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Inter- and intra-molecular interactions in anionic polymerization of polar vinyl monomers

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Dedicated to Acad. Dimiter Ivanov on the occasion of his 120th birth anniversary

This review article presents the results on the nature of the active centers of propagation (AC) in anionic polymerization of polar vinyl monomers such as acrylates, methacrylates, vinyl nitriles and vinyl ketones and especially their interactions with donor-acceptor ligands, carried out in the Laboratory of Polymerization Processes of the Institute of Polymers, Bulgarian Academy of Sciences. Particular attention to the interactions involving AC with lithium and magnesium counter-ions was paid due to their strong tendency of interacting with a variety of ligands, as well as in reactions of self-association resulting in numerous possibilities of controlling the structure of the polymers as well as the composition of copolymers. The model compounds or “living”oligomers of polar vinyl monomers were studied intensively by using IR spectroscopy and conductometry. Their physicochemical characteristics in solution, before and after adding of ligands, were investigated. A typical feature is the use of lithium picrate as a model in studying the interactions with monomers, compounds with polar groups, and most typical additives: alkoxide, LiCl, tetraalkylammonium salts and trialkylaluminum compounds.

Key words: anionic polymerization, polar vinyl monomers, “living”oligomers, propagation active centers, polymer tacticity, ambifunctional nucleophilic species, ligands

INTRODUCTION

The chemistry of carbanions is a traditional subject for research in Bulgaria. The first studies in the field of the chemistry of organometallic compounds are placed by acad. D. Ivanov and his world-known school. Carbanions are the centers for the growth of the polymer chain in the anionic polymerization. By means of anionic polymerization can be obtained the so-called “living” polymers in which the growing centers or propagation active centers (AC) retain their reactivity after full consumption of the monomer. Indeed, living anionic polymerization is the first successful method for the synthesis of polymers with very narrow molecular weight distribution (MWD), for the synthesis of macromers and active polycondensation oligomers, as well as for the preparation of well defined block copolymers. Until now “living” polymerization is the best method for achieving good control over the molecular weight and the polymer tacticity. It is apparent that the anionic polymerization is far more complex process as compared to the radical polymerization. To study the mechanism of anionic polymerization researcher must be familiar with the chemistry of carbanions, all modern spectral methods, kinetic methods for fast reactions in solution, non-aqueous solutions electrochemistry, etc.

There are several reviews (cited below) describing anionic polymerization of (meth)acrylates: mainly kinetic results and MWD of the polymers obtained. The present review article presents the results on the nature of the active centers of propagation in anionic polymerization of polar vinyl monomers (PVM) such as acrylates, methacrylates, acrylonitriles, and vinyl ketones and especially their interactions with donor-acceptor ligands, carried out in the Laboratory of Polymerization Processes of the Institute of Polymers, Bulgarian Academy of Sciences. Mostly works of our own are presented, since our approach is not so much popular as the kinetic investigations.

Anionic polymerization of PVM is by far more complex than that of styrene and dienes. In contradiction with the simplicity of polymerization of nonpolar monomers, the polymerization of PVM is rather complicated due to the presence of polar groups. Indeed, PVMs are bidentate species, and each polar group competes with the double ›C=C‹ bond for the initiator or the propagating centers. A problem arises from: a) the side reactions by nucleophilic attack of the AC onto the monomer or polymer unit due to the reactive side group (e.g.

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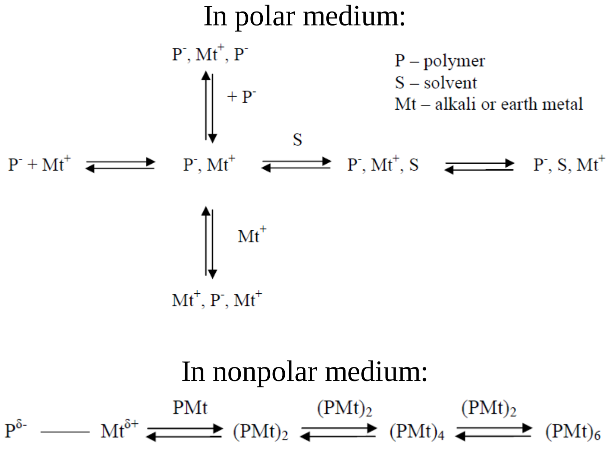
ester, nitrile, amide, or keto groups); b) different, sometimes competitive, available forms of aggregation of AC, as in contrast to polystyrene active chain, the AC aggregation in the case of PVM occurs also in polar solvents like ethers; c) ambident nature of the AC, which refers to active species containing two centers susceptible to monomer attack, in other words, two nucleophilic sites. Table 1 represents the most important ambident nucleophilic species, typical for the anionic polymerization of PVM.

Characteristic of our investigations is the wide use of IR spectroscopy of carbanions having a cyano- or a carbonyl group adjacent to the anion. From the pioneering works of Juchnovski [7,8] on nitriles and Lochmann on ester enolates [5,9], it is well known that in such cases the IR C≡N and C=O stretching frequencies decrease by 20 to 200 cm^{-1}.

On account that the AC of the anionic polymerization of PVMs are ambident nucleophiles, different forms of active species coexist such as free ions, contact or solvent-separated ion-pairs, triple ions, dimers, and higher associates (see Scheme 1) depending on the solvent medium nature (polar or non-polar), size of counter ion, concentration and temperature. The above mentioned ionic forms are in dynamic equilibrium and most of them are capable of initiating the polymerization, but with different rates and mode of addition.

Each active site for a certain time can exist in any of the ionic forms shown in Scheme 1 involved in the propagation reaction in a manner consistent with the current state. A slow equilibrium between ionic species results in broadening and even multimodality of the MWD. Obviously, aggregation and ion dissociation of anionic AC direct the course of the anionic polymerization. Hence, the propagation rate, the MWD and the polymer stereoregularity strongly depend on the reaction conditions.

The mechanism of living anionic polymerization is associated primarily with the nature of the active centers of growth and donor-acceptor interactions in which they participate.



Scheme 1. Different forms of active species in anionic polymerization of PVM.

There are five main interactions involving the active site of growth:

1. AC – solvent molecules or other cation-binding ligands (e.g. ethers, glymes, crown-ethers, cryptands)
2. AC – polar groups from polar vinyl monomer or monomer unit

   AC – additives:
3. AC – μ-type ligands (e.g. LiCl, $LiClO_4$, *tert*-BuOLi)
4. AC – Lewis acid agents (e.g. AlR_3, BR_3, ZnR_2)
5. AC – quaternary ammonium salts

Another characteristic feature of our research is that for the purpose of estimating the interactions of the AC with different ligands, the approach of studying a reference system was adopted, i.e. lithium picrate (LiPi) in dioxane (DO). We look upon the picrate as a model of ambident organolithium compound imitating the AC. The interacttion LiPi/ligands were studied in DO, a solvent of comparatively low solvation capacity and low polarity. This avoids the formation of solvent separated ion pairs and free ions and, hence,

Table 1. Ambifunctional nucleophilic growing centers in anionic polymerization of PVM.

