Complex bases:
10. New complex bases. Application to solution anionic polymerization of vinyl monomers

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Numerous new complex bases, MNH_2-ROM (M = Li, Na, K) are described. It is shown that these bases are able to initiate the polymerization of vinyl monomers in solvents such as tetrahydrofuran or toluene. The characteristics of the polymer obtained depend on the nature of the activating agent ROM. Moreover, the living nature of the polymer is demonstrated.

INTRODUCTION

Organometallic derivatives[1] are commonly used as initiators for anionic polymerizations. Numerous works have been done in order to increase the reactivity of anionic initiators by adding, for instance, tertiary amines[2], linear and macrocyclic polyethers[3,4], cryptands[5]. Some alcohols[6] and alkali alkoxides[7,8] have also been used. Finally acceleration effects have been shown to occur on adding alkoxy alcohols to magnesium alkyls[9] as well as on mixing sodium or potassium tert-butoxides with sodium alkyls or with sodium or potassium salts[10].

Use of these conventional initiators on a large scale is restricted by their high cost and difficulty in handling. In order to reduce these inconveniences we have investigated the possibilities offered by a new class of cheap and easily handled potential initiators.

We have fully demonstrated[11-13] that the concept of bases synergy applied to sodamide and sodium alkoxides led to the preparation of new reagents $NaNH_2$-RONa called Complex Bases.

These bases have properties different from those of $NaNH_2$ and RONa (called activating agent) taken separately and may be powerful bases even in weakly polar solvents such as tetrahydrofuran (THF) or benzene. Thus it might be expected that the enhanced reactivity of the amide anion could be used for anionic polymerizations.

In two short preliminary notes[14,15] we showed that our expectations were justified and that not only was it possible to initiate anionic polymerization with complex bases but also that varying the nature of the activating agent led to variations in the nature of the polymers formed.

Here, we wish to report on a full description of the main results obtained in anionic polymerization of vinyl monomers using sodamide as well as lithium and potassium amides containing complex bases as initiator agents.

EXPERIMENTAL

Materials

Degussa broken sodamide was used, 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 32.

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. Alcohols were either commercial (Fluka, Aldrich) or prepared by classical procedures (condensation of Grignard reagent on suitable ketone for aliphatic alcohols and condensation of tosylates of commercial alcohols or polyethyleneglycols monoalkyl ethers on mono sodium salt of glycols or polyethyleneglycols[33]). Silica column chromatography was performed by using Kieselgel (Merck 0.063–0.200 mm). The monomers were distilled on calcium hydride under argon or high vacuum.

General

All melting points (Kofler) reported are uncorrected. Infra-red spectra were recorded with a Perkin-Elmer 457 Spectrometer and n.m.r. spectra with a Perkin-Elmer R 12 B instrument using TMS as an internal standard. The molecular weights were determined by v.p.o. ($\bar{M}_n$) with a Knauer instrument and by g.p.c. ($\bar{M}_n$, $\bar{M}_w$) with a Waters 200 instrument. U.v. and visible spectra were recorded with a Varian Cary 118 C Spectrophotometer. All reactions were performed under nitrogen R or argon U.

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General procedure

Relative ratios of reagents and reaction conditions are given in the theoretical section

Complex base preparations

A solution of the activating alcohol in the chosen solvent was added dropwise to a suspension of the alkali amide in the same solvent at room temperature (NH_3 must evolve). The mixture was then heated for 2 h at 45–50°C. Note that during these operations, if a light pink colour appears, the corresponding reagent will give bad results. The colouration is due to too large a concentration of peroxides in the reactants or the solvent.

BRP *determinations*

A solution of triphenylmethane in the chosen solvent (1.5 ml/mM) was added to the complex base. As soon as the red colour appeared, a solution of benzyl chloride (0.5 ml of solvent/mM) was added until decolouration was observed. The procedure was then repeated. The reaction times used for *BRP* determination correspond to the duration between the first and ultimate red colouration. After cooling the reaction mixture was poured onto ice, extracted with diethyl ether and the organic phase dried over $CaCl_2$. After removing of the solvent under vacuum, 1,1,1,2-tetraphenyl ethane was isolated in quantitative yield for complete reactions (M.pt = 143–144°C; M.pt = 145°C [34]).

CGP *determination*

A solution of triphenyl methane in the chosen solvent (1.5 ml/mM) was added to the complex base and stirred for 3 h at 60°C. After rapid cooling to room temperature, the reaction mixture was quenched by adding a well stirred solid CO_2 suspension in THF. After returning to room temperature, the mixture was hydrolized, the aqueous phase washed with light petroleum ether to remove the unreacted triphenyl methane, then acidified and extracted with diethyl ether. After drying over $MgSO_4$, the solvent was removed under vacuum. Pure triphenyl acetic acid was obtained from ethyl acetate and identified by comparison with an authentic sample. Yields of triphenyl acetic acid were used for *CGP* determination.

