

## DONOR-ACCEPTOR AND SOLVATION INTERACTIONS IN ANIONIC POLYMERIZATION OF SOME HETEROCYCLES

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**Abstract** - The effects of donor-acceptor interactions or of strong specific ("stoichiometric") solvation of active species in anionic polymerization of some heterocycles - epoxides, cyclosiloxanes, lactones, lactams, episulphides - are considered. All the components of polymerizing systems, namely, the monomer, solvent, solvating additives, macrocyclic ones including, and the polymer being formed possess cationic affinity and therefore participate in solvation of the growing ion pair. Relative role of these components is considered, which is different for various classes of anionically polymerizable monomers. In a number of cases, particularly in epoxides and cyclosiloxanes polymerization, the interaction of the growing centre with heteroatoms of its own macromolecule is supposed to be predominant. Analysis is based on the results of study of the polymerization kinetics, conductivity of living and model systems, the interaction of heterochain polymers with inorganic salts and with active centres models, and on quantum-chemical calculations.

### INTRODUCTION

For a number of heterocycles the main polymerization mechanism is anionic; some classes of such heterocycles, which are studied in detail, their main representatives, as well as the types of structures of monomer units and active centres are given in Table 1.

TABLE 1. Anionically polymerizable heterocycles

Class of monomers	Main representative	Monomer unit	Active centre
Epoxides	Ethylene oxide	$-\text{CH}_2\text{CH}_2\text{O}-$	$\sim \text{CH}_2\text{CH}_2\text{O}^- \text{Mt}^+$
Cyclosiloxanes	Hexamethylcyclotrisiloxane	$-\text{SiMe}_2\text{O}-$	$\sim \text{SiMe}_2\text{O}^- \text{Mt}^+$
Lactones	$\beta$ -Propiolactone	$-(\text{CH}_2)_2\text{COO}-$	$\sim (\text{CH}_2)_2\text{C} \begin{array}{l} \text{O} \\ \diagdown \end{array} \text{Mt}^+$
Lactams	$\epsilon$ -Caprolactam	$-(\text{CH}_2)_5\text{NHCO}-$	$\text{O}=\text{C}-\text{N}^- \text{Mt}^+$
Episulphides	Propylene sulphide	$-\text{CH}_2\text{CHMeS}-$	$\sim \text{CH}_2\text{CHMeS}^- \text{Mt}^+$

Specific features of heterocycles polymerization, how trivial it may seem to repeat, are determined by the presence of heteroatom and by its nature. The heteroatom, being usually on the charged end of the growing chain, contributes to a considerable localization of the negative charge, and in this way substantially increases the strength of ion pair. As a result, the role of the latter in the processes of anionic polymerization of most of heterocycles is more significant than in similar processes with vinyl monomers. Some characteristics of the polymerizing systems, which reflect the relative role of ions and ion pairs in anionic polymerization of heterocycles, are collected in Table 2. Only in the case of propylene sulphide (with  $\text{Na}^+$  in tetrahydrofuran) and  $\epsilon$ -caprolactam the kinetic contribution of free

ions proves to be predominant. In other systems a similar situation may be reached only by the addition of strongly solvating agents, such as crowns or cryptands.

TABLE 2. Ions and ion pairs in anionic polymerization of some heterocycles<sup>a</sup>

Monomer	Solvent	Counterion	$K_D$ , mol / l <sup>b</sup>	$k_p^-/k_p^\pm$ <sup>c</sup>	Ref.
EO	THF	K <sup>+</sup>	$1.8 \times 10^{-10}$		1
EO	THF	Cs <sup>+</sup>	$2.7 \times 10^{-10}$	$< 20^f$	1
EO	THF	K <sup>+</sup> + [2,2,2]	$2.0 \times 10^{-7}$	67	2
D <sub>3</sub>	D <sub>4</sub>	Na <sup>+</sup> , K <sup>+</sup>	$\sim 10^{-15}$ <sup>f</sup>		3
D <sub>3</sub>	D <sub>4</sub> + THF	Na <sup>+</sup>	$\sim 10^{-13}$ <sup>f</sup>		3
$\epsilon$ -CL	$\epsilon$ -CL	Na <sup>+</sup> <sup>e</sup>	$6.7 \times 10^{-5}$	50	4
$\epsilon$ -CL	$\epsilon$ -CL	Na <sup>+</sup> <sup>e</sup>	$1.0 \times 10^{-4}$		5
$\beta$ -PL	CH <sub>2</sub> Cl <sub>2</sub> <sup>d</sup>	K <sup>+</sup> + DB18C6	$1.3 \times 10^{-4}$	220	6,7
PS	THF	Na <sup>+</sup>	$5.1 \times 10^{-9}$	1600	8
PS	THF	K <sup>+</sup>	$2.0 \times 10^{-8}$	16.5	8
PS	THF	Na <sup>+</sup> + [2,2,2]	$4.2 \times 10^{-5}$	0.5	8

<sup>a</sup> EO - ethylene oxide, D<sub>3</sub>, D<sub>4</sub> - cyclosiloxanes (see 6),  $\epsilon$ -CL -  $\epsilon$ -caprolactam,  $\beta$ -PL -  $\beta$ -propiolactone, PS - propylene sulphide, [2,2,2] - cryptand-[2,2,2], DB18C6 - dibenzo-18-crown-6, THF - tetrahydrofuran; <sup>b</sup> dissociation constant of living polymer or active centre; <sup>c</sup> ratio of propagation rate constants of ions and ion pairs; <sup>d</sup> with monomer concentration equal to 3.0 mol / l; <sup>e</sup> Na-salt of  $\epsilon$ -CL; <sup>f</sup> estimated values.

On the other hand, the presence of donor heteroatom in the monomer and in the polymer chain provides a possibility for them to participate, together with the bulk solvent, in the solvation of the ion pair cation. The consequences of such solvation for activation of ion pairs, be it interionic or peripheral, have been demonstrated sufficiently broad. A particularly important role in these interactions may be played by the resulting polymer which, in contradistinction to low-molecular donors, is capable of multi-centre binding of cations. Lately such binding has been extensively studied and widely employed.

Relative capability of monomers, solvents and chain fragments to interact with the cation cannot be determined within the framework of traditional approach to evaluation of the donation power. As a rule, it is estimated from the strength of the hydrogen bond between donors and a standard acceptor, and some characteristics of donating power for the selected series of systems are given in Table 3. There are also some other approaches, e.g. through complexes with iodine, but in any case all these criteria reflect only monodentate donation ability, whereas most of the counterions employed in anionic processes have high coordination numbers.

The above-mentioned specific features of the polymerizing systems with the participation of heterocycles must lead to the conclusion that in these systems the interactions between donor components on the one hand and an ion pair on the other hand should play an important role. The results of experimental studies carried out in recent years show this is really so.

Some specific features of the polymerization kinetics, the influence of the chain length of living polymers and their models on the reactivity and dissociation of the active centres, the character of the influence of acyclic and macrocyclic polydentate solvating agents, and a number of other facts are indicative of an essential role played particularly by the macromolecules in the propagation process. These effects are most noticeable in the

TABLE 3. Donating power of some heterocycles and models of their chain fragments (Ref. 9-12)<sup>a</sup>

Compound	$\Delta\nu_{\text{MeOD}}$	$K_{\text{MeOD}}$	$\Delta\nu_{\text{PhOH}}$	$K_{\text{PhOH}}$
Propylene oxide	59	0.45	320	5.95
Tetrahydrofuran	90	1.05	295	9.83
Diethyl ether	78	0.72		
1,2-Dimethoxyethane	71	0.68		
Propylene sulphide			222	1.08
Tetrahydrothiophene			262	2.49
Diethyl sulphide			263	
$\beta$ -Propiolactone	34	0.25		
$\epsilon$ -Caprolactone	82	0.97		
Ethyl propionate	32	0.32		
N,N-Dimethylacetamide	113			
Hexamethylcyclotri-siloxane			167	
Octamethylcyclotetra-siloxane			144	
Hexamethyldisiloxane			169	

<sup>a</sup>  $\Delta\nu_{\text{MeOD}}$ ,  $K_{\text{MeOD}}$  - frequency shift and equilibrium constant of hydrogen bond formation with MeOD;  $\Delta\nu_{\text{PhOH}}$ ,  $K_{\text{PhOH}}$  - same, but for PhOH; frequencies - in  $\text{cm}^{-1}$ , equilibrium constants - in l/mol.

anionic polymerization of epoxides and cyclosiloxanes.