No	Nucleophilic site	Anion structure	υ_{CN} or υ_{CO} IR absorption (cm^{-1})	Polymer
1	Alkyl cyanide anions	$\overbrace{>C(R)CN}^{-}$	2000 – 2050 alkali cations [1,2] 2050 – 2080 Mg^{+2} [3]	Polyacrylonitrile (R = H) Polymethacrylonitrile (R = CH_3)
2	Ketoenolate anions	$\overbrace{>C(R)CO}^{-}$	1560-1610 [4]	Polyvinylketone
3	Esterenolate anions	$\overbrace{>C(OR)CO}^{-}$	1620 – 1680 [5,6]	Polyacrylate Polymethacrylate

reduces the number of possible structural types of AC when small amounts of ligands are introduced. The method was firstly applied to investigate weak interactions of organic compounds with polar groups and LiPi [10].

These AC/ligand interactions have a decisive influence on the overall mechanism of the polymerrization process and the polymer properties. A striking example of the importance of the additives is the influence of LiCl on the MWD of *tert*- butyl acrylate as shown in Fig. 1 [11].

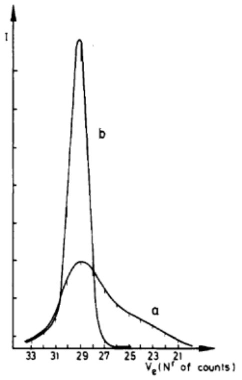
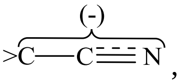


Fig. 1. Influence of LiCl as additive in anionic polymerization of *tert*-butyl acrylate: no salt (a); LiCl/AC = 5 (b) [11].

Clarification of the nature of AC/polar group and AC/additive interactions contributes to finding the most suitable conditions under which polymerization process takes place with minimal involvement of side reactions, preparation of polymer with defined molecular mass and narrow MWD, as well as stereocontrol of the propagation step. In this review, we will pay particular attention to the interactions involving AC with lithium or in some cases magnesium counter-ions. As opposed to the other alkali ions, they show strong tendency of interacting with a variety of ligands, as well as in reactions of self-association. This results in numerous possibilities of controlling the structure of the polymers as well as the composition of copolymers.

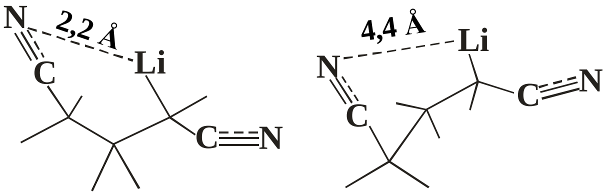
TYPES OF INTERACTIONS INVOLVING AC OF ANIONIC POLYMERIZATION OF VINYL NITRILES

The AC in the anionic polymerization of AN or MAN are ambident anions. Therefore, the negateve charge is distributed on the group



$$\overbrace{>C\!-\!C\equiv N}^{(-)},$$

the nitrogen atom being partially charged. This might result in increased electrostatic interaction between the counterions, which hampers the formation of loose or solvent separated ion-pairs. In order for a clearer distinction of the interactions, typical for the closest to the AC cyano-groups, the following model compounds were used: α-lithiated isobutyronitrile ($P_{1(CN)}Li$) and 1,3,3-trimethylglutaronitrile ($P_{2(CN)}Li$). The quantum-chemical calculations indicate the existence of different conformers of $P_{2(CN)}Li$ in non-polar media [12]. The distance between Li^+ and the penultimate CN group is 2.2 to 4.4 Å (see Scheme 2). Obviously, the structure in which the distance is smallest, i.e. 2.2 Å, is characterized by the strongest interaction between Li^+ and the penultimate CN group in $P_{2(CN)}Li$:



Scheme 2. Conformers of $P_{2(CN)}Li$, according to [12].

The results on measurements of the dissociation constant in THF are consistent with the calculations: they show very low values for K_D of order 10^{-11}M and close to the theoretical values of counterion distance [13] (see Table 2).

Table 2. Dissociation constants of ion pairs (K_D) and ion triples (k_T) of lithium salts of ambident anions ($P_{n(X)}Li$) as model living oligomers of PVM in THF at -30°C [13,14].

“Living” oligomer	K_D **x** 10^{12} **M**	k_T **x** 10^4 **M**	**[ABA]⁻/[A]⁻**
$P_{1(X)}Li$			
$P_{1(CN)}Li$	69	7.0	7
$P_{1(COC(CH3)3)}Li$	75	6.5	8
$P_{1(COOR)}Li$	0.4	0.2	250
$P_{2(X)}Li$			
$P_{2(CN)}Li$	6.0	1.0	50
$P_{2(COOR)}Li$	1.5	3.0	16

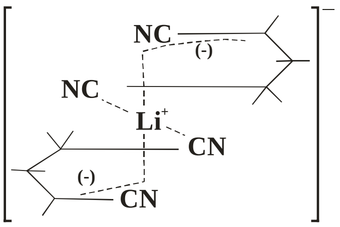
It should be noted that the calculations of the dissociation constants were made by using Woosters equation [15]. The anion triple A^-,Li^+,A^- is energetically more stable than the triple Li^+,A^-,Li^+ [16], so we suppose the existence mainly of negative ion triple. The ionic equilibrium can be described by the following equations:

$$A^-,Li^+ \overset{K_D}{\rightleftarrows} A^- + Li^+ \qquad A^-,Li^+,A^- \overset{k_T}{\rightleftarrows} A^- + A^-,Li^+$$

K_D values are in agreement with data for the dissociation constants of other anions, containing a heteroatom, e.g. 2-ethylpyridine salts [17], and "living"MMA oligomers [14]. Mainly tight ion pairs are formed with the interionic distance of about 2.5 Å. Importantly, the dissociation constants of the studied salts are smaller than these of polybutadienyl lithium and polyisoprenyl lithium [18], and diminish in the following order:

K_D	> **K_D**	~ **K_D**	> **K_D**
("living" poly butadienyl lithium)	(α-lithiated ketone)	(α-lithiated nitrile)	(α-lithiated ester)

In the case of lithium derivatives of nitriles, the dissociation constant of the dimer $P_{2(CN)}Li$ is one order of magnitude less than that of $P_{1(CN)}Li$, which is indicative of chelate complex formation [19]. Both $P_{1(CN)}Li$ and $P_{2(CN)}Li$ tend to form ion triples, the concentration of ion triples in $P_{2(CN)}Li$ solutions being much higher than in solutions of $P_{1(CN)}Li$. We consider the most probable structure of the ion triple to be as shown:



Obviously, the –CN group competes with THF molecules for the lithium coordinating sites. The formation of ion triple is consistent with the results on measurements of binding constants (K_L) between lithium picrate, used as model of ambident AC, and some nitriles and THF as presented in Table 3 [20,21]. It is widely assumed that interacttions of alkali metal cations with oxygen donor atoms are stronger than with the softer nitrogen atoms, contrary to the data for aliphatic nitriles shown in Table 3. In our opinion, the rod-like structure of the most nitriles suggests that in complex formation with LiPi steric hindrance is less important than for the cyclic ethers. This could be the reason why K_L (THF) ‹ K_L (CH_3CN) in spite of the higher DN for THF. In addition to a favorable steric factor, interaction of Li^+ with the π system of the nitrile group may contribute to the binding energy.