Relative activating properties in THF

(1) *Basic renewal power of RONa*

Primary alkoxides: $R = Me, Et, (CH_2)_n$ ($n = 2,3,4,6$) $\ll CH_2{=}CH\text{-}CH_2$, Pr, Bu, $Me(CH_2)_4$, $Me(CH_2)_5$, $Me(CH_2)_7 < Me(CH_2)_{11} < Bu(Me)_2CCH_2 < iPrCH_2 < tBuCH_2$

Secondary alkoxides: $R = Et(C_5H_{11})CH$

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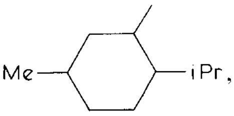

, $Me(C_6H_{13})CH < iPr_2CH$, $Me(Pr)CH$, iPr, $Me(Et)CH < Et_2CH$

Tertiary alkoxides: $R = Me_2C(CH_2)_2CMe_2$

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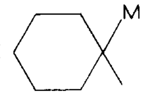
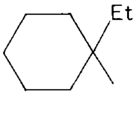


, $Et(Me)(C_8H_{17})C <$ t-Bu, $Me_2(C_8H_{17})C$, $n.Bu_3C <$



$< Me_2(Et)C$, $Me_2(Bu)C < Et_2(Me)C$

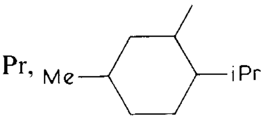
Alkoxy alkoxides: $R = C_{10}H_{21}(OCH_2CH_2)_2$, $Et(OCH_2CH_2)_5$, $Et(OCH_2CH_2)_6$, $CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2 \ll PhOCH_2CH_2 < MeOCH_2CH_2$, $BuOCH_2CH_2 < Et(OCH_2CH_2)_4$, $Bu(OCH_2CH_2)_3 < C_6H_{13}(OCH_2CH_2)_2 < Bu(OCH_2CH_2)_2$, $Et(OCH_2CH_2)_3 < EtOCH_2CH_2$, $Me(OCH_2CH_2)_2$, $Et(OCH_2CH_2)_2$

Alkoxides with aromatic ring: $R = p.MeOC_6H_4$, $p.MeOC_6H_4CH_2 < C_6H_5$, $o.MeOC_6H_4CH_2$

(2) *Carbanionic generation power of RONa*

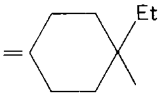
Primary alkoxides: $R = Me, Et, (CH_2)_n$ ($n = 2,3,4,6$) $\ll$ Pr, Bu, $Me(CH_2)_7$, $Me(CH_2)_{11}$, $iPrCH_2$, $tBuCH_2 < Me(CH_2)_4$, $Me(CH_2)_5$, $Bu(Me)_2CCH_2 < CH_2{=}CH\text{-}CH_2$

Secondary alkoxides: $R = Me(Et)CH$, $iPr_2CH < Me(Pr)CH$, $Et(C_5H_{11})CH <$ iPr,

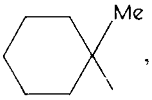


$< Me(C_6H_{13})CH$, Et_2CH

Tertiary alkoxides: R =

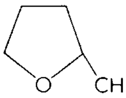


$n.Bu_3C$, $Et(Me)(Bu)C$, $Me_2C\text{-}CMe_2 < Me_2(Bu)C$, $Et(Me)(C_8H_{17})C <$



, $Me_2(C_8H_{17})C <$ t-Bu, $Me_2(Et)C$, $Et_2(Me)C < Me_2C(CH_2)_2CMe_2$

Alkoxy alkoxides: $R = CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}CH_2 \ll Et(OCH_2CH_2)_5$, $Et(OCH_2CH_2)_6 < Et(OCH_2CH_2)_4$, $Et(OCH_2CH_2)_3 < C_{10}H_{21}(OCH_2CH_2)_2$, $Bu(OCH_2CH_2)_3$, $Me(OCH_2CH_2)_2 < MeOCH_2CH_2$, $EtOCH_2CH_2$,



$< BuOCH_2CH_2$, $PhOCH_2CH_2$, $C_6H_{13}(OCH_2CH_2)_2$, $Et(OCH_2CH_2)_2$, $Bu(OCH_2CH_2)_2$

Alkoxides with aromatic ring: $R = o.MeOC_6H_4CH_2 < p.MeOC_6H_4$, $p.MeOC_6H_4CH_2 < C_6H_5$

Inversions were observed in DME. Precise data may be obtained from reference 20.

Note: Experiments reported in *Tables 1* and *2* were performed by the same procedure.

Polymerization procedure

In the same reactor used for the preparation of complex bases, the polymerizations were carried out under nitrogen or argon. After bringing this reactor 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 the 2-vinyl pyridine in the cyclohexane. In studying the ratio $NaNH_2$/activating agent (*Figure 1*) the polymerizations were carried out with 88 mM of monomers at 45°C. The polymerization time was 18 h with tBuONa and 6 h with $Et(OCH_2CH_2)_2ONa$ in 40 ml of solvent at 45°C.

