of interaction of MLA with a suitable donor of cations. For example:



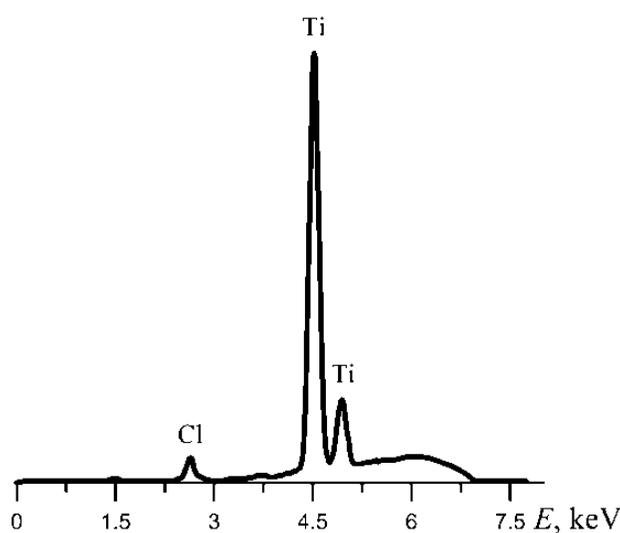
In this case a more stable carbonium ion is formed. Therefore, in order to a direct initiation we need to create conditions for guarantee the complete absence of cationogen impurities in the system. Only in this case MLA themselves can play a role of initiators.

Nevertheless, the polymerization of highly active monomers by initiation of the MCL self-ionization is possible. One of these monomers is a 9-vinylcarbazole (VC), it is very easy polymerizing for cationic mechanism [24–26]. Authors of Ref. [27] showed that the rate of chain growth in cationic polymerization of VC under the action of stable organic cations is more than 100 times higher than the corresponding value for vinyl ethers.

Authors [28] studied kinetics of polymerization of VC in toluene solution under the action of titanium tetrachloride by thermometric method [29–33] and found that the polymerization

process begins with the formation of complex compounds  $\text{TiCl}_4$  with 1-6 solvent molecules forming the solvation shell. It was established that complex formation is accompanied by a large thermal effect, which is reflected in the curve recorded a sharp jump in temperature at the initial time of polymerization. Since the system contains monomer (VC) with a developed system of  $\pi$ -electrons, the latter one competes with toluene and partially displaces it from the solvation shell of  $\text{TiCl}_4$ . As a result of new resolution a complex compound of a rather complex structure is formed where the vinyl bond of the monomer is partially polarized. This facilitates the subsequent process of opening the double bond and leads to increasing reactivity of the monomer.

The active particle is formed by the further polarization of the monomer vinyl bond in the solvation shell of titanium tetrachloride. This is followed by the accession of the last one to the monomer double bond forming the corresponding ion (direct initiation). Direct connection  $\text{TiCl}_4$  to monomer is confirmed by data of X-ray fluorescence analysis of the polymer samples. Diffractogram shows that the polymer contains a small amount of titanium chloride as terminal groups (Fig. 1).

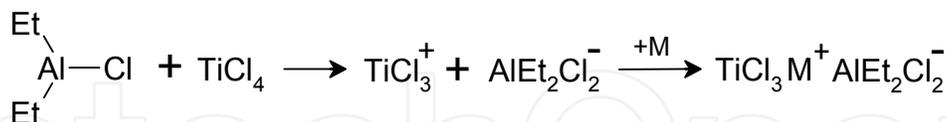


**Figure 1.** X-ray Fluorescence Spectrum of the sample Polyvinylcarbazole obtained under the action of  $\text{TiCl}_4$  in toluene solution

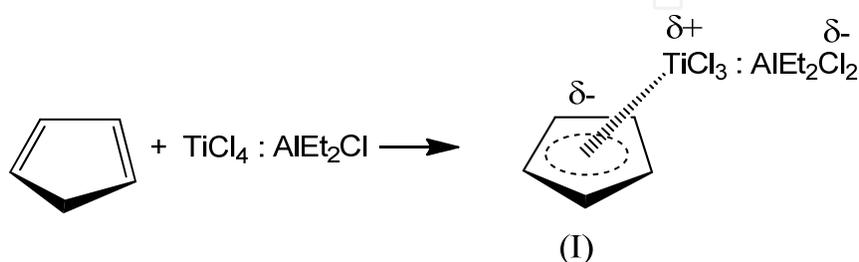
Concentration of active sites may increase during the slower stage; it causes S-shaped kinetic curves. The chain growth on contact or separated ionic pairs is the most probable mechanism of the polymerization in the studied system. It is confirmed by permanency of the chain growth constant depending on the initial concentration of the initiator.