IR spectroscopy is especially convenient for studying the character and changes of the AC during the polymerization process. It should be noted that the study of mechanism of chain propagation of AN/MAN polymerization by IR assisted measurements is complicated because of insolubility of the polymers. In order to prepare soluble species, polybutadiene and polystyrene "living" chains were used as initiators. Thus, a technique of "capped" polymers was successfully used by addition of small number (n = 1-6) of AN/MAN monomer units to the quite soluble polybutadiene or polystyrene active ends [22,1]. Thus, polymerization does not lead to precipitation and made it possible to study the solution properties of AC in the anionic propagation of AN/MAN directly in the range of AC concentrations $1.10^{-1} – 1.10^{-3}$ M.

Table 3. Complex formation constants K_L of lithium picrate with THF and some nitriles, ketones and esters in dioxane at 25°C [20,21].

Ligand	K_L, M^{-1}	DN	ε
THF	0.95	20	7.6
Acetonitrile	1.22	14.0	36.2
Acetone	1.16	17.0	20.7
Ethylacetate	0.75	17.1	6.0
iso-Butyronitrile	1.80	15.4	20.8
Propionitrile	2.80	16.1	27.7
Methacrylonitrile	0.55		
Acrylonitrile	0.46		38
Methylmethacrylate	0.16		

The carbanion next to the cyano group reduces the absorption frequency of the latter by 20 - 200 cm^{-1} [23]. It should be noted that the wave length of the nitrile absorption bands at the AC are strongly dependent on the nature of the counterion and solvent as well on the presence of donor or acceptor additives, but remain unchanged within the whole temperature range between 20°C and -60°C in THF [24,2].

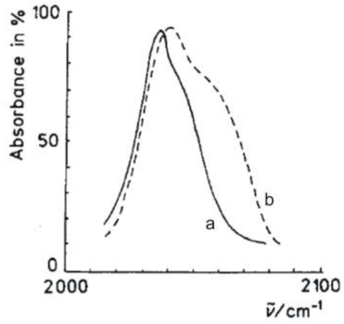


Fig. 2. IR spectra of $P_{1(CN)}Li$ (a) and $P_{2(CN)}Li$ (b) in THF [25].

$P_{2(CN)}Li$ resembles to a greater extent the real AC in comparison to $P_{1(CN)}Li$, because it possesses one more monomer unit. As in the case of conductivity measurements, the characteristics of IR band have to be greatly influenced by the second nitrile group being in interaction with lithium counterion. Indeed, as seen from Fig. 2, the ν_{CN} band of the active site for $P_{2(CN)}Li$ is significantly wider and shifted to higher wave numbers (2037 cm^{-1} → 2042 cm^{-1}).

The result is in full agreement with the data obtained in the synthesis of "living" oligomers of MAN at different initial ratio M/In [1] as shown in Fig.3.

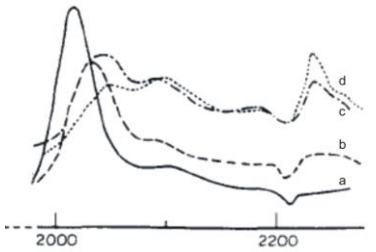


Fig. 3. IR spectra of MAN active species in the reaction of oligostyryllithium with different M/In ratio: MAN/In=1 (a); MAN/In=2.2 (b); MAN/In=3.6 (c); MAN/In = 5.5 (d); THF, ambient temperature [2]

The shift of the band at 2020-2060 cm^{-1} towards higher frequencies, as the number of adjacent monomer units is increased (Fig. 3) is explained by interaction of the AC with the nitrile groups of the polymer chain next to the growing end. The dependence of the shift of the maxima in the IR spectra on the number of the groups attached is shown in Fig. 4.

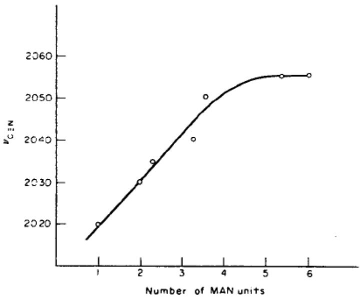


Fig. 4. Dependence of the band (ν_{CN}) shift of MAN AC on the number of MAN units attached to the polymer chain [2].

The addition of about 3-4 monomer units changes the position of the IR spectral bands. At higher ratios ν_{CN} levels off. The results are direct evidence of the intramolecular interaction of active centers with neighboring monomer units (penultimate effect), which was hinted at in conductivity studies.

With the aid of IR spectroscopy it is possible to follow the interaction of AC's with the cyano group of the monomer. The intermolecular interaction Li^+…CN characterized by the appearance of a band at 2255-2285 cm^{-1} is of special importance and it is quite similar to that between LiI and a nitrile [26,27]. Indeed, in non-polar solvents the AC's of oligomethacrylonitrile with lithium and magnesium counterions form complexes with nitriles having characteristic bands in the range 2250-2280 cm^{-1} [2,3]. In case of organomagnesium compounds, used as initiators, the AC or the initiator itself form complexes even with the monomer without addition reaction. This observation is especially worth noting, since it permits a more detailed investigation of the initial act of complex formation between the initiator and the monomer or between the AC and the monomer before the propagating step:

$$P_nMt + M \overset{K_c}{\rightleftharpoons} P_nMt.M \xrightarrow{k_p} P_{n+1}Mt$$

The organomagnesium compounds are very suitable for such studies because of their lower reactivity: thus in hydrocarbon media, they do not initiate AN, or MAN polymerization at temperatures below -60°C. No polymer formation takes place on mixing the ether-free organomagnesium halide $[(C_{12}H_{35})_3Mg_2Br]_n$ in toluene with MAN [25]. The IR spectrum of the mixture at room temperature exhibits an absorption band at 2225 cm^{-1} (free monomer), and at 2263 cm^{-1} (initiator/monomer complex) as shown in Fig. 5.

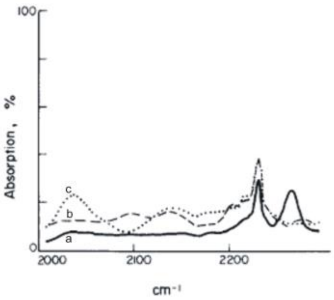
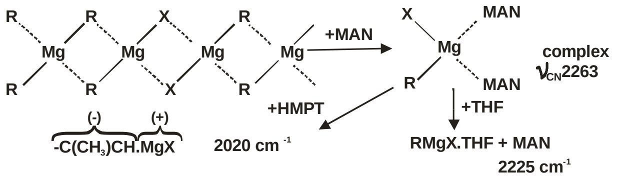


Fig. 5. IR spectra of the reaction mixture MAN/ $[R_3Mg_2Br]_n$ in toluene (a); after adding THF (b); after adding hexamethylphosphortriamide (HMPT) (c) [3]

Addition of equivalent amount of THF, causes increasing of intensity of the band for free monomer and disappearance of band at 2263 cm^{-1}. This is due to the greater binding constant of THF as compared to that of MAN (Table 3). When the additive is HMPT, the new band for AC appears.

The observed interactions can be represented schematically (Scheme 3) thus:



Scheme 3. Complex formation between MAN and $[R_3Mg_2Br]_n$ in toluene [3].