Some experiments showing the presence of living

Table 1

$$Ph_nCH_{4-n}(20\,mM) + base \xrightarrow[THF\,(70\,ml)]{3h,\ 50^{\circ}C} Ph_nCH_{3-n}^{\ominus}K^{\oplus}$$

$$Ph_nCH_{3-n}^{\ominus}K^{\oplus} \xrightarrow[②\,H_3O^{\oplus}]{①\,Ice\,CO_2} Ph_nCH_{3-n}COOH$$

Hydrocarbon n	Base (mM)	Acid isolated yield %
3	KNH_2 (90)	90
	KNH_2 (60)–ButOK (30)	93
2	KNH_2 (90)	83–87
	KNH_2 (60)–ButOK (30)	61–67
	KNH_2 (60)–$Et(OCH_2CH_2)_2OK$ (30)	73

Table 2 Reaction

$$Ph_3CH(20\,mM) + base \xrightarrow[C_6H_6\,(70\,ml)]{3h,\ 50^{\circ}C} Ph_3C^{\ominus}K^{\oplus}$$

$$Ph_3C^{\ominus}K^{\oplus} \xrightarrow[②\ H_3O^{\oplus}]{①\ Ice\ CO_2} Ph_3CCOOH$$

Base (mM)	Acid isolated yield %
KNH_2 (90)	15–17
KNH_2 (60)–ButOK (30)	65–72
KNH_2 (60)–$Et(OCH_2CH_2)_2OK$ (30)	58–60
KNH_2 (60)–$Me_3C–CH_2OK$ (30)	31
KNH_2 (60)–Me_2CHOK (30)	21
KNH_2 (60)–$Me(C_6H_{13})CHOK$ (30)	23
KNH_2 (60)—$Me_2\underset{OK}{C}—(CH_2)_2—\underset{OK}{C}Me_2$ (30)	23

polymers (*Figure 2*) were done with 44 mM of styrene for complex bases prepared in 50 ml of solvent at 40°C.

The polystyryl spectra were studied as a function of solvent (THF, toluene), temperature and alkali amide. The living polymer solution was introduced into an optical cell by filtration on a glass-frit. Recording of the spectrum was realized every five min. All compartments of the Carry 118 were modified to allow variable temperature measurements over the range of −80 to +80°C. The temperature was controlled by means of a Secasi TBT variable temperature control unit and measured with a thermocouple.

The operating conditions for other experiments are reported on the corresponding Tables.

NEW COMPLEX BASES

Sodamide containing complex bases

The interpretation of bases synergy[13] showed that the phenomena are much too complicated to be quantitatively predicted. Moreover the number of activating agents previously found[16,17] was too small to be of interest in the polymerization field. Thus our first task was to study the behaviour of a large variety of potential activating agents taken from among the most current alcohol families and to determine some general reactivity laws. As usual[11,16–18] the reactions used in this preliminary study were the carbanion formation from Ph_3CH in THF or dimethoxyethane (DME) followed by benzylation with $PhCH_2Cl$ or carbonation.

The time needed for condensation of a given amount of benzylchloride on a given amount of triphenylmethane (the condensation being carried out as for a titration,[11,16]) represents the ability of a complex base to regenerate a carbanion (Basic Renewal Power: *BRP*). The yield of acid formed by carbonation indicates the ability of a complex base to form a carbanion (Carbanionic Generation Power: *CGP*). The results obtained have been shortly summarized in the experimental part. From this study it appears that salts of methanol, ethanol and primary glycols do not activate sodamide sufficiently.

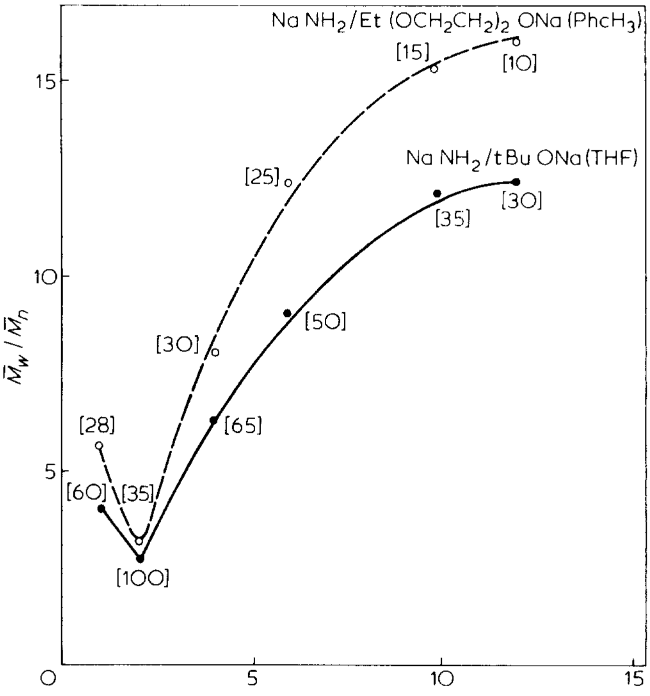


Figure 1 Polymerization of styrene by complex bases: Influence of $NaNH_2$/activating agent ratio [% yield]

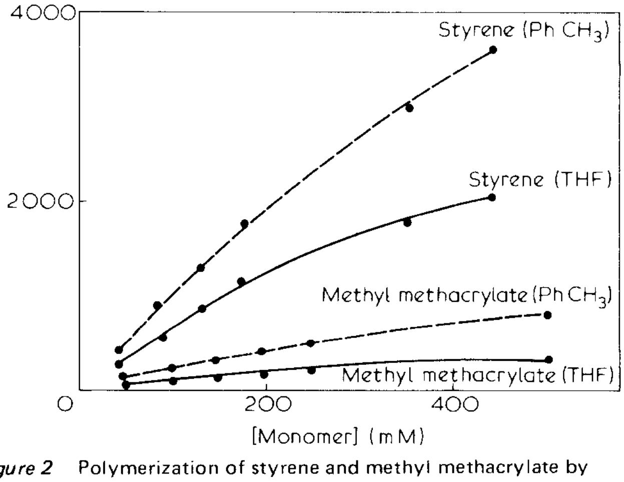


Figure 2 Polymerization of styrene and methyl methacrylate by complex base $NaNH_2–Et(OCH_2CH_2)_2ONa$: Influence of monomer concentration

Linear primary alkoxides are acceptable activating agents but they may suffer from poor reproducibility. Interestingly, the presence of a branched carbon atom bound to the hydroxylic carbon atom dramatically improves reproducibility as well as the *BRP* of primary alkoxides. Note the unexpected high value of allylic alkoxide's *CGP* in THF indicating that this activating agent may be used in this solvent when a high level of basic sites is desired.