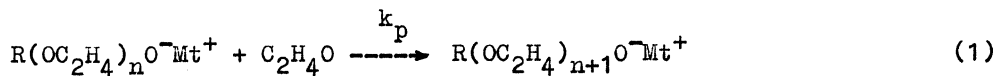
It is an object of the present review article to give critical consideration of the donor-acceptor interactions of active species in the processes of living anionic polymerization of some heterocycles (within the set given in Table 1) and to discuss the ways of their more direct study. It should be emphasized that only one aspect of such interactions, namely, their influence on the kinetic and equilibrium properties of the growing centre itself will be analysed. The reverse aspect - activation of the bonds in the monomer and polymer by such coordination - will be practically ignored here.

## EPOXIDES

Anionic polymerization of ethylene oxide (EO) has been studied in this class of monomers in most detail. In ether media it proceeds without termination and chain transfer by the living mechanism. Chain propagation proceeds via ion pairs of contact type, which are practically not dissociated under the experimental conditions (Ref. 1). A number of specific features of polymerization make EO outstanding among other anionically polymerizable heterocycles.

Selfsolvation as an ability of the macromolecules being formed to solvate terminal ion pairs provides a key to the understanding of many phenomena which accompany anionic polymerization of EO. The term "selfsolvation" itself was introduced by J.Ugelstad (13) in discussion of low-molecular reactions of oxoalkoxide salts. It should be emphasized that here one deals with just intramolecular effects, i.e. with the interaction of the growing ion pair with oxygen atoms of the same chain. So, in what way do these interactions display themselves?

Autoaccelerated character of the chain propagation, which is observed even at the concentration of active centres 0.0001 mol/l and lower, is probably the result of progressing solvation of the ion pair by the growing macromolecule (Ref. 14,15). The chain propagation rate constant



increases with the chain length, reaching the limit value at  $n = 4 - 6$  as it is shown on Fig. 1. Recently a more detailed analysis has been given to this phenomenon (Ref. 16). Similar chain length effects were observed also in the MWD of oligomeric adducts of EO (Ref. 17 as an example).

Electric conductivity of short-chain EO living polymers in THF is also a function of the chain length with a tendency to saturation at the same values of  $n$  equal to 6-10 (Fig. 2). As it has been shown recently by I. Panayotov's group (19), this is also characteristic for ion pairs with  $\text{Cs}^+$  as counterion which is commonly considered as non-solvated in THF and other ethers.

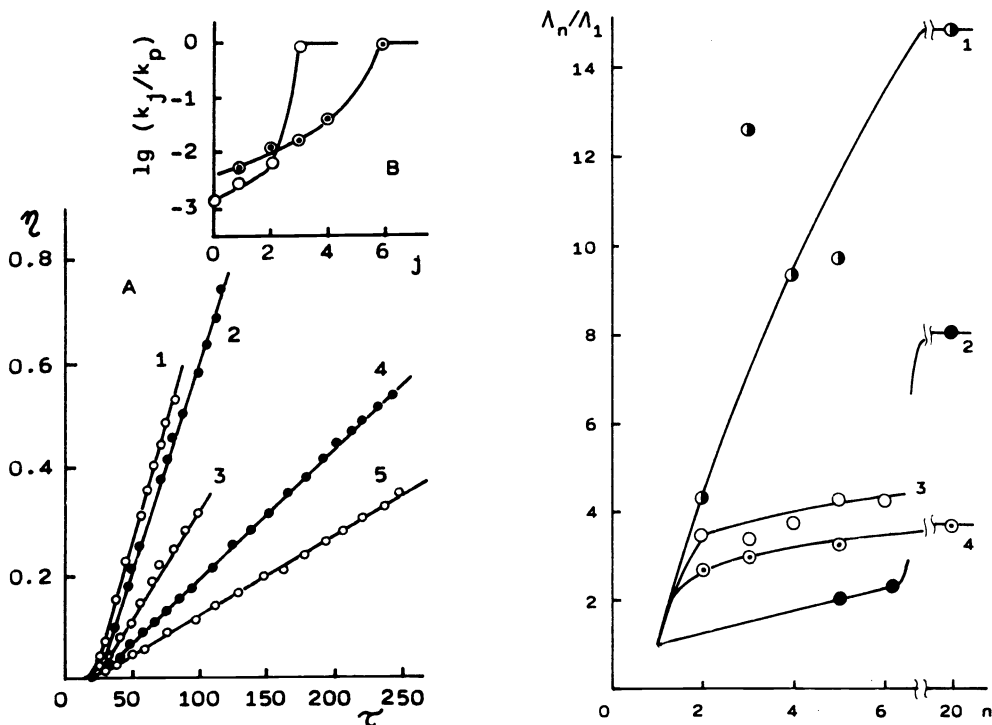


Fig. 1 (left). Autoacceleration in anionic polymerization of EO in THF with  $\text{K}^+$  as counterion (Ref. 14,15). Kinetic curves (A) are calculated by the scheme (1) under the assumption of the rate constant being dependent on the chain length ( $j$ ) as it is shown in Fig. B; concentrations of active centres for kinetic curves are  $2.7 \times 10^{-5}$  (1),  $4.3 \times 10^{-5}$  (2),  $6.4 \times 10^{-5}$  (3),  $1.47 \times 10^{-4}$  (4) and  $1.55 \times 10^{-4}$  mol / l (5);  $\tau$  is conventional (integral) time.

Fig. 2. Change of equivalent conductivity of low-molecular models of two-end (1,2,4) and one-end (3) living poly(ethylene oxide) with the chain length ( $n$ ); THF as a solvent,  $\text{Cs}^+$  (1) and  $\text{K}^+$  (2-4) as counterions (Ref. 14,15,18,19).

The mechanism of relative liberation of the cation, which determines mainly the level of conductivity, is not yet clear. There is a version of interpreting these phenomena through a change of the dissociation mechanism (Ref. 18,19), but in any case the true reason lies in the dependence of the properties of the ion pair itself on the chain length.

Anionic polymerization of EO is practically insensitive to an "external" solvent because of strong shielding effect of macromolecule (in the sense of preferable solvation). Analysis of the conductivity of low-molecular models of active centre shows (Ref. 14,17) that this effect appears only in the case of long chains which are, evidently, able to form a saturated solvate shell of the counterion. The influence of such powerful solvating additives as dibenzo-18-crown-6, dicyclohexyl-18-crown-6 and even cryptand-[2,2,2], on the contrary, sharply weakens with the growth of the macromolecule. That is why crowns do not exert noticeable influence on the kinetics, and only use of cryptand have made it possible to attain some activation of this process (Ref. 2).

Finally, in anionic polymerization of asymmetric epoxides the chirality of active centres and the process stereoselectivity, which was observed in a

series of systems (Ref. 20-22), is attributed to the interaction of active centres with the chiral chain.

The majority of manifestations of selfsolvation are to a greater or lesser extent indirect, and though in total they appear to be rather convincing, additional arguments were required. In this connexion we took up quantum-chemical calculations and began to study the alkali cations binding by poly(ethylene oxide) (PEO).

Quantum-chemical simulation. Reliability of quantum-chemical calculations is progressively becoming close to that of the experimental methods. Having been approved and reliably parametrised with regard to simple molecules, these calculations, when applied to complicated systems, also allow the obtaining of data which are often unavailable with the experimental approach. Naturally, we do not imply that numerical characteristics can be obtained in this way; the point is that in such a manner certain tendencies in the series of systems under investigation can be revealed. The series of works carried out by Eizner and Erussalimsky (23), by Kysel and coworkers (24) are examples of successful formulation and solution of ionic polymerization problems by the methods of quantum chemistry.

