Complex bases:
11. Solid complex bases. Application to the bulk anionic polymerizations of vinyl monomers

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Solid complex bases, easily obtained from complex bases MNH_2-ROM by removing the solvent or by direct reaction between MNH_2 and ROH, constitute good initiators for bulk polymerization of vinyl monomers. The influence of the nature of the activating agent and of the solvent used for the preparation of the complex base have been examined. Finally the polymers thus formed appear to be living ones.

INTRODUCTION

Among the many different methods allowing the production of bulk polymers from vinyl monomers[1-20] anionic initiation is of particular interest. It has been shown that the anionic mechanism is well suited to obtaining low reaction times, low monomer residue and relatively monodispersed polymers[19,20].

Moreover the thermal anion of a living polymer may be used in order to obtain a functional polymer or to initiate a new monomer polymerization[21]. It is well known that anionic polymerization may be performed with or without a solvent[21]. However if the presence of a solvent is necessary in order that the polymerization occurs, the reaction will be of interest only for the elaboration of expensive polymers with special properties. On the contrary, when common and inexpensive polymers are desired, the presence of a solvent must be eliminated and mass polymerization must be used.

In the preceding paper[22] we showed that Complex Bases MNH_2–ROM might be used as anionic initiators for vinyl monomer polymerization in solution.

Taking into account the above observations we pondered the question as to whether complex bases should also constitute bulk polymerization initiators. We shall see that this was the case and in the present paper, we wish to present our main results in this field.

EXPERIMENTAL

Solid complex base preparations

Relative ratios of reagents are given in the theoretical section. In the case of solid complex bases prepared without a solvent, the activating alcohol was added dropwise to the ground alkali amide at room temperature (NH_3 must evolve). The mixture was then heated for 2 h at 45–50°C with stirring.

With the solid complex bases prepared in a solvent the experimental technique used is the same as in the preceding paper[22]. After the formation of the complex base the solvent is evaporated under vacuum at room temperature.

Note: The experimental techniques (materials and polymerization procedure) used in this study were outlined in the preceding paper[22]. In the study of the ratio $NaNH_2$/activating agent the polymerizations are realized with 88 mM of monomers at 45°C with Bu^tONa and 40°C with $Et(OCH_2CH_2)_2ONa$. The polymerization time was 18 h with ButONa, 0.5 h with $Et(OCH_2CH_2)_2ONa$ prepared in THF and 1 h with $Et(OCH_2CH_2)_2ONa$ prepared without a solvent.

The experiments reported on *Figure 2* were carried out with 44 mM monomers at 40°C. The operating conditions for other experiments are reported on *Tables 1–4.*

SOLID COMPLEX BASES

It was of paramount interest to know if it was possible to remove the solvent from the complex bases without loss of activity. However complex bases are heterogeneous reagents comprised of a limpid liquid, a colloidal suspension and some residual alkali amide[23-26]. From a careful study not reported in detail here, performed with $NaNH_2$-Bu^tONa of $NaNH_2$–$Et(OCH_2CH_2)_2ONa$[24] using generation and carbonation of $Ph_3C^-Na^+$ as a reaction test[22], it appeared that: After careful filtration there was a low concentration of active complex base in the limpid liquid. Nearly all the active part was concentrated in the white colloidal suspension, and as expected residual sodamide was found without reactivity.

However for non-instantaneous reactions, the presence of sodamide led to better results. This observation agrees with our hypothesis[23-26] on the alkoxide transfer of the amide during the reaction from the surface of the solid sodamide toward the solution as more or less soluble aggregates.

With these data in hand, we decided to study the possibility of obtaining solid complex bases from the

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Table 1 Polymerization of vinyl monomers by complex bases $NaNH_2$ (16.7 mM)–RONa (8.3 mM)