Most secondary and tertiary alkoxides are good activating agents and are reproducible. Note that the best results were obtained with not too large a molecular mass. Phenol itself may also be considered as a good activating agent.

Finally the most efficient activating agents were found among alkoxy alkoxides. It is noteworthy that polyethylene glycolate monoalkyl-ethers may be good activating agents when the corresponding glycolates are not activating agents. The best reactivities were obtained with monoalkyl-ether of diethyleneglycol where the alkyl group was not too large.

In summary: In THF the best *BRP* have to be expected from diethyleneglycol alkoxide monoalkylethers. In the same solvent, good *BRP* may also be obtained from primary and secondary alkoxides (provided that they contain a light branched chain) as well as from tertiary alkoxides.

DME led to a levelling effect on the *BRP* values with numerous inversions relative to the order defined in THF.

Concerning *CGP* values, THF as well as DME orders are similar to *BRP* order in THF, again with a levelling effect of DME

Extension of the above results to much less polar solvents such as benzene showed that only $R(OCH_2CH_2)_2ONa$($R = Me$, Et, Bu) and $Et(OCH_2CH_2)_3ONa$ were able to properly activate $NaNH_2$. (*BRP* being about 35, 35, 50 and 240 respectively). However it is worth nothing that the simple addition of current alcohols to an excess of sodamide led to a base strong enough to react with triphenylmethane in an extremely weak polar solvent. Even in cyclohexane a *BRP* of 180 was found for $Et(OCH_2CH_2)_2ONa$.

Lithium and potassium amides containing complex bases

Lithium amide is much less basic than sodium amide. Using the above reaction tests we found that only $R(OCH_2CH_2)_2OLi$ ($R = Et$, Bu) were able to lead to the characteristic red colouration of triphenylmethyl carbanion.

On the contary, potassium amide is a strong base which is able to react with triphenyl as well as diphenylmethane in THF[19]. As exemplified by the results reported in *Table 1*, potassium alkoxides did not activate potassium amide in THF. Some lower reactivity of KNH_2 might even be observed. This result may be explained since KNH_2 is certainly much more soluble and dissociated in THF than $NaNH_2$. Moreover, its dissolution rate must be much higher. Thus this amide does not need alkoxides to pass in solution. However aggregates (complex bases) are formed between KNH_2 and potassium alkoxide (we shall later see that polymerization experiments support this hypothesis). In these aggregates, the electronic availability of the amide group is certainly equal or slightly lower than for KNH_2 dissolved in THF.

If this hypothesis is correct, it might be thought that completely different results should be obtained in low polar solvents such as benzene. Indeed, it might be expected that solubility, dissociation as well as the dissolution rate of KNH_2 should all be much lower than in THF. Thus an alkoxide activation effect should be observed. This was verified as may be seen from the experiments reported in *Table 2*. Some experiments not reported here, showed that, as for $NaNH_2$ [18] the best activation was obtained when the ratio $KNH_2/ROK = 2$. Interestingly, in benzene, the best activating agent allows obtaining basic properties approaching those observed in THF with KNH_2 along. This brings to mind the comparison between $NaNH_2$ in HMPA and $NaNH_2$–RONa in THF[11–13,20].

ANIONIC POLYMERIZATION OF VINYL MONOMERS

Complex bases $NaNH_2$–RONa as initiators

Some preliminary experiments on styrene and vinyl monomers rapidly showed that complex bases $NaNH_2$–RONa, might constitute rather good anionic initiators in THF or toluene and that the nature of the polymers depended on the nature of the activating agent[14,15]. Thus with the goal of obtaining more information on the mechanism and of determining the best practical polymerization conditions, we undertook the study of the influence of different parameters.

Influence of the $NaNH_2$/activating agent ratio

This study was performed on styrene polymerization. Taking our preliminary experiments into account, Bu^tONa and $Et(OCH_2CH_2)_2ONa$ were chosen as activating agents in THF and toluene respectively. *Figure 1* illustrates the simultaneous variations in dispersity and yield *versus* $NaNH_2$/activating agent ratio. All experiments were performed in the same conditions. (See Experimental section).

It appears clear that when the ratio was 2, the best results were obtained, i.e. the same result as for trityl anion formation[16,18], and this ratio has been used in all the following work.

Influence of the nature of the activating agent. It was of interest to determine the role played by the activating agents. For this study, twenty alkoxides chosen from among the families already examined (*vides supra*) were tested. The results obtained are presented in *Table 3*.