Initialization of the monomer polymerization by the way of ionization of complex Lewis acids can be illustrated by oligomerization of dicyclopentadiene (DCPD) under the action of catalytic system  $\text{TiCl}_4 : \text{Et}_2\text{AlCl}$  [34–35]. This catalyst (similar to individual  $\text{TiCl}_4$  [30]) causes process of cationic polymerization of DCPD. Lower value of  $k_p$  as compared with the process based on individual  $\text{TiCl}_4$  can be explained by the presence of less hard counter ion on the base of  $\text{AlEt}_2\text{Cl}$ .

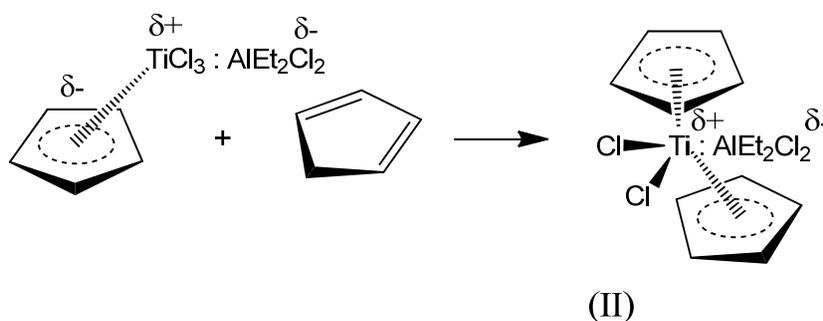
In both cases dicyclopentadiene polymerization goes according to the following mechanism: Firstly, active complex (solvated ion pair) is formed as a result of self-ionization of Lewis acids:



Also, we can suppose formation of  $\pi$ -complex (I) MLA with cyclopentadiene which is present at the system in small amount:



Then sandwich-complex is formed (II):

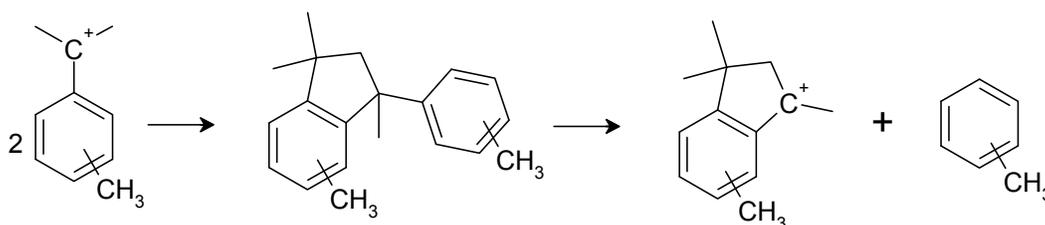


Complex equilibrium during initialization may be completed by regrouping the  $\pi$ -complex to  $\sigma$ -complex and isomer carbonium ion or by transformation of the sandwich-complex to semi-sandwich-complex (I):



Then the reaction is also completed by regrouping the  $\pi$ -complex to  $\sigma$ -complex and isomer carbonium ion. Further chain growth occurs using one of two unsaturated bonds of DCPD – norbornene or cyclopentene [36].

In the case of initiation of oligomerization of vinyltoluene by  $\text{TiCl}_4$  the active particle is formed due to further polarization of vinyl bond of the monomer in solvate shell of  $\text{TiCl}_4$ . Finally it adds to the double bond forming the respective ions (direct initialization). The obtained carbocation transfers to indane dimer and oligomeric products. At room temperature of the reaction mixture the indane dimer finally decomposes into toluene and indanyl cation [37, 38]:



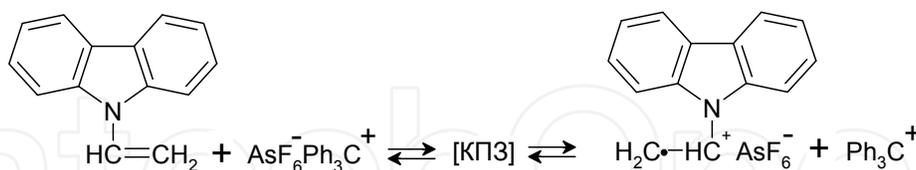
Then the cationic oligomerization of vinyltoluene takes place. In the case of use of catalytic system  $\text{TiCl}_4 : \text{Et}_2\text{AlCl}$  (1:1) oligomerization of vinyltoluene occurs under similar conditions and is characterized by the presence of counter-ion of more complex composition.