Dielectric susceptibility and electric conductivity measurements carried out on the $[R_3Mg_2Br]_n$ solution during "titration" with MAN reveal that the MAN/Mg complex is 2:1.

The investigations have shown also that two types of AC (AC I and AC II) are formed during polymerization of MAN initiated by organo-magnesium compounds. Growth of the polymer chain in ether solvents proceeds through AC I. AC II are found by polymerization in toluene, initiated with R_2Mg. This is in agreement with studies of Joch *et al.* [28], who suggested, on the basis of MWD, the existence of two types of AC in the polymerization of MAN in toluene initiated with diethylmagnesium:

$$\text{-}\overbrace{C(CH_3)CN}^{(-)},\overbrace{MgR}^{(+)}\ (\text{AC I}) \qquad [(CH_3)C\ CN]_2{}^{-}\ Mg^{2+}\ (\text{AC II})$$

Li^+…RCN complex was formed also when trimethylacetonitrile (TMAN) is added to the benzene solution of "living" MAN oligomers [2]. The complex formation is characterized by a new IR band at 2260 cm^{-1}. As in the case of $[R_3Mg_2Br]_n$ and MAN, the complex is in equilibrium with the free nitrile and AC:

$$\text{-}\overbrace{C(CH_3)CN}^{(-)},Li^+ + (CH_3)_3CCN \overset{k}{\rightleftharpoons} \text{-}\overbrace{C(CH_3)CN}^{(-)},Li^+\ldots NCC(CH_3)_3$$

Scheme 4. Equilibrium between AC and complex of AC with TMAN in benzene. Equilibrium constant at 20°C, K = 0.25 ± 0.05 M [2].

The result reveals the possibility for intermolecular interaction with the participation of –CN groups attached to the monomer units. This is clearly shown in the case of $P_{2(CN)}Li$. In the IR spectrum of a mixture of $P_{2(CN)}Li$ and non-metalated dimer $P_{2(CN)}H$ in benzene along with the band of the unperturbed CN-group a band at 2265 cm^{-1} is again observed (Fig. 6).

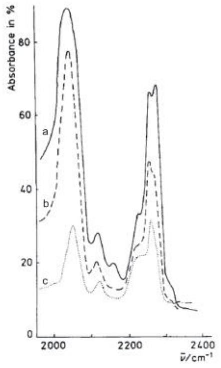


Fig. 6. IR spectra of a mixture of lithiated and non-metallated dimer in benzene, $P_{2(CN)}H/P_{2(CN)}Li=50$. $[P_{2(CN)}Li]=0.071$ M (a); $[P_{2(CN)}Li]=0.06$ M (b); $[P_{2(CN)}Li] = 0.33$ M [25]

Evidences for the interaction of AC with tert-BuOLi

The serious drawback of the anionic polymerization of AN and MAN is that it is accompanied by several side reactions. The reason for the formation of these byproducts is the high capacity of the nitrile group to react with strong bases, as well as to take part in donor-acceptor interactions. It is well known that *t*-BuOLi is able to interact with the AC of acrylates and methacrylates [29,30] and is successfully used to improve the mode of polymerization. Therefore, it is of great interest to study the interactions of polyAN and polyMAN AC with lithium alkoxide in order to use it as additive in more efficient polymerization process.

The interaction between $P_{n(CN)}Li$ and *t*-BuOLi is very different from P_nLi…NC- complex formation. *t*-BuOLi affects the association equilibria of the AC of PVM transforming them into mixed associates and on these ground this kind of interaction can be formulated as associative.

The interaction of AC and *t*-BuOLi causes a shift of the band of the $\nu_{CCN}{}^{-}$ toward higher wave numbers. The IR spectrum of the system $P_{1(CN)}Li$/*t*-BuOLi shows changes that indicate a specific interaction between AC and *t*-BuOLi (Fig. 7) [25]. The intensity of the absorption of the group

$$>\overbrace{C\text{—}C\equiv N}^{(-)}$$

decreases in the presence of additive depending on the mole ratio of the two compounds. At the same time, there is an increase in intensity of a new band at 2047 cm^{-1}. The assumption for complex formation is confirmed by the conductometric measurements of $P_{1(CN)}Li$ solutions with different [*t*-BuOLi]/$P_{1(CN)}Li$ ratios, which indicates the existence of adduct with 1:1 stoichiometry. It should be noted, that both $P_{1(cN)}Li$ and *t*-BuOLi and their adducts are aggregates in THF, which hampers more detailed study.

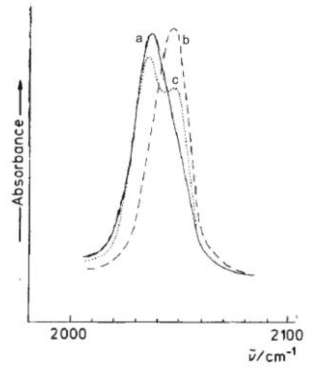


Fig. 7. IR spectra of $P_{1(CN)}Li$ without and in the presence of *t*-BuOLi in THF: $[P_{1(CN)}Li]=0.06$ M (a); [t-BuOLi]/$[P_{1(CN)}Li]=3$ (b); t-BuOLi]/$[P_{1(CN)}Li] = 1$ (c) [25]

The interaction of $P_{2(CN)}Li$ and *t*-BuOLi has a more complicated character. At the ratio [*t*-BuOLi]/$P_{2(CN)}Li] = 2$, however, unlike $P_{1(CN)}Li$, the larger part still exists in a form of free AC. Most probably, the explanation is in the possibility *t*-BuOLi to interact both with AC and the second nitrile group of $P_{2(CN)}Li$.

INTERACTIONS INVOLVING AC OF ANIONIC POLYMERIZATION OF VINYL KETONE

The ACs of vinyl ketones resemble enolates, the most characteristic representatives of ambient anions. The negative charge in an enolate is delocalized between a carbon atom and an oxygen atom, and their site may act as a nucleophile depending on the reaction conditions. Thus, enolate are capable of forming covalent bonds with both carbon and oxygen atoms, when interacting with electrophilic compounds [31,32]. The effects of solvent, counterion, and temperature as well as the structure of the nucleophile and the electrophile on this C/O competition, have been studied extensively. It should be noted that the data of dissociation constants $\boldsymbol{K}_D$ and $\boldsymbol{k}_T$ of α-lithiated ketones and nitriles are very close (see Table 2).

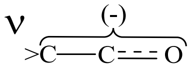
As it is the case in the anionic polymerization of vinyl nitriles, the AC of vinyl ketones are able to interact with the adjacent monomeric units, thus forming intramolecular complexes. The keto groups of the last one unit and the next to it are situated near the cation as shown (Scheme 5) for the trimer conformations.

The intramolecular interactions, shown in Scheme 5 are in agreement with the results of Lyons and Catterall [33] who proposed the formation of cyclic products with the growing AC as a result of interaction between the Li^+ counterion and the carbonyl group of the next to the last but one monomeric unit. Indeed, for some conformers, shown in Scheme 5, the distance between the lithium and the carbonyl group does not exceed 3.5 Å, which proves the formation of coordinative bonds.