Monomer (mM)	Styrene (88)[a]								Methyl methacrylate (100)[a]							
Solvent	THF				–				THF				–			
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	39 200	121 500	3.1	28	45 100	157 850	3.5	37	5200	11 950	2.3	30	5600	19 050	3.4
C_5H_{11}–	53	74 200	252 300	3.4	50	99 500	358 200	3.6	40	6400	13 450	2.1	35	8050	25 750	3.2
C_6H_{13}–	50	75 000	247 500	3.3	47	97 750	361 650	3.7	38	6550	16 350	2.5	32	7400	26 600	3.6
C_7H_{15}–	51	77 000	269 500	3.5	45	94 500	330 750	3.5	50	8700	20 900	2.4	40	10 400	36 400	3.5
C_8H_{17}–	55	99 100	485 600	4.9	53	120 850	640 500	5.3	45	7650	19 900	2.6	37	10 450	31 350	2.0
$C_{10}H_{21}$–	39	74 100	377 900	5.1	40	103 000	535 600	5.2	40	7850	23 500	3.0	35	10 500	43 050	4.1
$tBuCH_2$–	26	18 200	56 400	3.1	20	18 000	73 800	4.1	60	5900	17 100	2.9	49	5900	19 500	3.3
$CH_2{=}CH{-}CH_2$–	100	310 000	837 000	2.7	80	396 000	1 188 000	3.0	47	23 950	57 500	2.4	75	55 500	160 950	2.9
iPr–	89	135 500	400 500	3.0	83	178 450	588 900	3.3	80	17 600	38 700	2.2	70	26 250	65 600	2.5
Et_2CH–	80	124 000	409 200	3.3	57	127 400	407 700	3.2	72	21 600	51 850	2.4	50	20 500	55 350	2.7
tBu–	90	153 000	443 700	2.9	78	175 500	508 950	2.9	88	30 800	64 700	2.1	85	40 800	97 900	2.4
nBu_3C–	52	53 350	198 200	3.7	61	92 400	378 850	4.1	78	23 000	57 500	2.5	40	16 000	41 600	2.6
$Et(OCH_2CH_2)$–	78	304 200	821 350	2.7	70	308 000	924 000	3.0	90	54 000	102 600	1.9	90	72 000	158 400	2.2
$Et(OCH_2CH_2)_2$–	100	480 000	1 152 000	2.4	95	570 000	1 482 000	2.6	95	190 000	361 000	1.9	92	184 000	386 400	2.1
$Et(OCH_2CH_2)_3$–	87	382 800	1 110 100	2.9	80	416 000	1 331 200	3.2	87	69 600	167 050	2.4	83	81 350	195 200	2.4
$Et(OCH_2CH_2)_6$–	53	212 000	890 400	4.2	45	216 000	950 400	4.4	80	48 250	120 600	2.5	78	62 400	156 000	2.5
$Me(OCH_2CH_2)$–	66	277 200	859 300	3.1	40	160 000	512 000	3.2	90	48 300	111 100	2.3	84	61 900	167 150	2.7
$Bu(OCH_2CH_2)_2$–	100	495 000	1 732 500	3.5	87	539 400	2 211 550	4.1	85	225 250	585 650	2.6	80	163 200	424 300	2.6
$Bu(OCH_2CH_2)_3$–	87	391 500	1 291 950	3.3	62	325 500	1 236 900	3.8	87	76 550	191 400	2.5	70	64 750	148 900	2.3
Furfuryl	100	375 000	1 087 500	2.9	87	346 250	1 108 000	3.2	83	59 350	136 500	2.3	60	48 000	96 000	2.0

[a] Temperature: 45°C, polymerization time: Styrene 1 h, Methyl methacrylate 0.5 h

[b] Measured by g.p.c. in THF at 30°C

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

Solvent of complex base preparation	Yield %	$\bar{M}_n$ [a]	$\bar{M}_w$ [a]	$\bar{M}_w/\bar{M}_n$
–	100	157 400	928 650	5.9
THF	100	121 600	522 900	4.3
DME	100	117 400	493 100	4.2
Diglyme	97	136 100	680 500	5.0
Toluene	75	95 750	450 050	4.7
Benzene	76	90 800	491 250	5.3
Cyclohexane	70	87 650	447 000	5.1

[a] Measured by g.p.c. in THF at 30°C

complex bases prepared in a solvent. The reactions were performed with complex bases $NaNH_2$-Bu^tONa and $NaNH_2$–$Et(OCH_2CH_2)_2ONa$ prepared as described[23–26] in THF, toluene or hexane.

After removal of the solvent under vacuum, yellow powders (called solid complex bases) were left which were moisture—and air—sensitive. Of course, some solvating residual solvent was included in these powders.

When the solvent used for preparation of the initial Complex Base was THF the solid reagent obtained was extremely reactive. Thus addition of melted triphenylmethane to solid $NaNH_2$–Bu^tONa or $NaNH_2$–$Et(OCH_2CH_2)_2ONa$ led to the instantaneous formation of the red triphenyl methyl carbanion. When the solid complex bases were replaced in THF the reactivity of the initial complex bases was recovered, showing that active aggregates were not destroyed during removal of the solvent. On the contrary, solid complex bases obtained from complex bases prepared in benzene or hexane showed a nearly complete loss of reactivity even when replaced in the initial solvent. Interestingly, these solid bases replaced in THF showed a reactivity approaching that of the corresponding complex bases prepared in THF.