Initially, it must be emphasized that comparison of these results with control experiments (not reported here for simplicity), showed that, concerning the yields as well as the nature of the formed polymer, the complex base behaviour was, as expected, completely different from the behaviour of its separate constituents. Thus yields were generally considerably lower and dispersities considerably higher.

Secondly from *Table 3* it may be generally concluded that the best activating agents are situated among those characterized by good *CGP* and/or good *BRP* (*vide supra*). Particularly striking was the efficiency of diethyleneglycol monoalkylethers.

Finally polymerizations performed with methacrylonitrile, acrylonitrile and vinyl pyridine using the same complex bases generally led to quantitative yields.

Table 3 Polymerization of vinyl monomers (88 mM) by complex base $NaNH_2$ (16.7 mM)–RONa (8.3 mM)

Monomer	Styrene (88)[a]								Methyl methacrylate (100)[a]							
Solvent	THF (40)				$PhCH_3$ (40)				THF (40)				$PhCH_3$ (40)			
Activating agent R–	Yield %	$\bar{M}_n$ [b]	$\bar{M}_w$ [b]	$\bar{M}_w/\bar{M}_n$	Yield %	$\bar{M}_n$ [b]	$\bar{M}_w$ [b]	$\bar{M}_w/\bar{M}_n$	Yield %	$\bar{M}_n$ [b]	$\bar{M}_w$ [b]	$\bar{M}_w/\bar{M}_n$	Yield %	$\bar{M}_n$ [b]	$\bar{M}_w$ [b]	$\bar{M}_w/\bar{M}_n$
nBu–	35	5100	9200	1.8	15	7950	38 150	4.8	40	3200	5450	1.7	37	1500	2700	1.8
C_5H_{11}–	50	10 300	20 600	2.0	15	10 650	57 500	5.4	50	5000	9000	1.8	43	2600	5450	2.1
C_6H_{13}–	52	12 750	34 400	2.7	10	9000	47 700	5.3	43	4500	8600	1.9	45	2950	6500	2.2
C_7H_{15}–	47	16 000	46 400	2.9	15	17 250	105 250	6.1	55	6350	10 800	1.7	47	3550	8500	2.4
C_8H_{17}–	53	18 650	61 550	3.3	19	24 400	153 700	6.3	75	9000	16 200	1.8	55	4700	10 350	2.2
$C_{10}H_{21}$–	22	11 200	50 400	4.5	25	45 000	342 000	7.6	70	10 500	15 750	1.5	70	7000	13 300	1.9
$tBuCH_2$–	15	1200	3400	2.8	30	19 500	159 900	8.2	60	4500	6750	1.5	50	2650	5300	2.0
$CH_2{=}CH{-}CH_2$–	87	53 500	85 600	1.6	37	100 000	600 000	6.0	60	6600	9900	1.5	100	10 000	17 000	1.7
iPr–	72	37 500	97 500	2.6	16	16 500	75 900	4.6	100	15 000	24 000	1.6	72	3950	6700	1.7
Et_2CH–	58	13 350	37 400	2.8	10	11 000	53 900	4.9	100	20 000	30 000	1.5	60	4200	7550	1.8
tBu–	62	18 600	39 100	2.1	35	45 500	163 800	3.6	100	25 000	40 000	1.6	83	5400	9700	1.8
nBu_3C–	40	5900	14 700	2.5	22	18 700	71 050	3.8	100	16 000	28 800	1.8	65	3900	7400	1.9
$Et(OCH_2CH_2)$–	40	6250	11 900	1.9	63	123 000	430 500	3.5	100	10 000	17 000	1.7	70	5600	8950	1.6
$Et(OCH_2CH_2)_2$–	100	60 500	90 750	1.5	78	245 700	786 250	3.2	100	30 000	48 000	1.6	100	12 500	18 750	1.5
$Et(OCH_2CH_2)_3$–	50	25 350	53 200	2.1	72	158 400	586 050	3.7	100	25 000	45 000	1.8	100	10 500	16 800	1.6
$Et(OCH_2CH_2)_6$–	27	5500	12 650	2.3	51	61 200	250 950	4.1	100	12 000	19 200	1.6	90	6300	10 700	1.7
$Me(OCH_2CH_2)$–	38	3800	6450	1.7	50	70 000	245 000	3.5	100	4300	6450	1.5	88	5050	8050	1.6
$Bu(OCH_2CH_2)_2$–	95	59 300	100 800	1.7	80	290 400	1 132 550	3.9	100	35 000	56 000	1.6	100	18 700	29 900	1.6
$Bu(OCH_2CH_2)_3$–	47	24 100	53 050	2.2	64	179 200	824 300	4.6	80	21 600	38 900	1.8	100	16 000	28 800	1.8
Furfuryl	100	72 200	137 200	1.9	22	30 800	194 050	6.3	100	8000	13 600	1.7	95	5700	10 250	1.8

[a] Styrene: temperature 30°C, polymerization time 3 h; Methyl methacrylate: temperature 40°C, polymerization time 2 h in THF and 6 h in $PhCH_3$

[b] Measured by g.p.c. in THF at 30°C

Table 4 Polymerization of styrene (88 mM) by complex base $NaNH_2$ (16.7 mM)–$C_2H_5(OCH_2CH_2)_2ONa$ (8.3 mM) at 45°C for 2 h

Solvent (40 ml)	Yield (%)	$\bar{M}_n$ [a]	$\bar{M}_w$ [a]	$\bar{M}_w/\bar{M}_n$
THF	100	81 000	187 000	2.3
DME	100	87 000	200 000	2.3
Diglyme	90	108 000	220 000	2.0
Toluene	35	70 000	190 000	2.7
Benzene	30	60 000	160 000	2.7
Cyclohexane	10	8400	45 400	5.4

[a] Measured by g.p.c. in THF at 30°C

However, $\bar{Mn}$ values varied between 3000 to 7000 in THF and 2000 to 3500 in toluene for methacrylonitrile and acrylonitrile; between 1200 to 6000 in THF and 1500 to 15 000 in toluene for 2-vinyl pyridine.