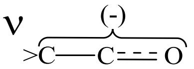
The negative charge distributed on 3 atoms


$>\overbrace{C-C{=}O}^{(-)}$

causes decreased adsorption of the carbonyl group, characterized by a band at 1560-1610 cm^{-1}, attributed to the stretching vibrations of the delocalized group

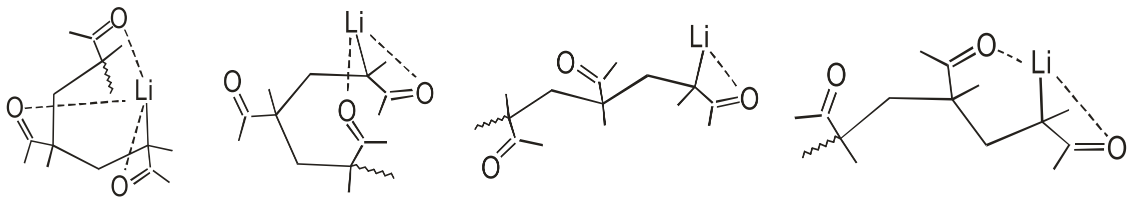

$\nu_{>\overbrace{C-C{=}O}^{(-)}}$ [4].

Alkali derivatives of acetone (ADA) are simplest model compounds of AC. In contrast to nitriles, the position of the


$\nu_{>\overbrace{C-C{=}O}^{(-)}}$

band strongly depends on the counterion dimensions (Fig. 8).

The most probable explanation for this dependence is the decreased electrostatic interacttion between the counterions from Li^+ to Cs^+, due to the increased average contact ion pair interionic distance. The band at 1688 cm^{-1} in the spectrum of acetone-lithium can be observed only in the presence of unreacted acetone in solution. If acetone is fully metalated only one band at 1602 im^{-1} is observed. The addition of acetone results in the appearance of maxima at 1688 and 1712 cm^{-1} (free acetone) as well as decrease of the band intensity at 1602 cm^{-1} (Fig. 9).



Scheme 5. Different conformations of $P_{3(COCH3)}Li$.

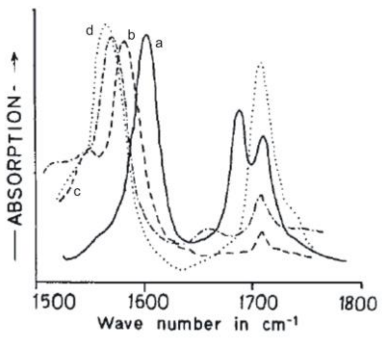


Fig. 8. IR spectra of ADA in THF with different counterions at 25°C, Li^+ (a); Na^+ (b); K^+ (c); Cs^+ (d) [4].

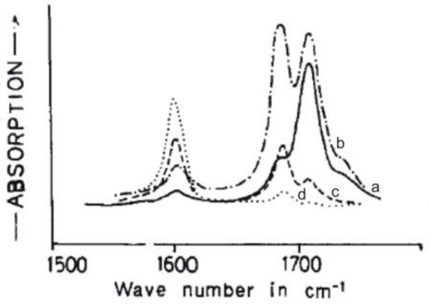


Fig. 9. IR spectra of ADA (Li^+) in THF at different [acetone]/[ADA] ratios: r = 13.3 (a); r = 3.8 (b); r = 1.2 (c); r = 0.27 (d) [4]

Temperature dependence between these three bands was established as well. At low temperature the peak at 1688 cm^{-1} increases in intensity, thus compensating the maxima at 1602 and 1712 cm^{-1}. Obviously, this is due to the formation of 1:1 complex, proved also by electroconductivity measurements:

$$>\overbrace{C—C=\!=O}^{(-)}, Li^+ + CH_3COCH_3 \rightleftarrows \text{complex}$$

The coordination of AC with the next carbonyl group (self-association) resembles the interaction between ADA and acetone. The IR spectra of solutions of “living” oligoisopropenylmethyl ketone exhibit nearly the same bands. They easily form intramolecular complex characterized by bands at 1685-1700 cm^{-1}. The equilibrium process in “living”oligomers is rather complicated since the AC of the trimer can form complexes with different monomeric units, each of them being characterized by a definite equilibrium constant. The strength of interaction decreases in the order $Li^+ > Na^+ > K^+ > Cs^+$. It is established that the MWD of the polymer narrows by diminishing the intramolecular $Mt^+ \ldots C=O$ interaction: e.g. by using Cs counterion the most narrow MWD is obtained (Fig. 10) [34].

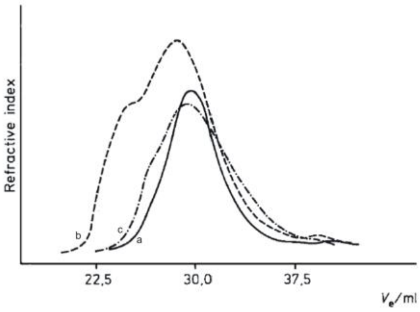
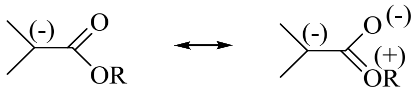


Fig. 10. GPC curves for poly(isopropenyl methyl) ketone by polymerization in THF at -70°C with counterions: Cs^+(a); Li^+(b); K^+(c) [34]

It should be noted that the intramolecular interaction Li… C=O is much stronger that the interaction Li…CN: IR spectra of α-lithiated oligomers of methyl isopropenyl ketone give evidence for intramolecular complex formation between the lithium counterion and the carbonyl groups of the neighboring monomer units even in THF at temperature as high as 20°C [4], whereas the IR spectra of the α-lithiated dimer of MAN indicates strong chelate formation only in benzene and toluene [2].

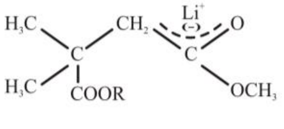
STRUCTURE OF LITHIUM ESTER ENOLATES IN THF

The dissociation constants of α-lithiated esters are smaller by about two orders of magnitude in comparison with lithium derivatives of nitriles and ketones (Table 2). This can be explained by the possibility for existence of mesomeric structures of ester anion:

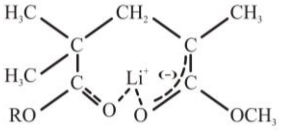


The partial charge distribution on –OR group leads to lower electron density of the ester enolate group in contrast to the same group in lithium keto-enolates, which may be judged by the different shifts of $\nu_{›CCO}$ bands in the IR spectra of α-lithiated esters [5] and lithium keto-enolates [4] (Table 1). The resonance structure is supported also by ^{13}C-NMR measurements of Vancea and Bywater [35], who reported reduced freedom of motion of the alkoxy groups in THF solutions of α-lithiated methylisobutyrate at low temperatures.

In contrast to lithium derivatives of nitriles, the difference between the dissociation constants of $P_{1(COOR)}$ Li and $P_{2(COOR)}$ Li is insignificant, the constants of the dimer being slightly higher (see Table 2). The values of $\boldsymbol{K_D}$ are of the order 10^{-12}M. It can be assumed that the AC of MMA exists in THF mainly as the nonchelated E form contact ion-pair:



E

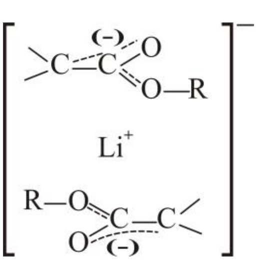


Z

^{13}C-NMR spectra of the lithiated dimer in THF are also not in accordance with the formation of chelate Z structures [36], neither are the IR spectra of the same model at different concentrations indicative for intramolecular complexation.

