Complex bases: 13. Salt complex bases as new initiators in anionic polymerization of vinyl monomers

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Inorganic salts have been used as activating agents of alkali amides, which led to salt complex bases MNH_2-M′Z. Salt complex bases or solid salt complex bases constitute good initiators for solution and bulk anionic polymerization of vinyl monomers. The influence of the nature of the activating agent and of the solvent used has been examined. Finally the polymers thus formed appear to be living ones.

Keywords Polymerization; initiation; activation; salts; complex

INTRODUCTION

Since our earlier work concerning the activation of sodamide by sodium alkoxides or sodium enolates[1-3] (complex bases abbreviated here CB) Biehl and coworkers[4,5] have observed the same type of phenomenon with inorganic sodium salts such as NaSCN or $NaNO_2$. In a comparative study of alkoxides, enolates and inorganic salts as activating agents we subsequently established that, in general, inorganic salts had lower activating properties[3].

However, we primarily established in previous publications that CB constituted good initiators for polymerization of vinyl monomers[6-9]. Thus we decided to further study the activation of $NaNH_2$ and KNH_2 by inorganic salts and to determine whether the best of them (called salt complex bases and abbreviated SaCB) could be used as initiators in polymerization of vinyl monomers.

EXPERIMENTAL

Materials

Degussa broken sodamide was washed several times with the solvent of the reaction and ground in a mortar under the same solvent. Fluka lithium amide was used as such. Potassium amide was prepared from potassium metal and liquid ammonia according to reference 11.

Badisch Anilin reagent grade THF was distilled from sodium or benzophenone–sodium couple before use. Reagent grade DME (Fluka), toluene and thiophene free benzene (Pursan) were refluxed on sodium metal, then distilled and kept on sodium wires. Salts were commercial grade (Fluka, Prolabo).

The monomers were distilled on calcium hydride under argon or high vacuum.

General

Infra-red spectra were recorded with a Perkin–Elmer 457 spectrometer. The molecular weights are determined by v.p.o. ($\bar{M}_n$) Knauer instrument and by g.p.c. ($\bar{M}_n$, $\bar{M}_w$) with a Waters 200 instrument.

All reactions were performed under nitrogen R or argon U.

General procedure

Relative ratios of reagents and reaction conditions are given in the Results and Discussion section.

Salt complex base preparations. The salt was added to a suspension of the alkali amide in the chosen solvent at room temperature. The mixture was then heated for 2 h at 45°–50°C. In the case of solid salt complex bases prepared without solvent the salt was added to the ground alkali amide at room temperature. The mixture was then heated for 2 h at 45°–50°C with stirring.

With the solid salt complex bases prepared in a solvent the experimental technique used was the same as the one with the salt complex bases in solution. After the formation of the salt complex bases the solvent was evaporated under vacuum at room temperature.

Polymerization procedure

In the same reactor used for the preparation of salt complex bases the polymerizations were carried out under nitrogen or argon. After stirring to polymerization temperature the monomer was introduced under stirring with a hypodermic syringe. The polymerization was stopped by adding a small amount of methanol, the polymer was precipitated by pouring the reaction mixture into a large excess of methanol except for 2-vinyl pyridine in cyclohexane.

In the study of $NaNH_2$/Activating agent ratio (*Figure 1*) the polymerizations were carried out with 88 mM of monomer at 45°C in solution and 40°C in bulk. The polymerization times were 6 h in 40 ml THF and 8 h in 40 ml toluene. In bulk polymerization, time was 1 h.

The experiments showing the influence of monomer concentration (*Figure 2*) were performed at 50°C in 40 ml

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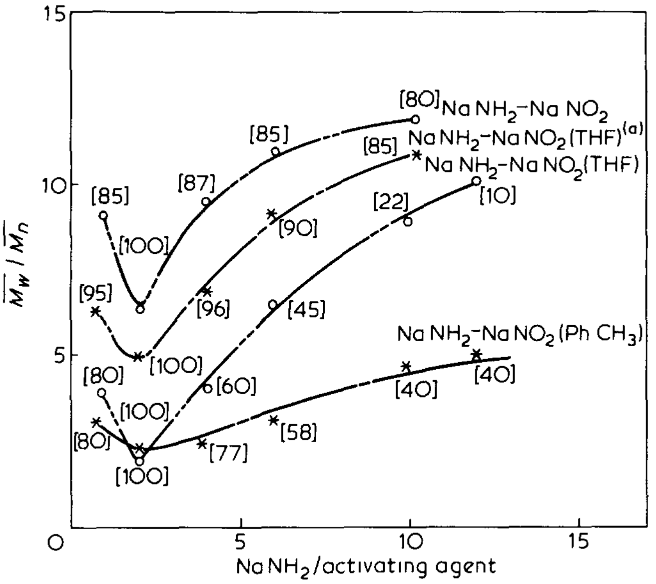