#### 4. Initiation of polymerization by electron transfer

Initiation of the polymerization by complete or partial electron transfer from the monomer to the initiator is a special case of interaction of the initiator with the monomer. This process is usually accompanied by the formation of intermediate charge-transfer complexes (CTC):



The last scheme is the most universal and attracts increasing attention in the field of polymerization of the polar electron-donor monomers. The phenomenon of charge transfer is evident not only in initiating the polymerization of such monomers with organic electron acceptors, but also occurs at the interaction with typical cationic polymerization initiators such as Lewis acids (including MLA) and stable organic cations, which act as acceptors relative to the electron-donating monomers [39, 40]. For example, in Ref. [41] it was shown that the initiation of polymerization of 9-vinylcarbazole under the action of  $\text{Ph}_3\text{C}^+\text{AsF}_6^-$  proceeds through the stage of formation of cation-radical:



Then dication 9-vinylcarbazole is formed; and it is responsible for the polymerization:



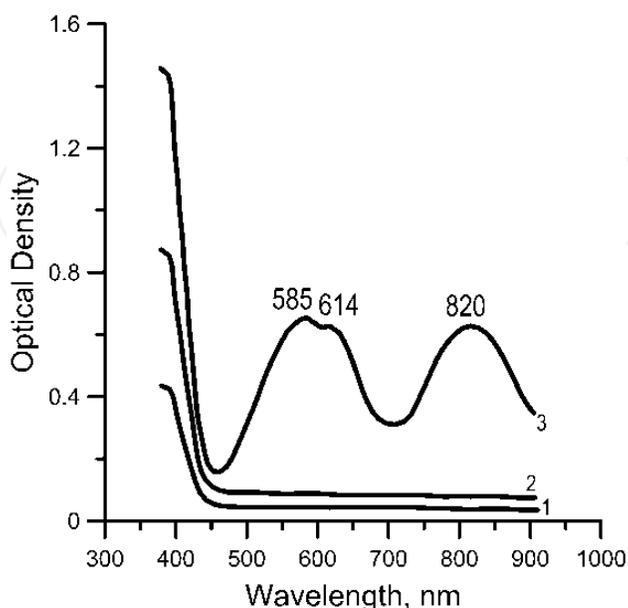
As MCL are very strong  $\nu$ -acceptors, their lowest molecular orbital is vacant  $\nu$ -valence orbitals of the metal atom. We can assume that stage of electron transfer from the monomer to a  $\nu$ -orbital of the MLA precedes the initiation process. Till now there is no adequate attention to the question of which kind of orbital electron-donating monomer delivers its

electron acceptor. It is usually assumed that  $\pi$ -complex is formed as a result of this interaction [42, 43]. However, data concerning formation of  $\pi$ -complexes of vinyl monomers with MCL are practically absent, that is probably associated with their rapid transition to the  $\sigma$ -complexes, ionic and radical products.

In [44] VC polymerization was studied in the presence of  $\text{Ph}_3\text{C}^+\text{AlEt}_2\text{Cl}_2^-$  in  $\text{CHCl}_3$  solution at 20 °C. Process kinetics was studied using the stopped flow method with the registration in the IR range [2, 45–47]. In this case, the active site of polymerization is a stable organic cation  $\text{Ph}_3\text{C}^+$ , which is formed from the reaction of equivalent amounts of  $\text{Ph}_3\text{CCl}$  и  $\text{AlEt}_2\text{Cl}$ . However, counter-ion  $\text{AlEt}_2\text{Cl}_2^-$ , in contrast with hexa-fluoro-arsenate, hexa-chloro-antimonate and the like inorganic counter-ions of low nucleophilicity [27, 41, 47–50], associates with the organic cation. It allows concluding that the most likely type of active sites are separated solvate-ion pairs or even complex between VC and the contact ion pair.

The first reaction order was observed until complete consumption of the monomer. It indicates the absence of the chain break reactions. Moreover, when new portion of the monomer is added the reaction rate is not changed. It indicates the presence of the “live chains” in this system [51–54]. The behavior of this system is similar to the system VC – DEAC – chloroform studied earlier [46]. However, kinetic correlations have some differences which mean other mechanism of the active site formation. Kinetic measurements revealed that the most probable polymerization mechanism in the studied system  $\text{CHCl}_3 \dots \text{Ph}_3\text{C}^+ + \text{Et}_2\text{AlCl}_2^- \dots \text{VC}$  is the chain growth on contact or solvate-separated ion pairs. It is confirmed by permanency of the  $k_p$  value depending on the initial concentration of the initiator as well as its similarity to the ones known from literature.