By using quantum-chemical calculations, we intended, in particular, to find out the ability of the chain oxygens to compete with the alkoxide one in the solvate shell of the cation, to estimate the energetic permissibility of intrachain complexes, to consider conformational peculiarities of these interactions, the reasons for and the extent of predominance of polydentate agents over monodentate ones, etc. Earlier (Ref. 15) we calculated by the CNDO method in BW-modification the energies and charge distributions in model oxoanions of type 1 with different number of oxygen atoms ( $n = 0, 1, 2$  and  $3$ ). In the calculation the conformation of the chain unit was assumed



to be TGT, which corresponds to 7/2 helix of PEO. Average values of the charge density were  $-0.811$  and  $-0.517$  for the alkoxide and intrachain oxygen, respectively, practically independent of the anion chain length. Now these data are supplemented with the calculations of ion pairs of type 2 both in "spiral" and cyclised conformations (Table 4). In connexion with the necessity of passing over to the CNDO/2 method which has parametrisation for Na, the anions 1 were also recalculated in accordance with this program.

TABLE 4. Quantum-chemical parameters of some oxoalkoxide anions and ion pairs (Ref. 25)<sup>a</sup>

Molecule	$E_{\text{total}}$ kJ/mol	Atomic charges		Na <sup>+</sup>	Bond order O...Na <sup>+</sup>
		O (alkox.)	O (chain)		
MeO <sup>-</sup>	72701	- 0.664			
MeONa	73064	- 0.580		0.747	
MeOC <sub>2</sub> H <sub>4</sub> O <sup>-</sup> <sup>b</sup>	165754	- 0.588	- 0.183		
MeOC <sub>2</sub> H <sub>4</sub> ONa <sup>b</sup>	166074	- 0.530	- 0.175	0.737	2.029
MeOC <sub>2</sub> H <sub>4</sub> ONa <sup>c</sup>	166463	- 0.572	- 0.206	0.719	1.984
Me(OC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ONa <sup>b</sup>	259231	- 0.534	- 0.158 <sup>d</sup>	0.736	1.973
Me(OC <sub>2</sub> H <sub>4</sub> ) <sub>2</sub> ONa <sup>c</sup>	260056	- 0.579		0.690	1.293

<sup>a</sup> CNDO/2 method; <sup>b</sup> in a spiral conformation; <sup>c</sup> in the form of cycle; <sup>d</sup> averaged value.

Let us pay attention to the following results among those presented in Table 4. The charge of the terminal oxygen is a weak function of the chain length, and, hence, the observed chain effects in kinetics and conductivity are not the result of negative charge redistribution in the anion. The charge density at the chain end somewhat drops with ion pairing, evidently, because of polarisation, but then it increases again in the course of cyclisation due to pumping of the electron density on the cation.

Donating power of internal oxygen atoms of the chain is obviously quite sufficient for them to interact strongly with the cation. This conclusion is confirmed by direct calculations of cyclic complexes in which the cation additionally coordinates with one oxygen atom or with several oxygen atoms of the chain. As can be seen from Table 4, such cyclisation is an essentially stabilizing factor and proceeds with a gain in energy. Because of inaccuracies in optimisation the absolute values of  $\Delta E$  are obviously unrealistic. As an example, the character of the energy change with a variation of the cation position in  $\underline{2}$  ( $n = 1$ ) is shown in Fig. 3. From the calculations it may thus be inferred that in this system non-cyclic forms are, evidently, not realised at all. The character of the change of  $O \dots Na$  bond orders in cyclisation shows a possible tendency of the additional coordination of the cation to influence the strength of the alcoholate bond. The latter to a considerable extent determines the reactivity of the ion pair.

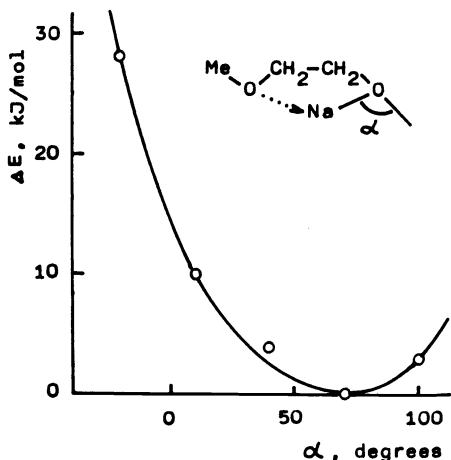


Fig. 3. Change of energy of the ion pair  $MeOCH_2CH_2ONa$  as a model of an active end of living PEO with variation of cation position.

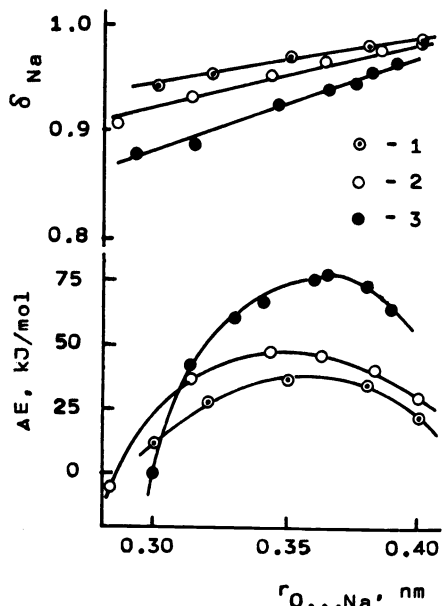


Fig. 4. Quantum-chemical simulation of complexes of EO (1), THF (2) and DME (3) with  $Na^+$ : energy gain ( $\Delta E$ ) and cationic charge ( $\delta Na$ ) as a function of  $O \dots Na$  distance (in Å); CNDO/2 method.

In order to compare the potential and the realised donating power of the oxygen atoms, the calculations have been carried for EO, THF and 1,2-dimethoxyethane (DME), and their complexes with  $H^+$  and  $Na^+$ . DME was taken as a model of the PEO monomer unit. The results of the calculations are presented in Table 5. Figure 4 shows the change of the energy and cationic charge with  $Na^+$  approaching the donors.

As can be seen, if the potential donor abilities (electron density on oxygen) are very close, the molecule, according to the real ability to complex formation, are arranged in the following natural series:  $EO < THF < DME$ . In our opinion, the character of charge density variation in the donor-cation bond formation shows that the donor-acceptor interaction play a significant role in this bonding: the cationic charge substantially diminishes with the approaching of the partners, this being attributable not to the nearest oxygen atom but to those from the periphery of the molecule. The distance of the maximum strength of the donor-acceptor interactions is 0.34-0.36 nm for  $O \dots Na$  in different systems. In the case of DME calculations give somewhat greater stability for the trans-conformation, this being not quite in agreement with the experimental data (Ref. 26). Complexation with  $Na^+$  strongly stabilises gauche-form, a weak tendency being observed to an additional diminution of the internal rotation angle  $OC-CO$  from 65-70° in the free state of DME to 45-50° in bonded one. To a lesser extent this is characteristic for the complex of  $H^+$ , where, because of distance effective bidentate interaction is, evidently, impossible.

Thus, the results of quantum-chemical simulation have made it possible to present qualitative confirmation of the reasons for the high strength of

TABLE 5. Ethers and their complexes with H<sup>+</sup> and Na<sup>+</sup> cations (quantum-chemical data)

Molecule	Method	E <sub>total</sub> kJ/mol	Atomic charges		r <sub>O...Na<sup>+</sup></sub> nm	E <sub>compl</sub> <sup>a</sup> kJ/mol
			O	Na		
EO	CNDO/BW	64461	- 0.427			
EO	CNDO/2	93688	- 0.236			
EO...H <sup>+</sup>	CNDO/BW	65200	- 0.473	0.500	0.096	739.0 <sup>b</sup>
EO...H <sup>+</sup>	CNDO/2	94727	- 0.066	0.366	0.097	1038.4
EO...Na <sup>+</sup>	CNDO/2	93726	- 0.272	0.967		38.3
THF	CNDO/2	139503	- 0.223		0.344	
THF...Na <sup>+</sup>	CNDO/2	139552	- 0.244	0.952		48.6
DME (tgt)	CNDO/BW	132353	- 0.506 <sup>c</sup>			
DME (ttt)	CNDO/BW	132366	- 0.509			
DME (tgt)	CNDO/2	191921	- 0.207			
DME...H <sup>+</sup>	CNDO/BW	132971	- 0.545	0.637	0.165	605.4
DME...Na <sup>+</sup>	CNDO/2	192006	- 0.231	0.936	0.365	85.0

<sup>a</sup> complexation energy; <sup>b</sup> experimental proton affinity of EO is 766.2 kJ/mol; <sup>c</sup> for DME averaged values of charges and distances are given in all the cases.

alkoxide ion pairs, to show the advantageousness of cyclic solvates formation in oxoalkoxide systems, which is the reason of selfsolvation, to elucidate the character and strength of the Na<sup>+</sup> complexes with ethers. On the other hand, these data again give no ground for considering polymeric ligand to be substantially more effective in the capture of cation, though such tendency has been undoubtedly detected in the calculation.