Influence of the nature of the solvent and the reaction conditions. Experiments performed with styrene using the best activating agent showed that, as expected[18], efficiency of the complex bases increases with solvent polarity (see *Table 4*).

Polymerization at different temperatures, using $NaNH_2$-$Bu(OCH_2CH_2)_2ONa$ showed that for styrene polymerization, the rate increased with temperature in THF as well as in toluene. On the contrary, for methyl methacrylate, the rate remained unchanged whatever the temperature in THF and decreased with increasing temperature in toluene. The same observations were described by Gole[21]. Side reactions were implicated by this author.

Finally, considering our hypothesis concerning the nature of the Complex Bases, it ought to be thought that new initiator sites should be formed during the reactions and that low rate polymerizations should be more sensitive to them. In agreement with this hypothesis, it was observed that for styrene polymerization in toluene, with Bu^tONa as activating agent, the ratio yield $\%\bar{M}_n$ (directly related to the polymer chain number) increases with time.

Complex bases $LiNH_2$–ROLi as initiators

We showed (*vide supra*) that $LiNH_2$ was hardly activated by lithium alkoxides. However, we were able to observe some activation with lithium salts of diethyleneglycol monoalkylethers, supporting the presence of aggregates. Therefore it might be thought that with other activating agents, aggregates should also be formed and that with some of them, activation was insufficient to form trityl lithium but strong enough to allow polymerization. This hypothesis was tested with activating agents chosen from among the best found for $NaNH_2$.

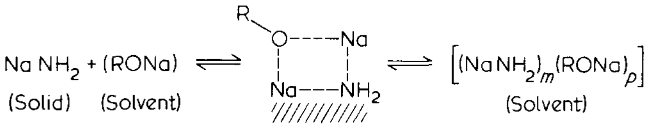
The results obtained are given in *Table 5*. Comparison with control experiments showed that behaviour of complex bases containing $LiNH_2$ was different from that of their separate constituents. However the number of activating agents leading to acceptable results was limited. The yields and molecular weight distribution of polymers are generally less interesting than those obtained with complex bases containing $NaNH_2$ and polymerizations are slow. Finally methacrylonitrile and acrylonitrile were also studied. The yields obtained varied between 20 to 50% and $\bar{M}_n$ values between 1200 to 3000.

From *Table 5*, it may be seen that results obtained for polymerization of vinyl monomers by complex bases containing KNH_2 are in agreement with *CGP* orders and that activation of KNH_2 by potassium alkoxides was observed in low polar solvents such as toluene.

It is noteworthy that comparison with KNH_2 and some potassium alkoxides taken separately showed greatest reactivity for complex bases. Considering that our systems were heterogeneous the molecular weight distribution appeared narrow and the reaction rapid. Methacrylonitrile and acrylonitrile led to quantitative yields with $\bar{M}_n$ varying from 1500 to 3500.

DISCUSSION OF THE POLYMERIZATION MECHANISMS

The activation of alkali amides by alkoxides has been interpreted by an alkoxide complexation of solid amide and formation of aggregates (Scheme 1).



Scheme 1

Clearly, the structure of the aggregates and their solubility depend on the nature of the activating agent and of the solvent. However, some parts of these aggregates constitute the active initiating centres. In other words, for a given amide, the number and the reactivity of active centres depend on the nature of the activating agent and of the solvent. It is thus possible to modulate the initiation of the polymerizations and thus the properties of the polymers formed. This possibility constitutes one of the interesting properties of complex bases as polymerization initiators.

At this point of the discussion, one interesting question should be asked: which part of the complex bases initiates the polymerizations?

The i.r. study of polystyrene oligomer prepared by the complex base $NaNH_2$-$Et(OCH_2CH_2)_2ONa$ in THF shows the presence of the peak arising from NH_2 at 3300 cm^{-1} proving that NH_2^- initiates the polymerization of styrene. Moreover one NH_2 group per macromolecular chain was identified by potentiometric titration of the polymer with $HClO_4$ in acetic acid.

One of the consequences of the initiation by the amide part of the base, is the destruction of the initiator centres with a simultaneous release of the alkoxide. The alkoxide returns to take up the amide and then new active centres may appear. Clearly in some circumstances, this regeneration of active centres may alter the homogeneity of the polymers formed.

Another interesting point was to know if the polymers were living or not. In order to answer this question, we studied the variation of $\bar{DP}_n$ (degree of polymerization) *versus* the monomer concentration for styrene and methyl methacrylate polymerizations in THF and toluene. The activating agent chosen was $Et(OCH_2CH_2)_2ONa$. As may be seen from *Figure 2*, a linear relation was found as long as the monomer concentrations were not too high. Note that this lack of linearity for high concentrations is well known for termination of polymerizations by transfer reactions[1]. The curves obtained strongly support the living nature of the polymers.