Thus it may be concluded that from low polar solvents the active aggregates evolved dramatically when the solvent was removed. The low reactive aggregates obtained in this way may be activated by THF which certainly allows the active aggregates to be partially reformed.

In summary this study showed that some reactive solid complex bases might be simply obtained from current complex bases. From the results described in the preceding paper[22] it might be expected that these new bases would be able to initiate mass polymerizations. We shall see below that this hypothesis was verified.

BULK POLYMERIZATION OF VINYL MONOMERS INITIATED WITH SOLID COMPLEX BASES

Sodamide containing solid complex bases

Some preliminary experiments showed that addition of styrene (265 mM) to the solid complex base $NaNH_2$ (17 mM)–$Et(OCH_2CH_2)_2ONa$ (8.5 mM) obtained from THF led to a temperature increase (about 10°C) and a rapid viscosity increase. Polystyrene was isolated with 93% yield. However the polymerization required a latent period.

Table 3 Polymerization of styrene (88 mM) by complex bases $LiNH_2$ (16.7 mM)–ROLi (8.3 mM) and KNH_2 (16.7 mM)–ROK (8.3 mM)

Amide	$LiNH_2$ [a]								KNH_2 [b]							
Solvent of complex base preparation	THF				–				THF				–			
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]	$\bar{M}_w/\bar{M}_n$
nBu–	15	26 250	141 750	5.4	10	20 500	125 050	6.1	53	30 750	83 000	2.7	50	41 500	141 100	3.4
$tBuCH_2$–	10	18 150	85 300	4.7	5	10 000	78 000	7.8	50	30 150	87 450	2.9	40	33 400	123 600	3.7
iPr–	22	46 200	235 600	5.1	20	49 600	297 600	6.0	55	39 050	136 700	3.5	45	46 150	184 600	4.0
Et_2CH–	15	32 250	170 900	5.3	7	18 200	107 400	5.9	45	33 100	119 150	3.6	45	45 900	201 950	4.4
tBu–	25	62 500	293 750	4.7	20	56 600	294 300	5.2	60	60 900	194 900	3.2	50	60 750	255 150	4.2
nBu_3C–	8	12 000	74 400	6.2	10	20 000	132 000	6.6	40	31 400	109 900	3.5	35	32 550	126 950	3.9
$Et(OCH_2CH_2)$–	35	156 000	577 200	3.7	25	14 000	546 000	3.9	65	78 000	234 000	3.0	70	140 000	490 000	3.5
$Et(OCH_2CH_2)_2$–	40	272 000	925 000	3.5	52	436 800	1 790 900	4.1	80	160 000	464 000	2.9	65	182 000	491 400	2.7
$Et(OCH_2CH_2)_3$–	28	168 000	1 041 600	6.2	30	192 000	1 171 200	6.1	70	105 000	283 500	2.7	60	120 000	396 000	3.3

[a] Temperature 45°C, polymerization time 6 h
[b] Temperature 45°C, polymerization time 30 min
[c] Measured by g.p.c. at 30°C in THF

Table 4 Copolymerization styrene–methyl methacrylate by complex base $NaNH_2$ (17 mM)–$C_2H_5(OCH_2CH_2)_2ONa$ (8.5 mM) prepared in THF at −30°C

	$\bar{M}_n$ (th)	$\bar{M}_n$ [a]
Sequence polystyrene	25 000[b]	25 000
Sequence poly MMA	32 600	19 300
Copolymer	57 600	44 300