Binding of alkali cations by monomeric and polymeric ethers. Solvation of alkali cations by low-molecular oligomeric linear ethers (glymes) and by macrocyclic ethers (crowns, cryptands), as well as by other, more complex systems is an important aspect of the anionic polymerization processes, since many of them proceed in ether media. It is well known that in linear systems solvating ability increases with the number of oxygen atoms, whereas macrocycles are sharply specific to the size of the cation.

In recent years the works on cation binding by polymeric ligands have become quite extensive, PEO and its analogues being occupied a leading place in them. However, in available publications (Ref. 27-29) we could not find such data which might throw light on the situation in the very polymerization process. That is why we undertook an investigation of our own with a view to elucidating the mechanism and quantitative characteristics of the alkali cations interaction with ethers - components of the polymerizing system. The methods of NMR on the alkali nuclei and conductometry were chosen as most informative ones. The problems of solubility of inorganic salts and their complexes dictated the use of nitromethane as the main solvent. Most of the salts are practically completely dissociated in this medium.

Monomeric oxides - EO, propylene oxide (PO) and THF bind Na<sup>+</sup> rather weakly, forming complexes with a 1:1 composition (Ref. 30). Binding isotherms according to the Na<sup>23</sup>-NMR data are shown in Fig. 5, and equilibrium constants of



are given in Table 6. A possibility of complexes of the NaO<sub>2</sub>-type cannot be altogether excluded, though it is less probable.

A considerably stronger binding of cations is observed in the case of PEO, this being shown as an example in Fig. 5. A more detailed investigation of this interaction (Ref. 31) made it possible not only to characterise it quantitatively, but also to formulate the mechanism of binding. The experimental dependences of NMR spectrum parameters (chemical shift, line width)

and of the equivalent conductivity of the salts on the ratio of molar concentrations of the oxygen and cation  $\beta = [O]/[M^+]$  are shown in Figs. 6 and 7 for some of the investigated systems.

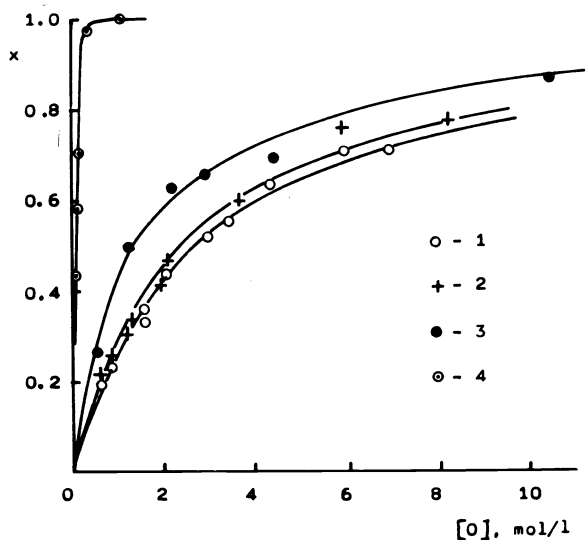


Fig. 5. Binding degree of  $\text{Na}^+$  as a function of concentration of ether oxygen in the interaction of  $\text{NaBPh}_4$  with EO (1), PO (2), THF (3) and PEO 400 (4) according to NMR data (Ref. 30).

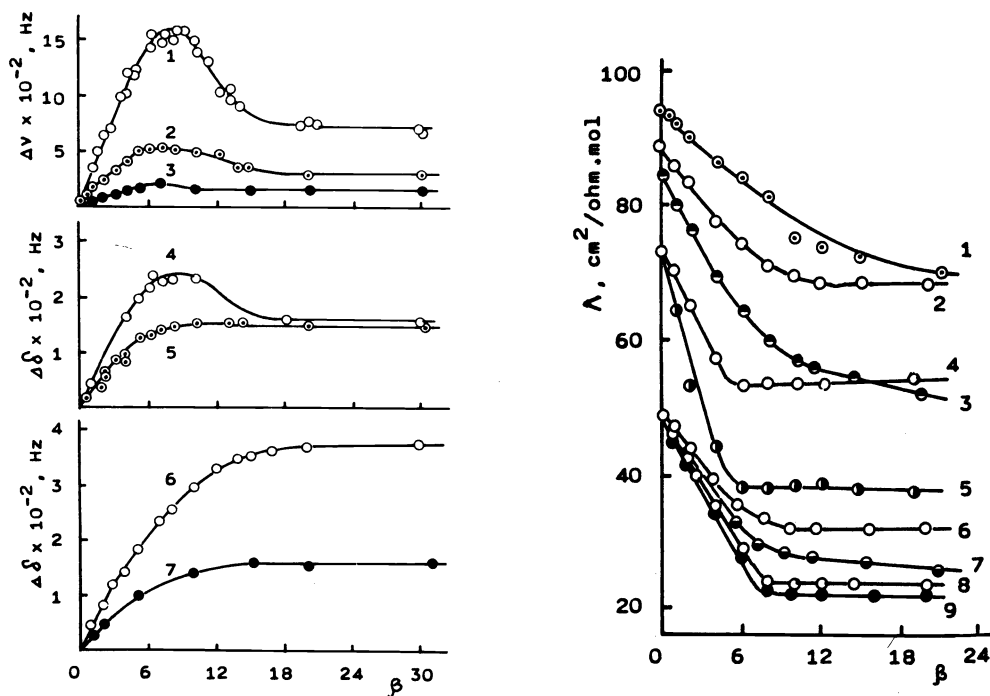


Fig. 6. Dependence of the chemical shift ( $\Delta\delta$ ) and line width ( $\Delta\nu$ ) of  $\text{Na}^{23}$  (1-5,7) and  $\text{Cs}^{133}$  (6) NMR signals on the concentration ratio  $\beta$  for PEO 1000 (3,7) and 6000 (1,2,4-6) at 298 (1,4,6) and 363 K (2,3,5,7) in  $\text{MeNO}_2$  (Ref.31).

Fig. 7. Change of equivalent conductivity ( $\Lambda$ ) of  $\text{CsCNs}$  (1),  $\text{KCNS}$  (2) and  $\text{NaBPh}_4$  in  $\text{MeNO}_2$  at 298 K with introduction of cation-binding agents: 18-crown-6 (4), PEO 400 (6), 1000 (7), 6000 (1,3,5,8) and



20000 (9);  $\beta$  is concentration ratio of ether oxygen and salt; initial salt concentrations are  $5 \times 10^{-4}$  (3),  $5 \times 10^{-3}$  (1,2,4,5) and  $5 \times 10^{-2}$  mol / l (6-9) (Ref. 31).

TABLE 6<sup>A</sup>. Equilibrium constants of formation of  $O_n Mt^+$  complexes between ethers and alkali salts in  $MeNO_2$ <sup>a</sup> (Ref. 31)

Ether	Cation <sup>b</sup>	n	$K_n$ , l/mol	Method
EO	Na <sup>+</sup>	1	0.41	NMR
PO	Na <sup>+</sup>	1	0.36	NMR
THF	Na <sup>+</sup>	1	0.69	NMR
PEO 400	Na <sup>+</sup>	6	60.5	NMR
PEO 1000 <sup>c</sup>	Na <sup>+</sup>	6	170	NMR
PEO 6000	Na <sup>+</sup>	6	3000	NMR
PEO 6000	Na <sup>+</sup>	6	2000	conduct.
18-crown-6	Na <sup>+</sup>	1	1800	conduct.
PEO 6000	K <sup>+</sup>	6	500	NMR, conduct.
PEO 6000	Cs <sup>+</sup>	6	200	conduct.
PEO 6000	Cs <sup>+</sup>	6	150	NMR

<sup>a</sup> in  $MeNO_2$  at 298 K; <sup>b</sup> cations were taken as  $NaBPh_4$ ,  $KCNS$  and  $CsCNS$  which are completely dissociated under the experimental conditions; <sup>c</sup> at 363 K.