The strong –O-Li bond in ester enolates tends to form aggregated species. The tendency of lithium ester enolates (P_{1COOR}Li and P_{2COOR}Li) to aggregate in THF was observed for the first time by Halaska and Lochmann [37] by using vapor pressure osmometry as presented in Table 4.

In contrast to the cyano derivatives, the concentration of ion triples in solution of $P_{1(COOR)}$Li is several times higher than that of $P_{2(COOR)}$Li solutions, which is in agreement with decreased aggregation tendency for $P_{2(COOR)}$Li shown in Table 2. In case the lithium cation lays over the plane of a nearly planar CCOOR group as postulated by Eizner *et al.* [38], the ion triples $(ABA)^-$ should possess a sandwich structure which is energetically more favorable for $P_{1(COOR)}$Li than for $P_{2(COOR)}$Li:



Obviously, the principal difference in the structure of ion triples of lithiated dimers of MMA and MAN consists in the assumption that the cyano group of the second monomer unit in the lithiated dimer of MAN has a share in the ion triple construction by formation of a coordinate bond, whereas complexation of counterion with the second ester group is not likely in the case of the α-lithiated dimer of MMA. This assumption is in agreement with the complexation order of nitriles and esters towards lithium picrate in dioxane: nitrile › esters [20] (Table 3). It should be mentioned, however, that lithium counterion in $P_{3(COOR)}$Li is able to coordinate intramolecular with the carbonyl group of the third monomer unit (γ-carbonyl) [39].

Ligated growing centers

In the last 20 years of 20th century efficient ligands have been discovered able to control the livingness and stereospecificity of anionic polymerization of (meth)acrylic ester monomers. The most important function of ligand additives is steric hindrance (steric shielding or electronic protecting of the functional groups of the polar vinyl monomers) providing space area around the AC contact ion pair. It appears to be determining factor for the controlled living polymerization. At least, steric hindrance leads to stabilization of the linear P_{3COOR}Li as rotational isomerization of P_{3COOR}Li is found to be the bottleneck in the intramolecular cyclization reaction. The efficient ligands, discovered to date are classified into the following main groups:

- Lithium alkoxides [40] and enolates [21].
- \- Inorganic salts:
- Lithium and magnesium halide i.e. LiCl, and $MgBr_2$ [41,42].
- Salts with bulky groups i.e. $LiClO_4$ or R_4NX [43,44].
- Aluminium and boron alkyls [45- 47].

Lithium alkoxide and enolate as additives

The role of lithium alkoxides as additives, studied in considerable detail by Trekoval, Lochmann, and Müller, turned out to be significant in both reaction kinetics and tacticity of the resulting polymers [29,48]. Cross-associates such as AC/*t*-BuOLi are acting as propagating centers. The AC's are "enveloped" by alkoxide molecules and the inner voids of the contact ion pair loses most of the solvent molecules. This makes the access to the AC more difficult. As a result, the polymerization process is practically insensitive to the solvent nature because of the strong shielding effect of *t*-BuOLi. Obviously, the mixed associate $P_{1(COOR)}$Li/*t*-BuOLi

Table 4. Average degree of aggregation for model ester enolates in THF [37].

Ester enolate	Degree of aggregation
$(CH_3)_2CLi\ COOCH_3$	3.5
$(CH_3)_2CHCO_2C(CH_3)_2CH_2C(CH_3)LiCO_2C(CH_3)_3$	1.7

is strong enough to withstand competitive solvation by solvent or monomer molecules, thus, preventing the influence of σ-ligands such as glymes or crown ethers on the mode of polymerization process. $P_{1(COOR)}Li$/*t*-BuOLi lowers the basicity of the AC but for steric reasons considerably restricts side reactions like intramolecular cyclization.

In $P_{1(COOR)}Li$ and $P_{2(COOR)}Li$ the cation is close to the O atom of the ester enolate group resembling the lithium alkoxide structure. Indeed, alkoxide, keto-enolates and ester enolates tend to form aggregates such as dimers, trimers or tetramers with a slow exchange rate [49]. Because, in the most cases, the initiator is not fully consumed during the polymerization process, the unreacted $P_{1(COOR)}Li$ plays the role of additive in the same manner as the ligation by *t*-BuOLi. This means that additive like *t*-BuOLi should compete with the unreacted lithium enolate in case of low initiator efficiency. This raises the question, which of both compounds has a higher binding capacity.

Table 5. Association constants, K_{ass} of LiPi complexes with different μ-ligands and $AlEt_3$ in dioxane [21].

Additive	K_{ass}, M^{-1}	λ_{max}, nm
LiCl	75	337
t-BuOLi	120	400
Pin-Li	150	390
$P_{1(COOR)}Li$	600	404
$AlEt_3$	350	325

Pin-Li = α-Lithiopinacolone

The problem was solved with the aid of LiPi, which services as a model compound for AC. According to measurements of the interaction LiPi-additive, shown in Table 5 the association ability of Li-alkoxide and Li-enolate ranges as follows:

K_{ass} Li-esterenolate › K_{ass} Li-ketoenolate › K_{ass} Li-alkoxide

The data, presented in the Table 5, indicate that the *t*-BuOLi associates several times less than lithium ester enolate. It is evident that in order to have an effect as an additive on the polymerization kinetics as well as on the stereochemistry on the polyaddition reaction, the ratio alkoxide/initiator should be much greater than the equimolar ratio. Indeed, Lochman and Müller [30] found that in order to decrease the propagation rate constant by one order of magnitude, addition of *t*-BuOLi at alkoxide/enolate ratio of 3/1 is needed. Wang *et al.* [50] also studied the effects of *t*-BuOLi on the stereochemistry of methyl methacrylate anionic polymerization upon addition of 10 equiv. *t*-BuOLi.

Lithium chloride as additive

It has been shown by the Teyssie group that LiCl-modified organolithium compounds initiate living anionic polymerization of methyl methacrylate, *t*-butyl methacrylate and *t*-butyl acrylate at low temperatures in THF [41]. This enables synthesis of (meth)acrylate based block copolymers with high efficiency and low polydispersity [51]. The explanation of the complexation behavior of LiCl with the lithium oligomers of *t*-BuMA was presented in [52]. The interaction between lithium ester enolate and LiCl is regarded as strong electrostatic interaction. The most pronounced effect of LiCl as an additive is the lowering of polydsipersity index of PMMA and PBuA. Addition of LiCl leads to only one type of complex growing center species with equimolar ratio. Our studies on the interaction between LiCl and lithium picrate in dioxane as reference system is in agreement with the equimolar complex ratio. The association constant K_{ass} 75 M^{-1} (Table 5) is several times less than K_{ass} for alkoxide and enolate derivatives. This gives us grounds to believe that by simultaneous presence of lithium alkoxide/lithium enolate and LiCl, the R-OLi additive will be favored by the interactions with ACs.