For assessing reactivity of VC in the cationic polymerization the kinetics of its polymerization in solution under the action of diethylaluminum chloride was studied [46]. It was shown that the reaction is greatly influenced by the complexation among the monomer and



**Figure 2.** The absorption spectra of solutions in chloroform BK (1)  $\text{AlEt}_2\text{Cl}$  (2) and complex of  $\text{BK-AlEt}_2\text{Cl}$  (3)

initiator. In particular, this leads to the fact that the polymerization process in general is limited by the formation of active particles that are supposed to be dication of VC. Appearance of new charge-transfer band in the electronic spectrum of the products of their interaction is clear evidence of the formation of donor-acceptor complexes between  $\text{AlEt}_2\text{Cl}$  and VC (Fig. 1, curve 3).

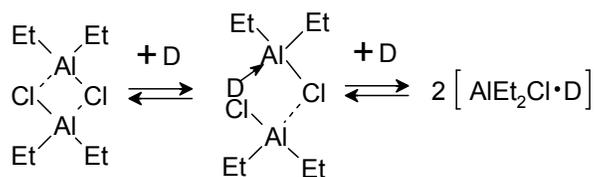
Figure 2 shows that the spectra of the initial VC (curve 1) or  $\text{AlEt}_2\text{Cl}$  (curve 2) similar band is absent, and the observed charge-transfer band actually consists of two bands with maxima at  $\lambda = 584$  and  $614$  nm. One of them, apparently, is associated with the transition of  $\pi$ -electron VC to the d-orbital  $\text{AlEt}_2\text{Cl}$ , and another one - with the transition of n-electron. The obtained data reveal that the interaction of VC with a molecule of the initiator in the initial phase of the formation of donor-acceptor complex of medium strength; and degree of charge transfer from donor to acceptor is 0.29 of electron charge. The resulting donor-acceptor complex between VC and  $\text{AlEt}_2\text{Cl}$  has  $\lambda_{\text{max}} = 584$  and  $614$  nm. It is close to the form shown in the literature for the complex value of  $\lambda_{\text{max}}$  VC with tetra-cyano-ethylene ( $590$  nm, [55]). The interaction between VC and  $\text{AlEt}_2\text{Cl}$  leads to the fact that the effective charge on the  $\beta$ -carbon atom of the vinyl group BK significantly decreases; the length of the vinyl connection increases and its order is reduced. This greatly facilitates the subsequent process of formation of the active particles.

Formation of VC cation-radical followed by merge of two these cation-radicals to the dication may be such process. In this case evidence of formation of the latter one is the appearance in the electron spectrum of products of interaction and VC  $\text{AlEt}_2\text{Cl}$  a band at  $\lambda_{\text{max}} = 820$  nm attributable to the long-wavelength absorption maximum dication VC (curve 3, Fig. 2). Authors [56] gave a value of  $\lambda_{\text{max}} = 850$  nm for the cation formed by the interaction of ethyl-carbazole with  $\text{SnCl}_4$ . Further cationic polymerization of VC mechanism takes place.

In all cases the polymerization of VC under the action of DEAC occurred until complete consumption of the monomer and accompanied by formation of colored intermediate. This color did not disappear after complete monomer consumption.

Such polymerization character indicates the absence of the chain break reaction in the system. It is confirmed by the fact that after contact of the reaction mixture with moisture in air the color disappeared and did not appear after addition of new portion of the monomer. However, stopping the growth of the molar weight of the polymer at repeated addition of the monomer proves availability of the chain transfer reactions in the system.

In some cases, the problem of donor site in the monomer molecule requires special study. For example, vinyl compounds containing a hetero atom in the structure (such as vinyl ethers, N-vinyl heterocyclic monomers, etc.) can function as both n-donors and  $\pi$ -donors, giving unshared electron pair of heteroatoms or electrons of the highest  $\pi$ -level for the intermolecular bond [57, 58]. It is largely dependent on the properties of an electron acceptor. When interacting with stronger acceptors (e.g., MCL metals of the third group of the Periodic table) sufficiently strong high polar nv-complexes are formed [59]:



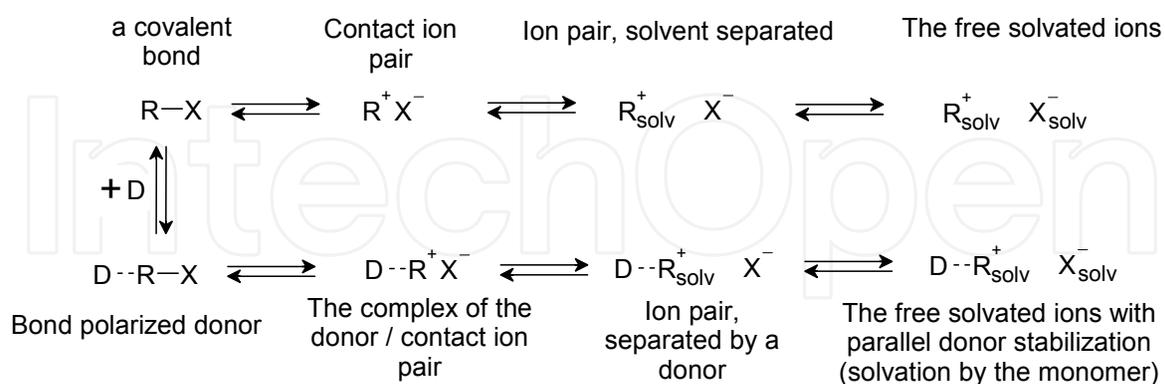
This will undoubtedly influence the formation of active particles in the system.

Thus, the generation of primary cations can pass through a series of relatively slow equilibrium stages, especially in the case of polymerization of monomers containing hetero atoms in the structure with an unshared electron pair. So often the formation of active sites becomes the limiting stage of the polymerization process as a whole, exerting a strong influence on the rest of the process.

## 5. Effect of reaction medium on the polymerization process

It is known that the influence of the reaction medium is a decisive factor, which determines the rate constants of individual stages of ionic polymerization [60]. We can distinguish two effects of medium influence: change of reactivity of the active sites and the stabilization of the formed ionized particles.

Process rate and reactivity of the active sites in various media will be determined by a number of factors: the influence of the polarity of the medium, co-catalytic action of solvents, specific solvation, and the formation of complexes with components of the reaction system. Experimental results show that the major factor is the polarity of the medium. It plays particularly noticeable role at the stage preceding the initiation and growth of the polymer chain. This is expected, since the processes occurring at the same time are due to the formation of intermediate active particles: free ions, contact and solvate-separated ion pairs, as well as other more complex aggregates:



The main problems associated with these particles in the initiation of polymerization were discussed at 6<sup>th</sup> International Symposium on cationic polymerization [61–67].

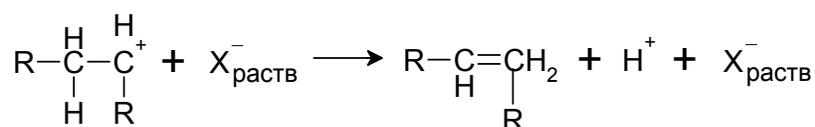
Large dipole moment of the ion pairs leads to a strong interaction with polar molecules including molecules of polar solvents. Solvate separated ion pairs exist only in mediums where at least one of the ions in a free state is coordinated with solvent molecules. In the

case of a slightly solvating solvents their function can be performed by the monomers, changing the dielectric constant of the medium, or other components that are directly involved in the polymerization. It results in a change in the kinetic order of reaction with respect to these components. This is explained by the fact that in media not providing the necessary solvation energy the ion pairs are stabilized by most polar or polarizable molecules from those ones presented in the system, i.e. monomer and initiator. They can be incorporated into the kinetic equation corresponding to the reaction, although they do not take direct part in it [8].

The existence of free ions in organic media because of their low stability is possible only under the following conditions [7]:

- ionization equilibrium is shifted toward preferably a covalent bond, i.e. there is a rapid reverse stabilization of charge;
- active formation of stabilized specific solvation of cations and anions with suitable solvents;
- nucleophilicity of the counter-ion is strongly reduced by acceptors in solvents with the prevailing acceptor character ( $\text{H}_2\text{CCl}_2$ , 1,2-diloretan, etc.); and there is no exchange with the cation except its electrostatic compensation.

The last condition, which would correspond to an almost "naked" cation takes place only at a strong intramolecular stabilization by delocalization of the charge (exchange interaction with the aromatic rings with a high density of  $\pi$ -electron, oxo-carbonium acids, allyl cations). Otherwise inductive effect of the ion carbenes on adjacent carbon atoms is so strong that the isomerization and cleavage for example,  $\beta$ -H-atoms will go faster than the reaction of chain growth:

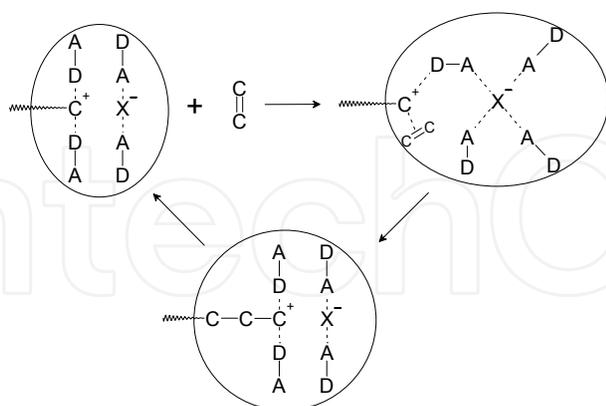


In such hard conditions the monomer itself is the strongest  $\pi$ -donor in the reaction system, which can reduce the high electrophilicity of carbonium ion. Therefore, the literature points to the special role the monomer solvation as a stabilizing factor for the active particles, helping them to implement the reaction growth [68].

Obviously, the ion pairs and free ions may have a different activity, and ion pairs are usually less active as compared with free ions. For example, for the polymerization of 9-vinylcarbazole in  $\text{H}_2\text{CCl}_2$  solution under the  $\text{Ph}_3\text{C}^+\text{SbCl}_6^-$  action at 20 °C a growth rate constants of the free ion and ion pair are equal  $6 \cdot 10^5$  и  $5 \cdot 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$  [69]. According to data of other authors [49] the corresponding values can differ by several orders of magnitude. This is due to the higher effective charge density of the free cation in comparison with the corresponding ion pairs [1].

In real systems the situation is complicated by the fact that the reaction of chain growth can be represented as the competition of the monomer, solvent, and counter-ions around the

electrophilic center [7]. The exchange interaction of solvent separated ion pair with the monomer leads to resolution of the ion pair and its expansion in order to the counter-ion:



1.3

The exchange interaction between the counter-ion and the growing carbonium ion can be controlled by charge and must depend on the effective electrophilicity of the latter one.

According to current ideas about the mechanism of chain growth in cationic polymerization at high electrophilicity of the cation (aliphatic vinyl monomers) and the high nucleophilicity of the counter-ion ( $CF_6^- \gg Cl^- \gg Br^- > I^-$ ) polymerization does not take place. Monomers forming a resonance-stabilized cations with low electrophilicity (e.g., vinyl esters, 9-vinylcarbazole, dienes, p-methoxy-styrene) with counter-ions having low nucleophilicity (e.g.,  $AsF_6^-$ ,  $SbCl_6^-$ ) at least at low temperatures are able polymerizing with a relatively small transfer chain. The growth occurs mainly through the free solvated ions. In the presence of counter-ions with the relatively high nucleophilicity (e.g.,  $Br^-$ ,  $I_{n+1}^-$ ,  $F_3CCO_2^-$  and others) these monomers are also capable for polymerization. Probably, the overall structure of the solution (scheme 1.3) reduces the potential energy [53], and wedging the monomer into an ion pair becomes favorable as compared with the monomer transfer to the chain.

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## 6. References

- [1] Reactivity, Mechanism and Structure in Polymer Chemistry; Jenkins, A.D.; Ledwith, A., Eds.; Wiley: London, 1974.
- [2] Kennedy J.P. // Indian J. Phys. – 1982. V. A56. – № 4. – PP. 41–50.
- [3] Miangos F. // Rev. Plast. Mod. – 1985. – V. 36. – № 346. – PP. 450–452.
- [4] Cheradame H., Gandiny A. // Amer. Chem. Soc: Polym. Prepr.–1985. – V. 26. – № 1. – PP. 42–43.
- [5] Sigwalt P. // Polym. J. – 1985. – V. 17. – № 1. – PP. 57–71.