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

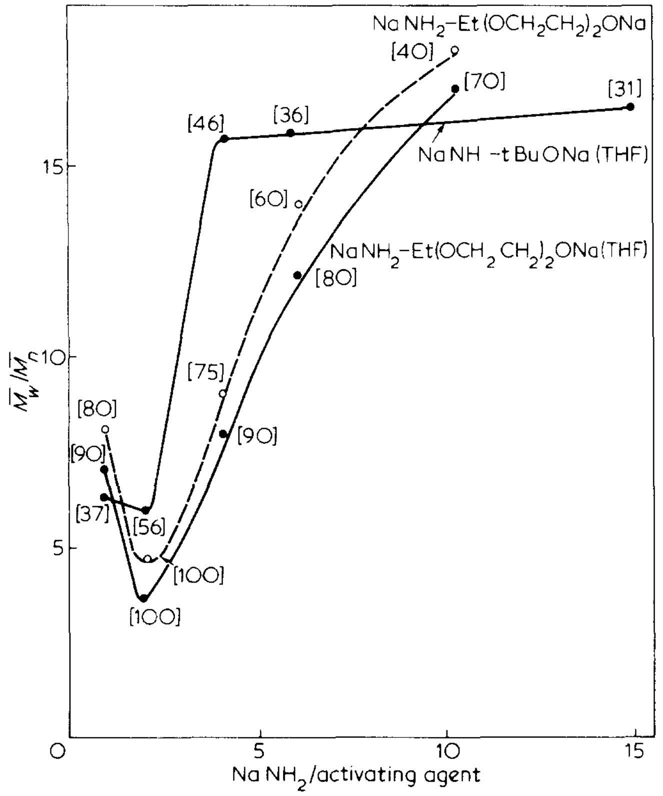

Figure 1 Polymerization of styrene by complex bases: Influence of $NaNH_2$/activating agent ratio [% yield]; (THF) as the solvent of complex base preparations

Interestingly, addition of $Et(OCH_2CH_2)_2OH$ (8.5 mM) to $NaNH_2$ (25.5 mM) without solvent led to a solid reagent also capable of polymerizing styrene. However the latent period was longer than with bases prepared from THF. The interpretation drawn from this is that without a solvent, the reaction between alcohol and sodamide cannot be completed, essentially for mechanical reasons. Addition of monomers increases the fluidity of the reaction medium, and the polymerization can start only when all the alcohol has disappeared.

With these first results in mind we undertook the study of the influence of some parameters on these polymerizations.

Influence of $NaNH_2$/activating agent ratio

In the preceding paper we showed that for polymerizations in solution, the optimum $NaNH_2/RONa$ ratio was found to be two. This value was also found as the best value for the preparation of carbanions as well as for elimination reactions. Here, (see *Figure 1*) it is worth noting that the same value was still found to give the best yields and the lowest molecular weight distribution whether the complex base was prepared in a solvent or not. Note that for a given activating agent, solid complex bases obtained from a complex base prepared in THF led to a lower ratio $\bar{M}_w/\bar{M}_n$ than when the base was prepared without a solvent.

Influence of the nature of the activating agent

From *Table 1* it appears that, broadly speaking, the best activating agents for polymerization in solution[22] were also the best activating agents for polymerizations initiated by solid complex bases, whether the solid bases were prepared in THF or not. The low ratio $\bar{M}_w/\bar{M}_n$ for bulk polymerizations must be emphasized. Moreover, control experiments showed that, for polymerizations in solution, solid complex base behaviours were completely different from the behaviour of their constituents taken separately. Finally bulk polymerization of methacrylonitrile, acrylonitrile and 2-vinyl pyridine with the same solid complex bases led to 60 to 90% yields. $\bar{M}_n$ values varied between 6000 to 100 000 for methacrylonitrile, 1000 to 75 000 for acrylonitrile and 10 000 to 300 000 for 2-vinyl pyridine.

Influence of the solvent used for the preparation of the solid complex bases

As found throughout this work, there were differences between solid complex bases obtained from complex bases prepared with or without a solvent. Therefore we decided to study briefly the influence of the nature of the solvent on the reactivity of the solid complex bases.

The main results obtained with $NaNH_2$–$Et(OCH_2CH_2)_2ONa$ and styrene are reported in *Table 2*. These data deserve some comments. It is clear that the solvent plays a role on the properties of solid bases. This observation supports the presence of some solvation. It is worth noting that solid complex bases prepared from non polar solvents were not able to given the carbanion of triphenyl methane whereas they allowed polymerization initiation. However the difference observed, as well as the larger ratio $\bar{M}_w/\bar{M}_n$ noted with bases prepared without a solvent, cannot be interpreted.

With styrene we briefly examined the possible polymerization with solid complex bases obtained from $LiNH_2$ and KNH_2. From *Table 3* it appears that these bases also initiate bulk polymerizations. Comparison with data of *Table 1* shows that, as expected from our results in solution, bases obtained from $LiNH_2$ were not very reactive. On the contrary, bases obtained from KNH_2 were comparable to bases obtained from $NaNH_2$. There appears no regular variation law as a function of the nature of the cation and in any case there are too many independent parameters to obtain good interpretation of the results observed.

Nature of the polymer formed

As for polymerizations performed in solution, we decided to determine whether the polymers were living or not with spectroscopic studies precluded. However, from *Figure 2* where $\bar{DP}_n$ *versus* monomer concentrations are reported, it might be concluded from the first part of the curves obtained that the polymers were living. This conclusion was confirmed by copolymerization experiments reported in *Table 4*.