Organometallic Lewis acids as additives

Tsvetanov *et al.* [45] first employed $AlEt_3$, Al(*i*-Bu)$_3$, Al(*n*-Bu)$_3$, BEt_3 , and $ZnEt_2$ as additives and *s*-BuLi as initiator in the polymerization of MMA in THF and toluene at -70°C. The AC of oligo-MMA form 1:1 complexes with trialkylaluminum and triethylboron. Addition of acceptors leads to decrease in the rate of MMA polymerization. The presence of such kind of additives increases substantially the syndiotactic sequences. Later on, Hatada *et al.*, studied anionic polymerization of MMA in toluene at -78°C by using *t*-BuLi as initiator and aluminum alkyls as additives [42,53]. Syndiotactic polymers with controlled molecular weight and narrow MWD were obtained. The steric hindrance due to the bulkiness of the aluminum alkyls plays important role. Ballard *et al.* [47] were able to polymerize alkyl methacrylates at elevated temperatures (0 – 40°C) in toluene by using bulky diaryloxyalkyl-aluminum as additives. The AC in the form of “ate” complexes is very stable.

Another improvement was the use of tetraalkylammonium halides as co-additives forming a complex with trialkylaluminium, e.g., $NBu_4[Al_2Et_6Br]$ [54]. The rate of polymerization is two orders of magnitude higher as compared to polymerization, initiated by $P_{1(COOR)}Li/AlEt_3$ and the MWD is very narrow (PDI ‹ 1.1).

The system AC/AlR_3 is much more complex than with the other additives because of the presence of three potential ligands for the acceptor additive: the growing species, the monomer, and the ester group of the monomer units. Moreover, AlR_3 is regarded as acceptor in contrast to Li-alkoxide or Li-enolates. This is clearly seen by comparing UV spectra of LiPi solutions in dioxane in the presence of $AlEt_3$ and $P_{1(COOR)}Li$ (Fig. 11) [21]:

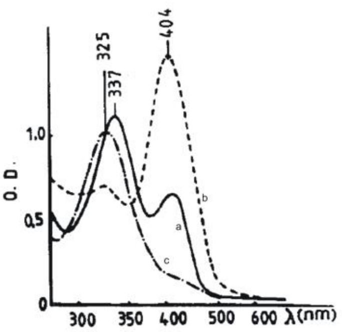
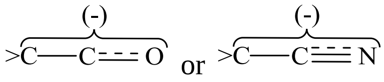
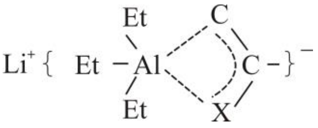


Fig. 11. UV spectra of LiPi (a); and its adducts with $P_{1(COOR)}Li$ (b) and $AlEt_3$ (c)

In the presence of $AlEt_3$ the UV spectrum of LiPi solutions in dioxane undergoes a slight blue shift from 337 to 325 nm. The interaction is fully reversible with well defined isosbestic points. The equilibrium constant is $\boldsymbol{K_{ass}}$ 350 M^{-1}, comparable with the association constants of LiPi and lithium alkoxide/lithium enolate (Table 5). IR measurements also confirm that [45,55] Al and B alkyls interact with the MMA and MAN AC as acceptors. The withdrawal of negative charge leads to decreased electron density on



groups and reduced reactivity of the AC. By analogy with similar complexes the following structure can be postulated:



The lithum counterion is substantially separated from the growing anion in contrast to the action of other additives. The oncoming monomer has to interact with the central aluminum atom.

In the case of LiCl and *t*-BuOLi additives no significant change in tacticity in THF was observed [39]. The different nature of the interaction AC/Ligand in the case of *t*-BuOLi and AlR_3 leads to entirely different structure of the resulting polymers especially in hydrocarbon solvent toluene as shown in Table 6.

Tetraalkylammonium salts as additives

The anionic polymerization of MMA, initiated by organolithium compounds in toluene, is characterized by complex kinetics and broad molecular weight distribution. Despite these drawbacks, the process is of great interest since it leads to highly isotactic polymer and has a definite advantage over the one in THF as far as the industrial application is concerned: it is desirable to carry out anionic polymerization of MMA in toluene at higher temperature and to obtain a highly syndiotactic PMMA (over 90%) with controlled molecular characteristics and low polydispersity. As already mentioned, Hatada *et al.* [42] were the first who succeeded in producing highly syndiotactic PMMA with narrow MWD using a *t*-BuLi/AlR_3 initiator system in toluene (Table 6). The AlR_3 addition changes the electron distribution and induces steric hindrance around the growing species. It may be inferred that the coordination sphere around the AC exerts a pronounced effect on

Table 6. Effect of additives on the PMMA tacticity.

Initiator	Solvent	T°C	Additive	[Add]/[In]	*mm*	*mr*	*rr*	Ref.
n-BuLi	Toluene	20	-		0.71	0.17	0.12	[29]
t-BuOLi			*t*-BuOLi	*	0.83	0.12	0.05	
t-BuLi	Toluene	-78	-	-	0.78	0.16	0.06	[42]
			$AlEt_3$	3	0.00	0.10	0.90	
			Al(*n*-Bu)$_3$		0.00	0.08	0.92	
s-BuLi	THF	0		-	0.22	0.35	0.43	[45]
			Al(*i*-Bu)$_3$	4	0.04	0.30	0.66	
			$AlEt_3$		0.06	0.24	0.70	

**t*-BuOLi efficiency as initiator is low, therefore, unreacted *t*-BuOLi acts as an additive.

the incoming monomer. The idea of industrial researchers is to prepare AC with high-volume complex counter ion, thus, it will “screen” the growing species from side reactions [47]. Thus, for example, the intramolecular cyclization reaction requires a metal ion like lithium for the activation of ester group and the expulsion of alkoxide ions. In order to avoid the influence of the metal counterion, Reetz [56] was the first, who used non-metallic tetrabutyl ammonium counterion in anionic polymerization of (meth)acrylic monomers.

We set ourselves the task to expand the research by examining the interaction of $P_{1(COOR)}Li$ with quaternary ammonium salts (QAS) with quite different structure and size [45,57]. Once again, LiPi was considered as a model of an AC of chain propagation as it is well known that the optical spectrum of the picrate anion is very sensitive towards changes in the interionic distance [58].

In contact with LiPi, the QAS can intervene in two ways. On one hand, counter ion exchange reactions are possible:

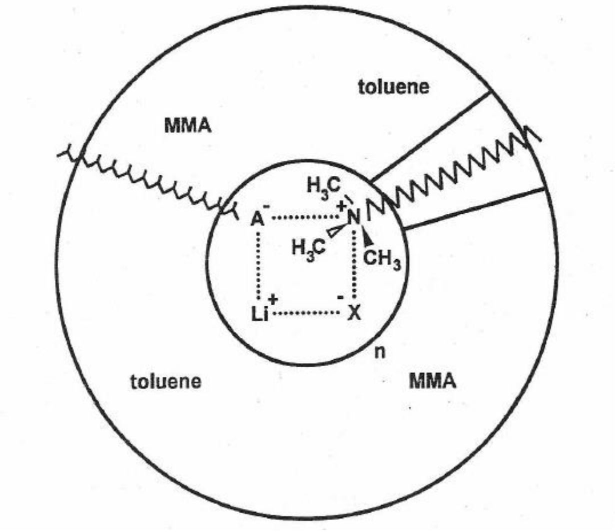
$$LiPi + N^+R_4,X^- \longrightarrow Pi^-,N+R_4 + LiX\downarrow$$

where R = alkyl substituent, X = Cl, Br

The exchange reaction leads to a definite change in the behavior of the picrate anion. The quaternary ammonium cation (Q^+) makes the organophobic picrate anion soluble, while LiX is insoluble in toluene. In case of $P_{n(COOR)}Li$/QAS system the exchange reaction leads to formation of AC with bulky Q^+.