- [6] Kennedy J.P. Cationic polymerization of olefins: a critical inventory. Wiley: London, 1975.
- [7] Reactions in polymer systems. / Ed. S.S. Ivanchev. – Chemistry, Leningrad. – 1987. – 304 p.
- [8] Cationic Polymerization. P.Plesh, Ed., Mir, Moscow, 1966, p. 584.
- [9] Kennedy J.P. // J. Macromol. Sci. – 1969. – V. A3. – № 5. – PP. 861–884.
- [10] Kennedy J.P. // J. Macromol. Sci. – 1969. – V. A3. – № 5. – PP. 885–895.
- [11] Heublein G. // Plaste und Kautsch. – 1981. – V. 28. – № 7. – PP. 361–364.
- [12] Kennedy J.P. // «Int. Conf. Struct. – Prop. Relat. Rubber, 29–31 Dec., 1980». – Kharagpur. – 1981. – PP. 5–8.
- [13] Kennedy J.P. // Rubber Chem. and Technol. – 1983. – V. 56. – № 3. – PP. 639–663.
- [14] Kennedy J.P., Langer A.V. // Progress of Chemistry. – 1967. – T.35. – № 1. – C. 65–141.
- [15] Sigwalt P. // Makromol. Chem. – 1974. – V. 175. – № 4. – PP. 1017–1034.
- [16] Chmelir M., Marek M., Wichterle O. // J. Polym. Sci. – 1965. – V. C16. – № 3. – PP. 833–839.
- [17] Plesch P.H. // «Macromol. Chem. 8 Plenary and Main.Lect. Int. Symp. Macromol., Helsinki, 1972». – London. – 1973. – PP. 305–318.
- [18] Plesch P.H. // Makromol. Chem. – 1974. – V. 175. – № 4. – PP. 1065–1076.
- [19] Tolstikov G.A. Aluminum-organic synthesis// Moscow, USSR Academy of Sciences Publishing House, 1978, 286 p.
- [20] Matsubayshi G., Wakatsuki K., Tanaka T. // Org. Magn. Reson. – 1971. – V. 3. – № 3. – PP. 703–711.
- [21] Rokhov Yu., Kherd D., Lewis R., Chemistry of Metalorganic Compounds, Moscow: Publishing House of Foreign Literature, 1963.
- [22] Ashby E.C., Smith M.B. // J. Amer. Chem. Soc. – 1964. – V. 86. – № 20. – PP. 4363–4370.
- [23] Chmelir M. // J. Polym. Sci.: Polym. Symp. – 1976. – V. 56. – № 2. – PP. 311–322.
- [24] Gorbachev S.G. // Abstract dissertation ... of candidate of chemical science. – Tomsk. – 1976. – 23 p.
- [25] Lyapkov A.A., Sutyagin V.M., Lopatinskii V.P., Kubits Z.G. // Polymer Science U.S.S.R. – 1987. – V. 29. – № 12. – PP. 2939–2942.
- [26] Sutyagin V.M., Lyapkov A.A. // Izvestiya Vuzov. Khimiya i Khimicheskaya Tekhnologiya. – 2000. – V. 43. – Issue 3. – PP. 87–91.
- [27] Bowyer P.M., Ledwith A., Sherrington D. // Polymer. – 1971. – V. 12. – № 8. – PP. 509–520.
- [28] Lyapkov A.A., Ionova E.I., Sutyagin V.M., Nikonova N.A. // Bulletin of the Tomsk Polytechnic University. – 2008. – V. 313. – №3. – PP. 59–64.
- [29] Ionova E.I., Lyapkov A.A., Bondaletov V.G., Shipilova N.S. // Bulletin of the Tomsk Polytechnic University. – 2009. – V. 314. – №3. – PP. 100–105.
- [30] Lyapkov A.A., Ionova E.I., Bondaletov V.G., Romanova A.A. // Bulletin of the Tomsk Polytechnic University. – 2009. – V. 314. – №3. – PP. 106–111.
- [31] Ionova E.I., Lyapkov A.A., Bondaletov V.G., Bondaletova L.I., Petrenko T.V. // Coke and Chemistry. – 2009. – V. 52. – № 11. – PP. 496–500.