Figure 1 Polymerization of styrene by salt complex bases: Influence of NaNH$_2$/activating agent ratio [% Yield]; (a) solvent for solid salt complex bases preparation

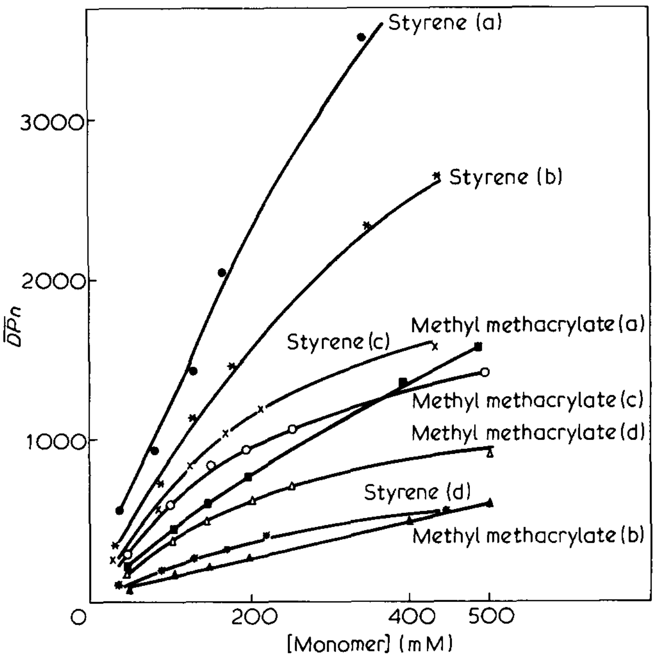

Figure 2 Polymerization of styrene and methyl methacrylate by salt complex bases: Influence of monomer concentration; (a) polymerization in toluene; (b) polymerization in THF; (c) bulk polymerization: solid salt complex bases prepared without solvent; (d) bulk polymerization: solid salt complex bases prepared in THF

of solvent with styrene, at 40°C in 40 ml of solvent with methyl methacrylate and at 30°C in bulk polymerization. The polymerization times were 6 h in THF, 8 h in toluene with styrene, 2 h with methyl methacrylate and 1 h in bulk polymerization.

The operative conditions for the other experiments are reported in the tables.

RESULTS AND DISCUSSION

Although complex bases are not very soluble in organic solvents, we found[8,9] that solution and bulk polymerizations led to different results. Therefore, in spite

Table 1 Polymerization of styrene by salt complex bases MNH$_2$ (16.7 mM)–ZM (8.3 mM)

Amides	LiNH$_2$						NaNH$_2$						KNH$_2$					
Solvent (ml)	THF (40)			PhCH$_3$ (30)			THF (40)			PhCH$_3$ (30)			THF (40)			PhCH$_3$ (30)		
Activating agent (ZM)	Yield (%)	$\bar{M}_n$^{a}	$\bar{M}_w$^{a}	Yield (%)	$\bar{M}_n$^{a}	$\bar{M}_w$^{a}	Yield (%)	$\bar{M}_n$^{a}	$\bar{M}_w$^{a}	Yield (%)	$\bar{M}_n$^{a}	$\bar{M}_w$^{a}	Yield (%)	$\bar{M}_n$^{a}	$\bar{M}_w$^{a}	Yield (%)	$\bar{M}_n$^{a}	$\bar{M}_w$^{a}
$NaNO_2$	26	22 200	71 050	20	24 400	82 950	100	75 700	151 500	100	95 600	210 300	100	14 500	37 700	100	21 200	40 300
NaSCN	24	19 700	68 950	15	16 200	56 700	100	70 000	140 000	100	82 000	180 400	100	13 700	32 900	100	20 000	44 000
NaCNO	14	10 700	43 900	10	8 850	33 350	95	63 800	153 100	90	69 600	174 000	100	10 800	27 000	100	16 600	44 800
NaCN	10	7 450	32 800	5	4 250	19 550	90	60 100	162 200	85	61 400	147 400	100	9 900	27 700	100	15 300	47 450
KNO_2	35	8 750	24 500	29	11 600	31 300	100	20 700	43 500	100	31 500	63 000	75	6 750	11 500	100	14 000	23 800
KSCN	30	6 750	20 900	25	8 750	25 400	100	20 000	34 000	100	30 100	69 200	70	6 100	11 000	100	13 500	25 650
KCNO	25	4 400	14 900	18	5 400	17 800	100	15 300	33 700	100	25 800	69 700	90	6 500	13 000	100	11 400	29 650
KCN	25	3 750	12 000	10	2 800	8 700	100	14 000	28 000	100	24 600	54 100	95	6 450	12 250	100	10 100	23 200