This hypothesis was confirmed by the preparation of

Table 5 Polymerization of vinyl monomers by complex bases $LiNH_2$ (16.7 mM)–ROLi (8.3 mM) and KNH_2 (16.7 mM)–ROK (8.3 mM)

	Monomer (mM)	Styrene (88)								Methyl methacrylate (100)							
	Solvent (ml)	THF (40)				$PhCH_3$ (40)				THF (40)				$PhCH_3$ (40)			
Amide	Activating agent R–	Yield %	$\bar{M}_n$ [c]	$\bar{M}_w$ [c]	$\bar{M}_w/\bar{M}_n$	Yield %	$\bar{M}_n$ [c]	$\bar{M}_w$ [c]	$\bar{M}_w/\bar{M}_n$	Yield %	$\bar{M}_n$ [c]	$\bar{M}_w$ [c]	$\bar{M}_w/\bar{M}_n$	Yield %	$\bar{M}_n$ [c]	$\bar{M}_w$ [c]	$\bar{M}_w/\bar{M}_n$
$LiNH_2$ [a]	nBu–	22	2200	18 050	8.2	10	6000	88 200	14.7	15	1850	2950	1.6	15	1650	5950	3.5
	$tBuCH_2$–	20	4600	41 850	9.1	10	6750	102 600	15.2	10	1250	1900	1.5	10	1150	4350	3.8
	iPr–	35	11 050	78 450	7.1	12	13 800	142 150	10.3	29	8700	12 200	1.4	25	4850	15 050	3.1
	Et_2CH–	30	11 550	79 700	6.9	10	12 500	125 000	10.0	20	7000	11 900	1.7	22	8150	34 200	4.2
	tBu–	35	14 300	90 100	6.3	27	41 200	391 400	9.5	32	16 550	23 200	1.4	31	9850	29 550	3.0
	nBu_3C–	30	10 500	65 100	6.2	20	26 500	249 100	9.4	25	11 250	16 900	1.5	25	12 500	48 750	3.9
	$Et(OCH_2CH_2)$–	40	8150	41 550	5.1	40	97 200	894 250	9.2	50	14 850	22 300	1.5	43	8150	25 250	3.1
	$Et(OCH_2CH_2)_2$–	42	30 050	126 200	4.2	62	212 050	1 929 650	9.1	60	38 650	50 250	1.3	54	11 450	32 050	2.8
	$Et(OCH_2CH_2)_3$–	31	20 150	92 700	4.6	57	154 500	1 606 800	10.4	39	20 550	30 800	1.5	30	3800	12 950	3.4
KNH_2 [b]	nBu–	80	4250	22 100	5.2	52	3100	26 950	8.7	87	5850	12 300	2.1	80	2400	5300	2.2
	$tBuCH_2$–	70	3850	19 250	5.0	50	3150	28 050	8.9	80	5600	13 450	2.4	70	2800	7300	2.6
	iPr–	68	4100	16 800	4.1	80	5600	35 850	6.4	100	13 300	27 930	2.1	100	4500	10 350	2.3
	Et_2CH–	65	4250	18 300	4.3	90	7200	46 800	6.5	90	13 500	31 050	2.3	100	6000	15 000	2.5
	tBu–	60	4100	15 150	3.7	100	7400	39 950	5.4	100	17 500	31 500	1.8	100	6100	12 800	2.1
	nBu_3C–	65	3550	13 900	3.9	95	6200	38 450	6.2	90	13 050	24 800	1.9	100	4500	9900	2.2
	$Et(OCH_2CH_2)$–	53	3050	8850	2.9	100	7100	38 350	5.4	100	8600	15 300	1.8	100	7200	17 300	2.4
	$Et(OCH_2CH_2)_2$–	50	4350	11 750	2.7	100	9600	45 100	4.7	100	25 700	43 700	1.7	100	10 400	19 750	1.9
	$Et(OCH_2CH_2)_3$–	54	3200	10 900	3.4	100	6700	38 200	5.7	100	8300	15 750	1.9	100	9700	25 200	2.6

[a] Styrene: temperature 50°C, polymerization time 6 h; Methyl methacrylate: temperature 40°C, polymerization time 2 h in THF and 6 h in $PhCH_3$

[b] Styrene: 30°C in THF and 50°C in $PhCH_3$, polymerization time 3 h in THF and 6 h in $PhCH_3$; Methyl methacrylate: temperature 40°C, polymerization time 2 h in THF and 6 h in $PhCH_3$

[c] Measured by g.p.c. in THF at 30°C

Table 6 Copolymerization styrene–methyl methacrylate by complex base: $NaNH_2$ (17 mM)–$C_2H_5(OCH_2CH_2)_2ONa$ (8.5 mM) in THF (10 ml) at –30°C

	$\bar{M}_n$ (th)	$\bar{M}_n$ measured[a]
Sequence polystyrene	35 000[b]	35 000
Sequence polymethyl methacrylate	41 600	15 000
Copolymer	76 600	50 000