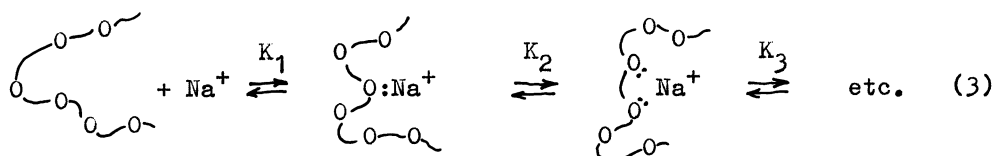
TABLE 6<sup>B</sup>. Equilibrium constants ( $K_j$ ) and probabilities ( $\alpha_c$ ) of cyclisation of PEO units in multicentre solvate complex formation with various alkali cations<sup>a</sup>

PEO	$Mt^+$	$\sigma$	$K_j$	$\alpha_c$
400	Na <sup>+</sup>	$5 \times 10^{-6}$	15	0.94
1000	Na <sup>+</sup>	$5 \times 10^{-6}$	18	0.95
6000	Na <sup>+</sup>	$5 \times 10^{-6}$	28	0.97
6000	K <sup>+</sup>	$4 \times 10^{-7}$	33	0.97
6000	Cs <sup>+</sup>	$1 \times 10^{-8}$	51	0.98

<sup>a</sup> all the conditions - as in Table 6<sup>A</sup>; averaged values of constants and standard entropies of ions in aqueous solution are employed in calculations of  $\sigma$  as the first approach;  $\sigma$  in l/mol.

What conclusions can be made on the basis of the model experiments of such kind? It is clear that in all the cases binding of cations by polyether is more powerful than by low-molecular ligands. The character of binding curves, especially at relatively high concentrations, show that in the complexes being formed the cation is coordinated with 6 to 8, and in some cases to 12 oxygen atoms. The stoichiometry of the complexes can be simply estimated from the position of the binding isotherm break point on the  $\beta$  axis. With large molar ratios even at small concentrations all the cations are captured by the chain into complexes with a limit stoichiometry, whose state does not change then within a wide range of  $\beta$  (plateau region). It should be emphasized that  $\beta$  is an analogue of the chain length of living PEO. Note that the polymer concentration values as such, at which clearcut binding effect is observed, as well as the form of binding isotherm being dependent not on the polymer or salt concentrations themselves but only on their ratio, indicate that the binding mechanism is predominantly intrachain. For instance, for PEO 6000 the concentration point at which the polymer coil begin to interact is about 1.0 mol / l, which could not be reached in experiments.

For cation binding by PEO the scheme can be adopted which is used when treating similar processes in proteins (Ref. 32,33):



Stepwise filling of  $n$  binding sites of cation (first solvation shell) by the chain fragments can be reduced to the simple Langmuir isotherm (Ref.33)

$$x = K_n [O] / (1 + K_n [O]) \quad K_n = \prod_{i=1}^{i=n} K_i \quad (4)$$

where binding degree  $x = [\text{complexed metal}] / [\text{M}^+]_0$ . The dependence  $x = f(\beta)$  in the majority of the investigated cases is quite well described by Eq.(4). The values of the equilibrium constants, obtained through calculations in accordance with (4) are collected in Table 6. Alongside of the binding isotherms for calculation of the constants the methods of dilution at  $\beta = \text{const}$  and displacement of one cation by another were also employed, which allowed, in particular, the obtaining of constants for  $\text{K}^+$  from NMR data for Cs.

The results in Table 6 clearly demonstrate an increase in the strength of solvate complexes from  $\text{Cs}^+$  to  $\text{Na}^+$ , as well as the increasing length of PEO chain. This fact and a relatively weaker solvating ability of crown-6 are conditioned, evidently, by greater conformational possibilities in the formation of the solvate shell from the donor units of the polymer chain.

Let us return to interpreting the sense of the equilibrium constants in scheme (3) and Eq. (4). It is obvious, that with equal enthalpies of formation of one  $\text{O}:\text{M}^+$  contact the difference of the first binding constant  $K_1$  from all other in the sequence (3) will be determined by the greater loss of the entropy at the first step, so that it will prove to be most difficult in this process. If we use elementary estimates which take into account the loss at this step in contrast to all others in the translational entropy of the cation and in the conformational entropy of the chain due to volume excluded by cation (Ref. 32), we shall come to the result:

$$\sigma = K_1/K_j = \exp(-\Delta\Delta S/R) = 10^{-4} + 10^{-8} \text{ l/mol} \quad (5)$$

where  $\sigma$  is cooperativity of binding, and  $K_j$  is the equilibrium constant of any step, except the first one. In a certain approximation, namely, in the case of the contact formation energies being equal and with the loss of only the vibrational entropy of the monomer unit, these constants will be practically equal to one another for the entire first solvation shell of the cation. Relationship (5) thus determines the possibility of cooperative behaviour of these systems, since only free and fully binded cations will be present here. This assumption is implicit in the calculations of the binding degree from the NMR and conductimetry data.

Using (5) and binding constants

$$K_n = \sigma K_j^n \quad (6)$$

it is possible to evaluate the values of cyclisation constants  $K_j$  and also the probabilities of capturing by the cation of the chain fragments adjacent to that already bound ( $\alpha_c$ ). The values obtained in such way are also presented in Table 6. The calculations thus show that with the presence or formation of one contact between the alkali cation and PEO chain the probability of other vacancies in the coordination sphere of the ion to be filled by the other donor fragments of the chain is very high. In such a case, as it also follows from quantum chemistry, it makes no difference (on condition that the number of binding sites one of which is occupied by the anion is left out of account) whether we consider the cation of the terminal ion pair or the free one. The values found in the last columns of Table 6(B) thus show the tendency to selfsolvation for PEO with various cations. The influence of solvent and anion will naturally change these values.

According to scheme (3), when the cooperativity is sufficiently high, the probability of interchain contacts which are determined by  $K_c$  value is obviously small; in this sense the scheme (3) explains the formation of only simplest complexes with low-molecular ethers. As regard the form of chain organisation in the cation solvate shell, from elementary consideration it is more or less clear that in the case of such flexible macromolecules as PEO the nearest fragments of the chain must enter in contact with the cation, since cycles and loops with a larger size are less advantageous. Preliminary analysis of changes of PEO viscosity in course of saturation by the cations is in qualitative agreement with such conclusion.

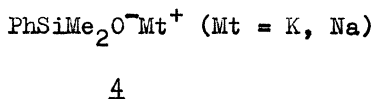
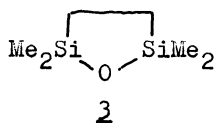
To summarise the results of this section, we may conclude that in anionic polymerization of EO the solvation of growing ion pairs from the very beginning of the process is fully determined by macromolecules, in the case of low active centres concentrations this solvation proceeding in an intramolecular way. This specific feature of the process is determined by the unique combination of the high donating power of heteroatom, flexibility of the chain, and preferable conformation of the monomer unit. In the case of substituted epoxides such interactions are, evidently, weakened, but, nevertheless, essential for the polymerization mechanism.

### CYCLOSILOXANES

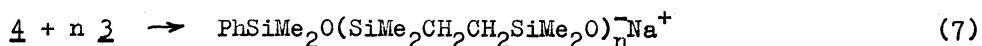
Cyclosiloxanes are readily polymerized by the anionic mechanism, in most cases without chain termination, but with a number of side reactions, in particular, macrocyclisation equilibrium. In the treatment of these processes, as in case of epoxides, considerable importance is attributed to a multicentre coordination or "internal multifunctional assistance" (Ref. 34) of the cations with polysiloxane fragments, both linear and cyclic. In this case both partners, the ion pair and the siloxane, are activated, which makes these systems distinct from polyether ones. Though the flexibility of polysiloxane chains is extremely high, reducing donor ability of the oxygen (see Table 3), conditioned by the p- $\pi$  interaction with silicon leads to solvation and selfsolvation effects in siloxane systems being easily suppressed even by weak donors - solvents and additives.

Polymerization of cyclosiloxanes has a number of features similar to epoxides. It proceeds only via silanolate ion pairs which are very similar to alkoxide ones and more liable to aggregation than to dissociation. Donor additives - so called "activators", including cryptands (Ref. 35), only destroy aggregates of ion pair, but do not change the nature of growing species.