The second possible reaction is the formation of mixed associates $(Q^+,Pi^-,Li^+X^-)_n$. In this case Li^+ remained in the solution. As already mentioned, the two cases are distinguished by the ability of lithium to be dissolved in toluene. Indeed, Table 7 reveals that depending on QAS salts structure, these two quite different types of interactions can be recognized. In the case of symmetrical R_4N^+X, almost quantitative counter ion exchange occurs, whereas the presence of QAS with very long chain alkyl groups namely $C_{17}C_{12}Me_2NBr$ or $(C_{12})_2Me_2NBr$, leads to increase in Li^+ solubility more than two orders of magnitude, i.e. to the formation of mixed associates. In order to diminish the steric hindrance, the Q^+ is oriented to the growing anion from the side of the smaller size groups, e.g. methyl groups (Scheme 6).

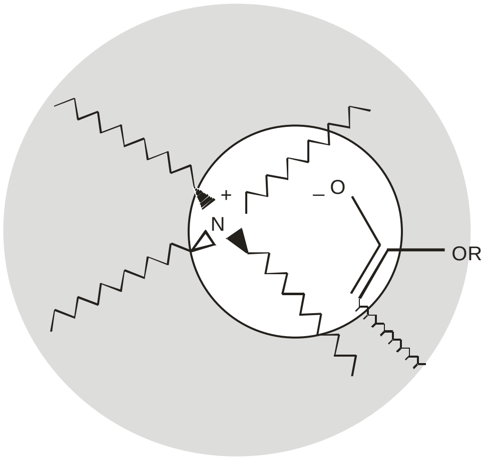
The longer fatty alkyl chains participate in the formation of the first solvation shell. This way the microenvironment is highly hydrophobic, shifting the mode of monomer addition to $P_{n(COOR)}Li$ towards isotactic structure.



Scheme 6. Sketch of the mixed associate $(Q^+,Pi^-,Li^+X^-)_n$ [44].

Completely different, when the QAS additive causes ion exchange, the syndiotactic addition is much more pronounced, the size of Q^+ being very important: ***rr*** Hex_4N^+ › ***rr*** Bu_4N^+.

Results, presented in Table 7 show that in both cases the ester enolate species are not “naked” as it is traditionally termed in the phase transfer catalysis reactions. Obviously, the growing species penetrate also into the void spaces of R_4N^+:



Due to the steric hindrance, the anion penetration suppresses the attack of the ester enolate anion to the carbonyl group of the third (γ) unit. This type of propagating species favors syndiotactic placement. The same trends were observed when using ***t***-BuOK [59] and Bu_2Mg [60] initiators.

Table7. Comparison between the solubility of LiPi in toluene in the presence of QAS and PMMA stereochemistry when $P_{1(COOR)}Li$ is used as initiator.

QAS	**LiPi**		**$P_{1(COOR)}$Li/QAS, PMMA triad placements**		
	λ_{max}, nm	**$[Li^+]/[PiQ]$ x10^3**	***mm***	***mr***	***rr***
-	337	-	80	17	3
Bu_4NBr	364	‹ 1	65	18	17
Hex_4NCl	361	‹ 1	16	28	56
$(C_{12})_2Me_2NBr$	360.5	214	77	16	7
$C_{17}C_{12}Me_2NBr$	360.5	299	95	4	1

CONCLUSION

The fine control of the anionic polymerization of polar vinyl monomers and especially of (meth)acrylates has been successfully realized in the 1980s and 1990s. One of the strategies that received a special attention is the ligated anionic polymerization. The interest in this field has produced a large number of excellent comprehensive reviews [39,61,62]. The attention of researchers has been focused mainly on the study of the polymerization kinetics and preparation of well defined poly(meth) acrylates or their blockcopolymers with narrow molecular weight distribution.

This review paper summarizes the research on the penultimate effects in anionic polymerization and the influence of ligands performed in the Institute of Polymers, BAS during 1980s and 1990s. The approach in our studies is slightly different. The main subjects of our study are model compounds or “living”oligomers of polar vinyl monomers, such as nitrile, esters, and ketons. Their physico-chemical characteristics in solution, before and after adding of ligands, were investigated with the aid of IR spectra and conductometry. In almost all cases the interactions involve lithium counter ion. A typical feature is the use of LiPi as a model in studying the interactions with monomers, compounds with polar groups, and most typical additives: alkoxide, LiCl, tetraalkylammonium salts and trialkylaluminum compounds.

We will mention some of the most important conclusions of the study:

1. The propagating species comprise contact ion pairs and ion triples in THF.

2. In THF the interaction growing center-penultimate monomer unit is not typical for PMMA, but it was demonstrated in living oligomers of AN, MAN, and vinyl ketone.

3. In the case of anionic polymerization in toluene of AN and MAN, initiated by lithium or magnesium compounds, interactions AC-monomer and AC-polar group of monomer unit are registered.

4. The approach by using reference system LiPi in dioxane distinguishes four types of interactions: LiPi-electron pair donors (polar groups of monomer or monomer unit); LiPi – μ ligands (LiCl, ROLi, Li-ketoenolate, and Li-esterenolate); LiPi – Lewis acids (R_3Al); and LiPi – quaternary ammonium salts.

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МЕЖДУ- И ВЪТРЕШНО МОЛЕКУЛНИ ВЗАИМОДЕЙСТВИЯ ПРИ АНИОННАТА ПОЛИМЕРИЗАЦИЯ НА ПОЛЯРНИ ВИНИЛОВИ МОНОМЕРИ

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(Резюме)

Настоящата обзорна работа представя резултатите от изследванията, проведени в лаборатория „Полимеризационни процеси” на Института по полимери – БАН, върху природата на активните центрове на нарастване (АЦ) в процеса на анионна полимеризация на полярни винилови мономери (ПВМ) – акрилати, метакрилати, винилови нитрили и винилови кетони, като е обърнато внимание на взаимодействията на АЦ с донорно-акцепторни лиганди. Обект на особен интерес са взаимодействията на АЦ с различни лиганди съдържащи литиев и магнезиев противойон, поради протичащите процеси на взаимодействие и самоасоцииране, които осигуряват възможност за осъществяване на контрол на структурата и състава на получаваните (съ)полимери. Използвани са и моделни съединения или „живи” олигомери на ПВМ, като чрез ИЧ спектроскопия и кондуктометрично са изследвани физикохимичните им характеристики в разтвор, преди и след добавяне на лиганд. Литиевият пикрат е използван като моделно съединение за изучаване на взаимодействието с мономери, съединения с полярни групи и най-типичните добавки: алкоксиди, литиев хлорид, кватернерни амониеви соли и триалкилалуминиеви съединения.