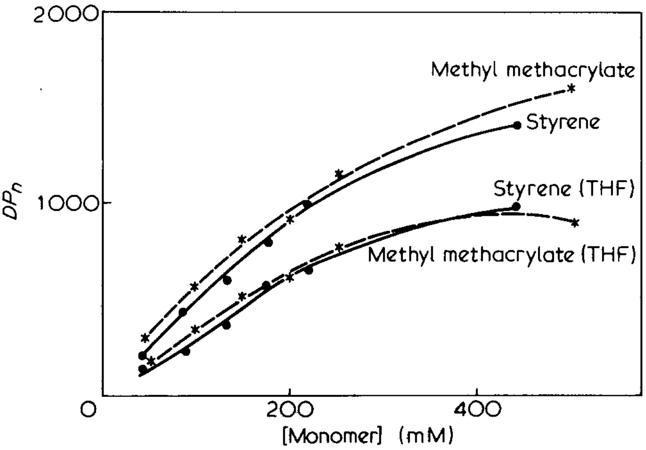

Figure 2 Polymerization of styrene and methyl methacrylate by complex base $NaNH_2$–$Et(OCH_2CH_2)_2ONa$. Influence of monomer concentration with (THF) as the solvent of complex base preparations

CONCLUSIONS

The conclusion of this work is that it is possible to obtain new bases able to initiate anionic bulk polymerization either from complex bases or directly by reaction between an alkali amide and an alcohol. These new initiators are of low cost, lead to living polymers and, as in solution, allow obtaining different results according to the nature of the reactants included in them.

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REFERENCES

1 Magat, M. *Polymer* 1962, **3**, 449
2 Kohlschutter, H. W. and Sprenger, L. *Z. Physik. Chem.* 1932, **16**, 282
3 Letort, M. *Compt. Rend.* 1936, **202**, 767
4 Travers, W. M. *Trans. Faraday Soc.* 1936, **82**, 246
5 Letort, M. and Petry, J. *J. Compt. Rend.* 1950, **231**, 519
6 Letort, M. and Richard, A. J. *J. Chim. Phys.* 1960, **57**, 752
7 Schmitz, J. V. and Larnton, E. J. *Science* 1951, **113**, 718
8 Mesrobian, R. B., Ander, P., Ballantine, D. S., Dienes, G. J. and Metz, D. J. *J. Am. Chem. Soc.* 1956, **78**, 2939
9 Hayashi, K. and Okamura, S. *Proc. Internat. Sympos.* Radiation Induced Polymerization and Graft Copolymerization, Rapport AEC, TID 1962, 7643
10 Schulz, R., Renner, G., Henglein, A. and Kern, W. *Makromol. Chem.* 1954, **12**, 20
11 Andreeva, I. V. and Koton, M. *Izv. Akad. Nauk. SSSR Otdel. Khim. Nauk.* 1959, 552
12 Okamura, S., Higashimura, T. and Takeda, K. *Makromol. Chem.* 1962, **51**, 217
13 Bamford, C. H., Jenkins, A. D. and Ward, J. C. *J. Polym. Sci.* 1960, **48**, 37
14 Bamford, C. H., Eastmond, G. C. and Ward, J. C. *Proc. Roy. Soc. (London)* 1963, **271**, 357
15 Morawetz, H. *Proc. Internat. Sympos.* Radiation Induced Polymerization and Graft Copolymerization, Rapport AEC, TID, 1962, 7643
16 Jakabhazy, S. Z., Morawetz, H. and Morosoff, N. *J. Polym. Sci.* 1965, **4**, 805
17 Kargin, V. A., Kabanov, V. A. and Zubov, V. P. *Vysokomol. Soedin* 1959, **1**, 265
18 Kabanov, V. A., Sergeev, G. B., Zubov, V. P. and Kargin, V. A. *Vysokomol. Soedin* 1959, **1**, 1859
19 Muller, D. *JEPO 3*, Le Mans, 1974
20 Sekiguchi, H., Tsourkas, P. and Coutin, B. *Makromol. Chem.* 1977, **178**, 2135
21 Szwarc, M. 'Carbanions Living Polymers and Electron-Transfer Processes', Interscience, 1968
22 Ndebeka, G., Caubère, P., Raynal, S. and Lecolier, S. *Polymer* in press
23 Coudert, G. *Thesis*, Nancy, 1974
24 Ndebeka, G. *Thesis*, Nancy 1979
25 Caubère, P. *Acc. Chem. Res.* 1974, **7**, 301
26 Caubère, P. Topics in Current Chemistry, 1978, **73**, 50