- [32] Lyapkov A.A., Ionova E.I., Bondaletov V.G. // Bulletin of the Tomsk Polytechnic University. – 2011. – V. 318. – №3. – PP. 97-101.
- [33] Ionova E.I., Lyapkov A.A., Bondaletov V.G., Karmanova O.I. // Bulletin of the Tomsk Polytechnic University. – 2011. – V. 319. – №3. – PP. 147-152.
- [34] Kuznetsov N.N., Ionova E.I., Lyapkov A.A., Bondaletov V.G., Manankova A.A. // Chemical Industry. - 2009. - V. 86. - № 7. - PP. 367-378. 22 V. 311. - № 3. - PP. 124-129. 25
- [35] Ionova E.I., Lyapkov A.A., Bondaletov V.G., Fiterer E.P. // Polzunov bulletin, 2009. – No 3. – PP. 163–167.
- [36] Peng Y.X., Liu J.L., Cun L.F. // J. Polym. Sci. – 1996. – V. 34. – № 17. – pp. 3527–3530.
- [37] M. Moreau, K. Matyjaszewski, P. Sigwalt. // Macromolecules. – 1987. – V. 20. – № 7. – PP. 1456–1464.
- [38] K. Matyjaszewski, P. Sigwalt. // Macromolecules. – 1987. – V. 20. – № 11. – PP. 2679–2689.
- [39] Shirota Y., Mikawa H. // Macromol. Sci.: Rev. Macromol. –Chem. – 1977. – V. C16. – № 2. – PP. 129–196.
- [40] Geylord J. // Uspekhi Khimii – 1972. – T. 41. – No 6. – pp. 1067–1110.
- [41] Rodrigues M., Leon L.M. // Eur. Polym. J. – 1983. – V. 19. – № 7. – PP. 585–588.
- [42] Viberg N. // Angew. Chem. – 1968. – V.80. – № 20.–PP.809–822.
- [43] Tinyakova E.I., Zhuravleva T.G., Kurenkina T.I., Kirilova I., Dolgoplosk B.A., Reports of USSR Academy of Sciences – 1962. – T. 144. – No 3. –pp. 592–595.
- [44] Lyapkov A.A., Sutyagin V.M. // Bulletin of the Tomsk Polytechnic University. – 2007. – V. 311. – № 3. – C. 124-129.
- [45] Novikov V.T., Lyapkov A.A., Kubits V.V. // Polymer Science U.S.S.R. – 1987. – V. 29. – № 12. – PP. 2942-2944.
- [46] Lyapkov A.A., Sutyagin V.M., Lopatinskii V.P. // Bulletin of the Tomsk Polytechnic University. - 2004. - V. 307. - № 4. - PP. 108-113.
- [47] Peper D.C. // Eur. Polym. J. – 1979. – V. 16. – № 5. – PP. 407–411.
- [48] Rooney J.M. // Makromol. Chem. – 1978. – V. 179. – PP. 165–171.
- [49] Rodrigues M., Leon L.M. // Eur. Polym. J. – 1983. – V. 19. – № 7. – PP. 589–591.
- [50] Bilbao E., Rodrigues M., Leon L.M. // Polym. Bull. – 1984. – V. 12. – № 4. – PP. 359–362.
- [51] Sigwalt P., Moreau M. // Progress Polym. Sci. – 2006. – V. 31. – № 1. – PP. 44–120.
- [52] Goethals E.J., Du Prez F. // Progress Polym. Sci. – 2007. – V. 32. – № 2. – PP. 220–246.
- [53] Puskas J.E., Shaikh S., Yao K.Z., McAuley K.B., Kaszas G. // Eur. Polym. J. – 2005. – V. 41. – № 1. – PP. 1–14.
- [54] Puskas J.E., Kaszas G. // Progress Polym. Sci. – 2000. – V. 25. – № 3. – PP. 403–452.
- [55] Wojciechowski P., Kryszewski M. // Potsdam. Forsch. – 1979. – V. B. – № 20. – PP. 141–145.
- [56] Partridge R.H. // Polymer. – 1983. – V. 24. – № 6. – PP. 733–738.
- [57] Kearns D.R., Gardner P., Carmody I. // J. Phys. Chem. –1967. – V. 71. – № 4. – PP. 931–937.
- [58] Gurianova E.N., Goltsshtein I.P., Romm I.P., Donor-acceptor bond, Moscow: Khimia – 1973. – 398 p.
- [59] Heublein G., Kumpfel W., Schutz H. // Z. Chem. – 1978. –V. 18. – № 1. – PP. 34–36.

- [60] Amis E. Influence of solvent on rate and mechanism of chemical reactions, Moscow: Mir, 1977
- [61] Pask S.D., Nuyken O., Visher A., Walter M. // «Cation Polym. and Relat. Process. Proc. 6th Int. Symp., Ghent, 30 Aug. – 2 Sept., 1983». – London. – 1984. – PP. 25–30.
- [62] Heublein G., Bauerfeind D., Spange S., Knoppel G., Wondra-czek R. // *ibid.* – PP. 69–75.
- [63] Plesch P.H. // *ibid.* – PP. 1–16.
- [64] Matyjaszewski K., Szymanski R., Kubisa P., Penczek St. // *Acta Polym.* – 1984. – V. 35. – № 1. – PP. 14–22.
- [65] Kunitake T., Takarada K. // *J. Polym. Sci.: Polym. Symp.* – 1976. – № 56. – PP. 33–38.
- [66] Puskas J., Kaszas G., Kennedy J.P., Tudos F. // *J. Macromol. Sci.* – 1982. – 1983. – V. A18. – № 9. – PP. 1353–1366.
- [67] Higashimura T. // *J. Polym. Sci.: Polym. Symp.* – 1976. – № 56. – PP. 71–76.
- [68] Heublein G. // *J. Macromol. Sci.* – 1981. – V. A16. – № 2. – PP. 563–577.
- [69] Rooney J.M. // *J. Polym. Sci.: Polym. Symp.* – 1977. – № 56. – PP. 47–56.