[a] Measured by g.p.c. at 30°C in THF
[b] Determined from measured $\bar{M}_n$

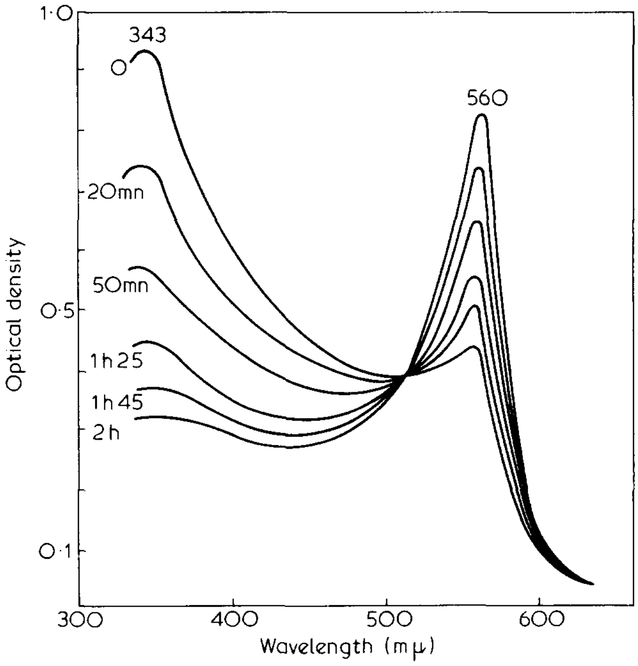
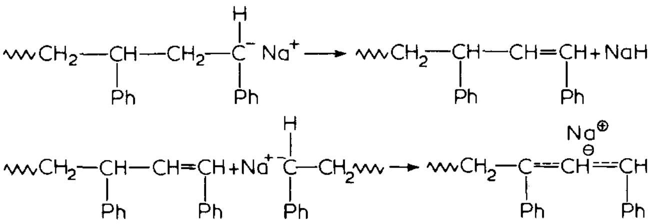


Figure 3 Absorption spectrum of carbanion polystyryl initiated by complex base $NaNH_2$–$Et(OCH_2CH_2)_2ONa$ in THF

block copolymers of styrene and methyl methacrylate (*Table 6*). The difference observed between theoretical and experimental $\bar{M}_n$ for methyl methacrylate was due to an incomplete reaction. The sequence length corresponds to 36% monomer incorporation. However, it is clear that the polymer chains formed from styrene carried active centres able to initiate polymerizations of other monomers.

Furthermore, we carried out a spectroscopic study of the stability of the carbanion leading to the propagation of the polymerization of styrene initiated by $NaNH_2$–$Et(OCH_2CH_2)_2ONa$.

In THF, as may be seen from *Figure 3* the absorption at 343 nm, which was due to benzylic carbanion[22–30] disappeared to give a new absorption at 560 nm corresponding to the benzyl allyl anion (scheme 2).



Scheme 2

In THF the complete disappearance occurs after 2 h and we were able to determine an isosbestic point.

The same study performed in toluene showed that the complete evolution occurs after 18 h. These results agree with the living polymer hypothesis. Note that the same changes were observed when we replaced the sodium cation by potassium. On the contrary, with the lithium cation, this evolution was much slower. Moreover at the beginning of the polymerization, disappearance of the 343 nm absorption occurred without formation of the 560 nm absorption. In other words, removing LiH was easier than allylic carbanion formation.

Franta and Rempp[27] observed similar results in HMPA. With a potassium counter-cation, the carbanion was stable below –50°C but it disappeared to give the benzyl allyl anion at –78°C with a sodium counter-cation.

Generally speaking it appears from the literature data[26] that the reactions pictured in scheme 2 are rather slow (for example 30% in 350 h in THF with a sodium counter-cation). The rates increase when the ion pair separation increases by increasing the solvent polarity[27,28] or through addition of complexing agents[29]. In the present case, the rather high rates observed may be interpreted as alkoxide activation of the carbanion which promotes polymerization, in the same way as alkali amide activation. Note that Lochman[31] proposed a similar scheme in the case of the alkali dialkyl amides.

Finally, in order to confirm the living nature of the polymers and generally demonstrate the possibility of preparing polymers with high $\bar{M}_n$ values we performed the reactions summarized in *Table 7* where different monomer/initiator ratios were used.

It is clear from these results that Complex Bases are able to give high polymers when high monomer/ initiator ratios are used.

CONCLUSIONS

From the present work it appears that complex bases constitute very interesting initiators for polymerizations as well as oligomerization in solution. They are cheap, easily prepared and handled. Moreover, their reactivity may be easily modified by changing the activating agent. It is therefore simple to change the nature of the polymers formed. Another interesting points is the possibility of preparing block copolymers. The only drawback may be a lack of homogeneity.

Table 7 Polymerization of acrylonitrile and methacrylonitrile at different monomer initiator ratios

Monomer mM	$NaNH_2$ mM	RONa mM	Yield %	$\bar{M}_n$
Acrylonitrile + $NaNH_2$ + $Et(OCH_2CH_2)_2ONa$ in THF (40 ml) at 25°				
100	16.7	8.3	100	15 000
100	8	4	95	35 000
150	4	2	90	72 000
Methacrylonitrile + $NaNH_2$ + Bu^tONa in toluene (50 ml) at 30°				
150	16.7	8.3	100	12 600
150	8	4	100	35 000
200	4	2	100	84 600

Finally we shall see in the next paper that complex bases may also be used as bulk polymerization initiators, thus extending the application field of the new initiators.

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