When initiated by low-molecular silanolates, polymerization of cyclosiloxanes proceeds with initial autoacceleration (Ref. 36,37) which is regarded as the result of positive effect of the chain being formed on the reactivity of the growing ion pair. Thus, in particular, such is the course of polymerization of cyclosiloxane **2** by sodium silanolate of type **4** in a heptane/dioxane mixture (95:5 by volume) (Ref. 37). Autoacceleration disappears with the initiation by living polymer (Ref. 37) or with the introduction of solvating additives into reaction mixture.



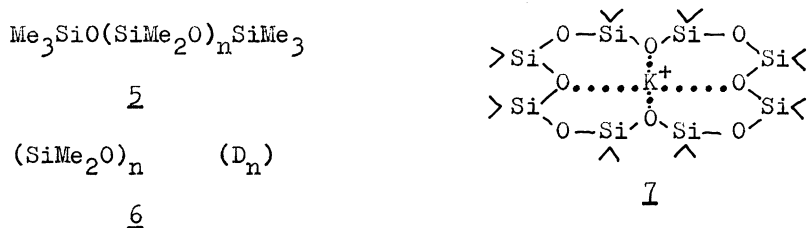
In spite of absence of spectral manifestations of the interaction of **2** with **4**, in the initiation reaction



in heptane there is observed a substantial increase of the initiator consumption rate constant with an increase of the concentration of **2**, which formally corresponds to the order of the reaction (7) with respect to **2** higher than the second. This effect also completely disappears upon introduction of small quantities of dioxane which is rather weak donor. Thus, here both the monomer and the polymer participate in solvation of silanolate ion pair, though neither of them is an effective complexing agent for the cation be-

cause of the absence of a sequence of siloxane bonds.

In polysiloxane systems the effects of donor-acceptor solvation are pronounced more definitely. This clearly shows the work carried out by Chojnowski and Mazurek (34) specially for the verification of this conception. These authors studied the kinetics of reactions of potassium silanolate of type 4 with a number of linear 5 and cyclic 6 polysiloxanes, as well as the influence of the medium on these reactions.



It turned out that the reactivity of the ion pair is a drastic function of the number of oxygen atoms in the polysiloxane fragment reacting with it (Fig. 8). This function monotonically increases in the case of linear reagents and passes through the maximum for cyclics, this, evidently, corresponding to an increase of conformational possibilities with the chain length and to the cycle being critical to the size of cation. Complexes of type 7 were proposed to explain these data.

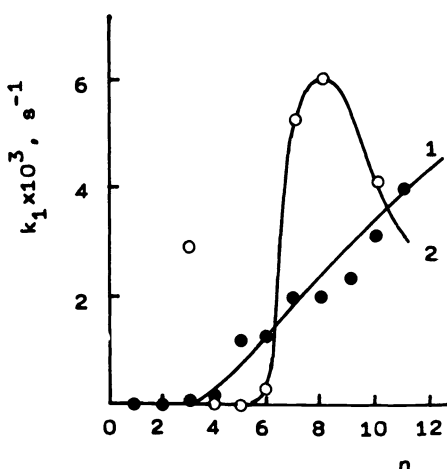


Fig. 8. Effect of the number of oxygen atoms ( $n$ ) on the reaction rate of potassium silanolate of type 4 with linear 5 (curve 1) and cyclic 6 (curve 2) siloxanes; solvent - heptane/dioxane (95:5 by volume, 303 K (Ref. 34).

Two factors, which are difficult to separate, determine the dependence of the reaction rate on the length of the polysiloxane sequence: activation of the ion pair and polarisation of the siloxane bond with an increase of its reactivity. We can believe, however, that the first of these factors is more essential, since one could hardly expect that with an increase in the number of siloxane fragments bonded in complex 7 with the cation each of them would be activated more strongly. It is most likely that the dominating factor here is loosening of silanolate bond by the effective solvation. The same is evidenced by the character of the solvating agents influence on model reaction of siloxane bond cleavage (Table 7). In the case of  $\text{D}_7$  (see 6) having a high solvating

ability the effect of "external" additives is substantially lower than in reaction with  $\text{D}_4$ .

Investigation of anionic polymerization of cyclosiloxanes and of model reactions with their participation thus show that polysiloxane sequences are capable of producing activation action on ion pairs by forming multicentre complexes of type 7 with them. A tendency to an increase in the ability of linear polysiloxanes to the solvation of such kind with the chain length shows that high-molecular polymers may play here the same decisive role as in epoxide systems. There are no sufficient data for making a rigorous decision whether in the given case these effects are intra- or interchain. In this connection it is interesting to note that contrary to expectation addition of  $\text{D}_7$  and  $\text{D}_8$  which, according to (Ref. 34), have strong activating effect on ion pair, in small amounts practically do not exert any influence on the rate of substituted cyclotrisiloxane polymerization, while THF and DME under the same conditions noticeably accelerate this process (Ref. 38). With close solvating powers of linear and cyclic polysiloxanes this fact may be indicative of preferable solvation of the growing centres by the polymer being formed. It is possibly the same shielding effect of polymer which is characteristic for EO polymerization.

TABLE 7. Solvent effect in the kinetics of anionic polymerization of cyclosiloxanes D<sub>4</sub> and D<sub>7</sub><sup>a</sup> (Ref. 34)

Solvent	k <sub>obs</sub> x10 <sup>4</sup> , s <sup>-1</sup> b	
	D <sub>4</sub>	D <sub>7</sub>
Heptane/dioxane (95:5 by vol.)	0.0037	0.60
Heptane/diglime (95:5 by vol.)	0.39	3.00
Heptane/HMPA (95:5 by vol.)	61	44
THF	0.49	7.5
THF + DB18C6 (1:1 to 4)	3.2	2.7

<sup>a</sup> 303 K; potassium silanolate 4 as initiator in concentrations 9.5x10<sup>-3</sup> mol /l in heptane mixture and 8.5x10<sup>-4</sup> mol /l in THF; [D]<sub>0</sub> is 2.5 to 2.7 mol /l; <sup>b</sup> observed rate constant of monomer consumption.

Complexes of polysiloxanes. The formation of complexes of cyclic and linear polysiloxanes with initiators which are models of active centres or with other alkali salts was established by H<sup>1</sup> and Na<sup>23</sup> NMR methods (Ref. 28,39) and by microcalorimetry techniques (Ref. 40). Some characteristics of these interactions are summarised in Table 8.

TABLE 8. Some characteristics of alkali salts interaction with cyclic and linear polysiloxanes

Siloxane <sup>a</sup>	ΔQ, J/l toluene <sup>b</sup>	Δδ, ppm THF <sup>c</sup>	Δδ, ppm toluene <sup>d</sup>
(SiPh <sub>2</sub> O) <sub>3</sub>	1361		0.20
D <sub>3</sub>		7.2 - 7.7	
D <sub>4</sub>	1884		
MD <sub>5</sub> M		8.1 - 8.2	
PMS (M = 1.5x10 <sup>4</sup> )	1256		
PMS (M = 1.2x10 <sup>5</sup> )		7.1 - 7.8	
PMS (M = 2.5x10 <sup>6</sup> )		6.4 - 6.5	

<sup>a</sup> (SiPh<sub>2</sub>O)<sub>3</sub> - hexaphenylcyclotrisiloxane, MD<sub>5</sub>M - 5 (n = 5), PMS - polydimethylsiloxane; <sup>b</sup> thermal effect of interaction of 0,05 M solution of sodium trimethylsilanolate with an excess of siloxane; for (SiPh<sub>2</sub>O)<sub>3</sub> equilibrium constant is 25 l/mol (Ref. 40); <sup>c</sup> chemical shift of Na<sup>23</sup> NMR signal of NaBPh<sub>4</sub> (0.02 - 0.08 mol /l) under the action of siloxane (Ref. 28); <sup>d</sup> H<sup>1</sup> NMR shift of methyl protons in sodium trimethylsilanolate (Ref. 39).

Though, proceeding from the available data, it is difficult to make quantitative comparison, nevertheless it may be concluded that cyclic and open chain polysiloxanes have a tangible cation-binding capacity. For instance, chemical shifts of the Na<sup>23</sup> NMR signal of NaBPh<sub>4</sub> in THF are only slightly smaller than similar characteristics for PEO in acetonitrile (Ref. 28). Linear and cyclic agents are, evidently, close in their affinity to Na<sup>+</sup>, this being fairly in agreement with the results of model reactions study. On the other hand, the published data on complex formation give absolutely no idea concerning the mechanism of the interaction of cations with sequences of siloxane bonds and the order of magnitudes of the equilibrium constants.