[a] Measured by g.p.c. at 30°C in THF

Styrene: 88 mM, temperature 40°C, polymerization time 4 h in THF, 8 h in toluene

Table 2 Polymerization of styrene (88 mM) by salt complex bases $NaNH_2$ (16.7 mM)–$NaNO_2$ (8.3 mM) at 40°C during 4 h

Solvent (40 ml)	Yield (%)	$\bar{M}_n{}^a$	$\bar{M}_w{}^a$	$\bar{M}_w/\bar{M}_n{}^a$
THF	100	75 700	151 500	1.3
DME	100	85 000	110 500	1.3
Diglyme	100	123 000	221 400	1.8
Toluene	45	55 600	122 300	2.2
Benzene	40	41 300	95 000	2.3
Cyclohexane	8	10 000	51 000	5.1

[a] Measured by g.p.c. at 30°C in THF

of the fact that salt complex bases were generally of poor solubility in usual organic solvent, we decided to examine both kinds of polymerization. We shall see later that here, too, different results were obtained.

Initially we studied the possible polymerization of styrene by numerous mixtures of alkaliamides with inorganic salts. In *Table 1* we have reported only the best results obtained. The polymerization experiments in solution as well as in bulk, performed with styrene with one of the best initiator agents $NaNH_2$–$NaNO_2$, showed (*Figure 1*) that the most powerful initiator was obtained when the ratio value $NaNH_2/NaNO_2$ was 2. That is the same ratio as that obtained for complex bases[8] and solid complex bases[9].

It is necessary to add a few comments to the results in *Table 1*. As far as the activating power is concerned, it appears that whatever the cation may be, counteranions of the activating part of the salt complex bases can be classified as follows:

$$NO_2^- \geqslant SCN^- > {}^-OCN \geqslant {}^-CN$$

The dispersity of the polymer is rather low considering the heterogeneity of the medium used. Moreover there are no large differences between solution and bulk polymerizations in contrast to what was observed with complex bases[8] and solid complex bases[9].

However, we have verified that, except for KNH_2, neither alkali amide nor alkali salts taken separately were able to initiate styrene polymerization. It is not usual that mixtures of such compounds, which are generally of low solubility in organic solvents, lead to activated initiators.

It is significant that MNH_2 activated by inorganic salt M′X generally leads to results similar to those obtained from $M'NH_2$ activated by MX (see *Table 1*). Thus it appears that aggregates must be formed so as to lead to actual exchanges of anions and cations and formation of new species. These observations confirm the generality of our concept concerning activation of reactivity of bases and, more generally, of salts A^-M^+ by another B^-M^{+3}.

Note that experiments not reported here, showed that a simple mixture of MNH_2 with an activating inorganic salt without solvent led to an initiator of styrene polymerization at 40°C. Moreover, a period of initiation was needed before the slow start of polymerization. This time certainly corresponds to the formation of the active aggregates. Apparently the low solubility in monomer was sufficient for the bases to be activated.

Taking into account these later observations we decided to study briefly the influence of the solvent on the polymerization in solution. The results obtained are shown in *Table 2*. It clearly appears that polar solvents

Table 3 Polymerization of vinyl monomers by salt complex bases $NaNH_2$ (16.7 mM)–ZNa (8.3 mM)

		Solution polymerization								Bulk polymerization							
Solvent (ml)		THF (40)				$PhCH_3$ (30)				THF (g)				—			
Monomer (mM)	Activating agent	$NaNO_2$	NaSCN	NaCNO	NaCN	$NaNO_2$	NaSCN	NaCNO	NaCN	$NaNO_2$	NaSCN	NaCNO	NaCN	$NaNO_2$	NaSCN	NaCNO	NaCN
2VP (80)[c]	Yield (%)	60	55	40	47	50	52	50	30	50	55	40	35	55	45	35	45
	$\bar{M}_n{}^a$	4900	3600	2000	2400	4600	3900	2800	1700	55 000	55 000	36 000	29 800	88 000	54 000	33 300	38 700
MMA (100)[d]	Yield (%)	100	100	96	90	100	100	90	85	70	65	75	55	60	75	55	60
	$\bar{M}_n{}^a$	43 500	22 000	19 200	16 200	41 000	19 000	15 300	12 800	63 000	53 900	51 000	34 100	72 000	66 000	38 500	40 800
	$\bar{M}_w{}^a$	56 500	46 200	48 000	38 900	195 600	87 000	62 800	71 400	151 200	140 300	158 100	143 200	172 800	191 400	134 800	195 900
	$\bar{M}_w/\bar{M}_n{}^a$	1.3	2.1	2.5	2.4	4.8	4.6	4.1	5.6	2.4	2.6	3.1	4.2	2.4	2.9	3.5	4.8
MAN (80)[e]	Yield (%)	100	75	63	50	100	95	74	57	85	80	75	60	85	87	80	75
	$\bar{M}_n{}^b$	20 000	11 250	8500	6500	19 500	10 000	6800	4800	63 800	50 400	34 500	28 200	72 300	56 600	42 000	37 500
An (80)[f]	Yield (%)	100	100	70	65	90	70	60	50	90	95	80	75	80	85	80	60
	$\bar{M}_n{}^b$	6300	4200	2800	2300	4000	2500	2100	1400	52 000	36 100	27 200	24 800	49 600	34 000	32 000	21 000

[a] Measured by g p c at 30°C in THF
[b] Measured by v p o at 130°C in DMF
[c] Solution polymerization temperature 40°C, polymerization time 4 h, bulk polymerization temperature 45°C, polymerization time 2 h
[d] Solution and bulk polymerization temperature 35°C, polymerization time 2 h
[e] Solution polymerization temperature 35°C, polymerization time 20 min, bulk polymerization temperature 45°C, polymerization time 30 min
[f] Solution polymerization temperature 40°C, polymerization time 30 min, bulk polymerization temperature 45°C, polymerization time 30 min
[g] Solvent of complex bases preparation

Table 4 Copolymerization styrene–methyl methacrylate by salt complex base NaNH$_2$ (16.7 mM)–NaNO$_2$ (8.3 mM) prepared in THF at –30°C

	Solution polymerization		Bulk polymerization	
	$\bar{M}_n$ (th.)	$\bar{M}_n{}^a$	$\bar{M}_n$ (th.)	$\bar{M}_n{}^a$
Sequence polystyrene	42500[b]	42500	13400[b]	13400
Sequence poly–MMA	20000	16300	32600	17500
Copolymer	62500	58800	46000	30900

[a] Measured by g.p.c. at 30°C in THF

[b] Determined from $\bar{M}_n$ measured. The difference observed between $\bar{M}_n$ (th.) and $\bar{M}_n$ (measured), in the case of copolymer, is likely to appear mainly because of the incomplete reaction of the sequence polymethyl methacrylate

gave the best results. Keeping those results in mind, we tried to extend the reaction performed to other vinyl monomers. The results obtained are summarized in *Table 3*. They demonstrate the general character of the initiating agents of salt complex bases. Moreover the low dispersity obtained with methyl methacrylate is particularly remarkable for anionic polymerization.

Finally experiments were conducted in order to determine the nature of the propagating species. Thus in *Figure 2* we have reported the variation of $\overline{DPn}$ (degree of polymerization) against monomer concentration in solution and bulk polymerization. It clearly appears that linear correlations occur at low concentrations showing the living nature of the polymer[10]. This property was confirmed by performing block copolymers between styrene and methyl methacrylate (*Table 4*).

Note that examination of i.r. spectra of a polystyrene oligomer prepared by the salt complex base NaNH$_2$–NaNO$_2$ in THF, showed absorption a 1610 cm^{-1} indicating the presence of a NH$_2$ group on the polymer. Potentiometric titration confirmed this observation which shows that, like complex bases and solid complex bases, salt complex bases initiate polymerization by the NH$_2^-$ part of the aggregates.

CONCLUSIONS

From this work it appears that alkali inorganic salts can activate alkaliamides to give salt complex bases very reactive as initiators for anionic polymerizations. The low cost and the easy handling of these new reagents must be emphasized.

Moreover it must be noted that, like alkoxides, inorganic salts allow the modulation of the properties of the salt complex bases.

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