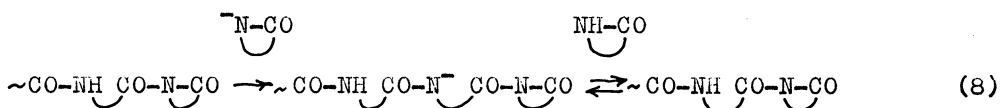
Thus, in the anionic polymerization of cyclosiloxanes in non-polar media monomers and the polymer being formed participate in solvation of ion pairs which are the only type of active centre in these systems. A specific feature of them resides in that in the course of the process siloxane fragments are redistributing among the cycles and the linear polymer, as well as among the cycles of different size, which differ in their cation-binding ability. This results in a more differentiated influence of the reagents on the reaction rates. However, all these interactions are completely suppressed even with an insignificant increase of the solvating power of the medium, so that in polar solvents or in the presence of specific solvating additives the process proceeds "normally".

#### OTHER MONOMERS

Lactams stand somewhat aloof from the other anionically polymerizable monomers. From the standpoint of the mechanism, the main peculiarities of them are the presence of a labile NH-proton and essential differences in the acidity of this group in the growing amide and monomer. The main form in which the anion exists is 8, usually employed as catalyst in the form of an alkali salt.



In the propagation step this anion, being an activated form of the monomer, attacks the uncharged end of the chain and is then regenerated through a rapid proton transfer from the monomer to the amide:



Such mechanism is adopted, in particular, for  $\epsilon$ -caprolactam ( $\epsilon$ -CL). Formal, but no less important specific features of lactams polymerization reside in that proceeds at high temperatures in bulk of the monomer (for instance, in  $\epsilon$ -CL case) and with considerable concentrations of active centres, the state of which is, thus, practically fully determined by the properties of monomer-polymer mixture, i.e. by the polarity and solvating power. Relatively high dielectric constants of lactams - 27.4 at 304 K for 2-pyrrolidone, 17.2/318 K for 2-piperidone, 15.0/483 K for  $\epsilon$ -CL (Ref. 41) - and some kinetic data have stimulated an opinion that the polymerization mechanism is free-anionic (Ref. 5).

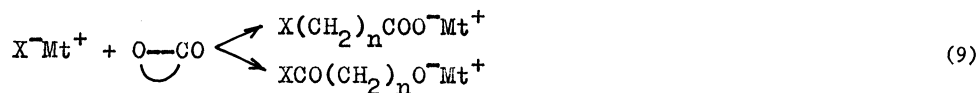
At present such point of view is prevalent and is in agreement with the majority of the experimental data. Weak effects of crown ethers and cryptands (Ref. 41,42), sharp suppression of the process by electrolytes with a common cation (Ref. 4), direct conductivity measurements and calculations of the dissociation constants (Ref. 4,5,41) show that kinetic contribution of free ions in lactams polymerization actually reaches 85 to 95%. Negligible variations are connected with the monomer polarity. The responsibility for the high dissociation in these systems lies, in the same time, also with ambidentate character of the anion, for which by the CNDO/2 method the distribution of the charge 2 has been obtained (Ref. 4). Usually such delocalisation reduces the ion pair strength.

Thus, the very conditions in which the polymerization proceeds unambiguously dictate here the mechanism of the process which allots no other role to solvation interactions but to increase the free ions concentration. We should think, however, that the situation here is not so simple, and the interactions under discussion may play an important role in these systems too. For instance, the character of the influence of activators - N-acyllactams, including the effect of the nature of acyl group, shows that they act as solvating agents with regard to the alkali salt of anion 8, enhancing its nucleophilicity. This is confirmed by the data of T. Frunze and co-workers (4) on a rapid and considerable increase of the conductivity of sodium salt of 8 by the addition of acyllactam. This point of view concerning the function of activators has for a long time been advocated by Sekiguchi.

In non-activated polymerization this role may be taken up by the polymer containing CO-NH-CO-sequences, as it gradually accumulates in the system. It would be noted that the nature of the initial autoaccelerated kinetics which is very characteristic for lactams is not quite clear here. Finally, the monomer itself is a sufficiently strong solvating agent. A confirmation of this can be found in recent results concerning the interaction of lithium chloride with  $\epsilon$ -CL and its polymer (Ref. 43): crystalline complexes of the composition  $\text{Li}(\text{CL})_4\text{Cl}$  have been isolated, and strong changes of  $T_g$  and  $T_m$  of nylon-6 by the addition of relatively small amounts of the salt<sup>m</sup> have been established. These results resemble the influence of salts on the properties of poly(propylene oxide), which are definitely conditioned by complex formation (Ref. 44).

A sufficiently strong interaction with sodium tetraphenylboron in THF was found recently for a number of vinyl polymers with amide side groups by the  $\text{Na}^{23}\text{NMR}$  method (Ref. 28). Chemical shift, e.g. for poly-N,N'-diphenylacrylamide, was 7.5 ppm and practically did not change within the range of amide to cation molar ratios from 0.6 to 2. These measurements indicate the presence of strong interactions, but again tell us nothing about the mechanism of them. In any case donor-acceptor and solvation interactions which take place in polymerization of lactams, by virtue of peculiarities of the process are intermolecular. The role of polymer chains in solvation requires more direct experiments, but the low flexibility of polyamides makes multi-centre coordination in these systems doubtful.

Lactones. In polymerization of lactones opening of the cycle under the action of alkali initiator may proceed in two ways:



It is supposed that the ratio between the alternative ways in (9) depends on the nature of nucleophile  $\text{X}^-$  and on the size the lactone cycle (Ref. 47, 48). In any of these variants, however, the ion pair formed which then participates in the propagation process is rather strong. In this respect lactones are very close to epoxides. Such similarity is confirmed by the order of cation activity in polymerization of  $\beta$ -propiolactone ( $\beta$ -PL):  $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{Ba}^{2+} > \text{Ca}^{2+}$  (Ref. 46,47), which is indicative of the contact nature of the ion pairs of the growing poly- $\beta$ -PL. As the result of that one can consider also a very inert reaction of the active centres and polymerization kinetics to the solvent (Ref. 47).

Recently rapid progress has been made in the study of anionic polymerization of lactones, especially of  $\beta$ -PL, with counterions complexed with crowns and cryptands (Ref. 6,7,45,48). In this case polymerization proceeds as a living one, and it is not complicated by side reactions. An increase of rate constant by crown or cryptand cannot be characterised quantitatively, since the same systems non-activated by macrocycles have not been investigated in detail. The dependence of the rate in case of  $\beta$ -PL polymerization on dibenzo-18-crown-6 concentration (Ref. 48) shows, however, that the equilibrium constant of ion pair complexation with crown is not very high, being hardly over 50 l/mol. This may be considered as an indirect evidence in favour of a weak shielding effect of polymer. Close point of view on polymerization of lactones was recently advanced by Ph.Teyssie (49) on the basis of the study of pivalolactone reactions with various carboxylates, including polymeric ones (PEO, polycaprolactone). It is supposed that in these systems multicentre intramolecular complexes are also formed, in which there participates a certain number of ester groups of the chain. At present there are no ground for more substantiated conclusions concerning the role of the solvation of active centres in these systems by polymer and monomer. The dependence of the rate and equilibrium constants of  $\beta$ -PL polymerization on monomer concentration which has been revealed by Slomkowski and Penczek (6,7) shows that these interaction here still should not be neglected.

Episulphides. Anionic polymerization of propylene sulphide, a most convenient and therefore popular member of cyclic sulphides family, has been studied, perhaps, in most comprehensive manner among all the other monomer classes considered here (Ref. 8,50). A very low donating abilities of the episulphide itself and the monomer unit, partly because of the really low electron density on the atom of sulphur and partly due to the steric effect

of methyl group, is, evidently, the main reason for the absence in episulphide polymerization of any effects which can be explained by solvation of the growing centre by monomeric or polymeric donor fragments. These systems are normally influenced with solvents and solvating additives, there are no noticeable effects of the chain length in the kinetics or conductivity, etc. So, it would be most justifiable to conclude now that the reagents in these systems practically do not make any contribution to the spectrum of specific interactions of the growing centre, dissociation and reactivity of which are completely determined by the bulk solvent. It is also important that in propylene sulphide polymerization, as has been mentioned above, the role of the ion pairs in propagation is minimal.

#### CONCLUSION

The above analysis shows that an essential component of the mechanism of anionic polymerization of some heterocycles is the participation of monomers, as well as the forming macromolecules and macrocycles, in solvation of the growing centres. The role of the monomer in such solvation is almost fully determined by its basicity (donating power), and taking into account the effect of monomer on the properties of the ion pair practically remains within the scope of traditional approach. In some cases (lactones, lactams) the contribution made by the monomer to the polarity of the medium is essential. Similar interactions of polymers proceed at a principally different level. A possibility of multicentre binding of the cation, which is determined by the donor ability of the heteroatom in the chain and by the flexibility of macromolecules, sharply increases the solvating capacity of heterochain polymers with respect to cations. As a result, in the case of epoxides, cyclosiloxanes, and, possibly, lactams, the process of the chain propagation proceeds, as it were, in a microreactor. In the mechanism of anionic polymerization for such systems comprehensive consideration should be given to the macromolecular nature of the growing centre, there having been no particular grounds for this heretofore. In subsequent studies of the effects under discussion, model and living systems should be, no doubt, drawn together. In the case of epoxides and some other heterocycles one of the possibilities is offered by spectrophotometric investigation of the reaction of anions, e.g. picrates, some carboxylates, etc., to binding of the cation in their ion pairs with heterocycles and heterochain polymers, as it has been done for polycrowns in the series of works by Smid and coworkers. It is necessary to point out in conclusion that the interactions of cations of ion pairs with side heterocyclic or other donor groups are rather frequent in the "vinyl world", but their consideration is reduced there, as a rule, to taking into account the penultimate effects only.

#### REFERENCES

1. K.S. Kazanskii, A.A. Solovyanov and S.G. Entelis, Europ. Polym. J. **7**, 1421-1433 (1971); Polym. Sci. USSR **14**, 1186-1195 (1972).
2. A. Deffieux and S. Boileau, Polymer **18**, 1047-1049 (1977).
3. V.V. Ptchelintzev, E.G. Kagan and Yu.A. Yuzhelevskii, Zh. Prikl. Khim. **46**, 1842-1843 (1973).
4. T.M. Frunze et al., Paper presented at the 21st IUPAC Microsymposium on Macromolecules, Carlsbad, 1980.
5. J. Sebenda, in Comprehensive Chemical Kinetics **15**, p.379-471, Elsevier, Amsterdam, (1976).
6. St. Slomkowski, St. Penczek, New Developments in Ionic Polymerization, p. 98-101, Strasbourg, 1978.
7. St. Penczek, St. Slomkowski and D. Kotinska, ACS Polymer Preprints **21** 53-54 (1980).
8. P. Hemery, S. Boileau and P. Sigwalt, J. Polym. Sci.: Polym. Symp. **52** 189-202 (1975).
9. T. Kagiya, Y. Sumida and T. Inoue, Bull. Chem. Soc. Japan **41**, 767-773, 773-778 (1968).
10. E. Lippert and H. Prigge, Annalen **659**, 81-92 (1962).
11. E.M. Arnett, E.J. Mitchell and T.S.S.R. Murthy, J. Amer. Chem. Soc. **96**, 3875-3891 (1974).
12. M.G. Voronkov, V.P. Mileshkewitch and Yu.A. Yuzhelevskii, Siloxane bond (in Russian), Nauka, Novosibirsk, (1976).
13. L.M. Thomassen, T. Ellingsen and J. Ugelstad, Acta Chem. Scand. **25**, 3024-3030 (1971).
14. K.S. Kazanskii et al., Doklady AN SSSR **234**, 858-861 (1977).



15. K.S. Kazanskii, New Developments in Ionic Polymerization, p. 15-18, Strasbourg, 1978.
16. S.A. Dubrovsky and K.S. Kazanskii, Kinetika i Katalyz **21**, 1056-1061 (1980).
17. J.A. Orvik, J. Amer. Chem. Soc. **98**, 3322-3325 (1976).
18. I.V. Berlinova, I.M. Panayotov and Ch.B. Tsvetanov, Europ. Polym. J. **13** 757-760 (1977).
19. I.V. Berlinova, I.M. Panayotov and Ch.B. Tsvetanov, Vysokomol. Soed. B **20**, 839-842 (1978).
20. V.A. Ponomarenko, Vysokomol. Soed. A **19**, 1670-1678 (1977).
21. A. Sato, T. Hirano and T. Tsuruta, Makromol. Chem. **176**, 1187-1190 (1975)
22. C. Kazanskii, M. Reix and N. Spassky, Polymer Bull. **1**, 793-799 (1979).
23. Yu.Ye. Eizner and B.L. Erussalimsky, Electronic Aspect of Polymerization Reactions (in Russian), Nauka, Leningrad (1976).
24. S. Miertus, O. Kysel and P. Majek, Macromolecules **12**, 418-422 (1979).
25. P.A. Berlin et al., Vysokomol. Soed. A **22**, 1600-1606 (1980).
26. K. Matsuzaki and H. Ito, J. Polym. Sci.: Polym. Phys. Ed. **12**, 2507-2520 (1974).
27. R.D. Lundberg, F.E. Bailey and R.W. Callard, J. Polym. Sci. A-1 **4**, 1563-1577 (1966).
28. A. Ricard, Europ. Polym. J. **15**, 1-4 (1979).
29. Sh. Yanagida, K. Takahashi and M. Okahara, Bull. Chem. Soc. Japan **50**, 1386-1390 (1977); *ibid.*, **51**, 1294-1299 (1978).
30. N.V. Ptitsyna et al., Doklady AN SSSR **247**, 1412-1415 (1979).
31. G.N. Arhipovitch et al., Paper presented at the 21st Microsymposium IUPAC on Macromolecules, Carlsbad, 1980.
32. Multiple Equilibria in Proteins, Ed. by J. Steinhard and J.A. Reynolds, Academic Press, New York, London (1969).
33. J. Engel and D. Winklmair, in Protein-Protein Interactions, Springer, Heidelberg (1972).
34. M. Mazurek and J. Chojnowski, Makromol. Chem. **178**, 1005-1017 (1977).
35. S. Boileau, ACS Polymer Preprints **21**, 25 (1980).
36. B. Suryanarayanan, B.W. Peace and K.G. Mayhan, J. Polym. Sci.: Polym. Chem. Ed. **12**, 1089-1107, 1109-1123 (1974).
37. J. Chojnowski and M. Mazurek, Makromol. Chem. **176**, 2999-3023 (1975).
38. Yu.A. Yuzhelevskii, E.G. Kagan and N.N. Fedoseeva, Vysokomol. Soed. A **12**, 1585-1592 (1970).
39. K.A. Andrianov et al., Doklady AN SSSR **207**, 1113-1116 (1972).
40. K.A. Andrianov et al., Doklady AN SSSR **219**, 607-609 (1974).
41. H. Sekiguchi, P. Tsourkas and B. Coutin, Makromol. Chem. **178**, 2135-2138 (1977).
42. B. Coutin and H. Sekiguchi, New Developments in Ionic Polymerization, p. 88-92, 1978.
43. E. Aglietto et al., Preprints of Short Communications presented at the 26th International Symposium IUPAC on Macromolecules, vol. 1, p. 169-171, Mainz, 1979.
44. J. Moacanin and E.F. Cuddihy, J. Polym. Sci. C **14**, 313-322 (1966).
45. A. Deffieux and S. Boileau, Macromolecules **9**, 369-371 (1976).
46. S. Okamura, T. Higashimura and K. Tanaka, Kogyo Kagaku Zasshi **65**, 707-718 (1962).
47. T. Shiota, Y. Goto and K. Hayashi, J. Appl. Polym. Sci. **11**, 753-771 (1967).
48. St. Slomkowski and St. Penczek, Macromolecules **9**, 367-369 (1976).
49. G. Broze, P.M. Lefebvre, R. Jerome and Ph. Teyssie, Macromolecules **12**, 1047-1051 (1979).
50. P. Sigwalt and S. Boileau, J. Polym. Sci.: Polym. Symp. **62**, 51-64 (1978).