Complex bases: 12. Application to the anionic polymerization of diene monomers

S. Raynal and S. Lecolier
Centre de Recherches du Bouchet, Société Nationale des Poudres et Explosifs, 91710 *Vert le Petit, France*

G. Ndebeka and P. Caubère*
Laboratoire de Chimie Organique I, ERA CNRS No. 476, *Université de Nancy I, Case Officielle* 140, 54037 *Nancy Cédex, France*
(*Received* 9 *December* 1980)

Complex bases and solid complex bases MNH_2–ROM (M = Li, Na, K) are able to initiate the anionic oligomerization of diene monomers. Although activation of alkali amide by alkali alkoxide was apparent in these reactions, variation of the alkoxides did not influence the microstructure of the oligomers.

INTRODUCTION

Compared with vinyl monomers, dienes possess the interesting property that polymerization can follow several pathways, 1,4-, 1,2- and 3,4- additions, being possible.

The properties of the polymer strongly depend on the nature of the reactions undertaken[1-8]. Attempts have been made to devise conditions under which definite mixtures of the possible products (or one of them) can be obtained. Among these, anionic polymerizations have proved versatile. Indeed, variation of the nature of the anionic initiator[3,8] and of the solvent[1-3] lead to variations in the relative proportions of the possible polyadditions. For example, polymerization of butadiene or isoprene by lithium or organolithium reagents in hydrocarbon solvents led essentially to 1,4 products[1,2]. However, in polar media, 1,2 and 3,4 were the principal products.

We have shown that the complex bases and solid complex bases are good new anionic initiators for performing polymerization of vinyl monomers[9-12]. Interesting results might also be obtained with diene monomers, and here we report results obtained with these monomers.

EXPERIMENTAL

Materials

Reagent grade butadiene (99.9%) was used without further purifications. Isoprene (Aldrich Chemical Company) was distilled over calcium hydride under argon. The purification of solvents and complex base preparations were described in our previous papers[11,12].

Polymerization procedure

The polymerizations were carried out under argon in the same reactor used for the preparation of complex bases. After standing at the polymerization temperature, isoprene was introduced with stirring using a hypodermic syringe. The polymerization was terminated by the addition of a small amount of methanol and the polymer was precipitated by pouring the reaction mixture into a large excess of methanol. With butadiene, a tube (a high pressure-glass reactor of 100 ml capacity) was used. The tube was sealed under vacuum and placed in an oil bath. The polymer was precipitated under the same conditions as those used for isoprene. The operative conditions for the experiment are reported in *Tables 1* and *4*.

Analytical data

Molecular weight measurements were obtained on a Machrolab Vapor Phase Osmometer using toluene as solvent.

Polybutadiene and polyisoprene structures were determined by ^1H n.m.r. measurements on 10–20% polymer solutions in carbon tetrachloride with a Perkin–Elmer spectrometer (R 12). Structural assignments were made using the Tanaka method[18] for polybutadiene and the Pham method[19] for polyisoprene.

RESULTS AND DISCUSSION

We simultaneously considered polymerization in solution by complex bases (CB)[11] as well as bulk polymerization by solid complex bases (SCB)[12] of butadiene and isoprene. Considering the results obtained in the previous publications, we chose to use a ratio $MNH_2/ROM = 2$. Control experiments, not reported here, showed that none of the amides or the alkoxides, except KNH_2, were able to initiate the polymerizations of the dienes.

The results obtained with $NaNH_2$ and KNH_2 containing complex bases are summarized in *Tables 1* and *2* and merit some comment. First, a large quantity of activating agent has been shown to lead to active CB and SCB in the polymerizations of vinyl monomers. With dienes, the only activating agents leading to acceptable results are those given in the Tables. Interestingly, these are also the best activating agents for polymerization of

---

* To whom correspondance should be addressed

0032-3861/81/101425-03$02.00

Table 1 Polymerization of isoprene (100 mM) by complex bases MNH_2 (16.7 mM)–ROM (8.3 mM) for 6 h

Solvent (ml)	THF (15)^a				$PhCH_3$ (15)^a				None^b			
Amide	$NaNH_2$		KNH_2		$NaNH_2$		KNH_2		$NaNH_2$		KNH_2	
Activating agent R–	Yield (%)	$\bar{M}_n{}^c$	Yield (%)	$\bar{M}_n{}^c$	Yield (%)	$\bar{M}_n{}^c$	Yield (%)	$\bar{M}_n{}^c$	Yield (%)	$\bar{M}_n{}^c$	Yield (%)	$\bar{M}_n{}^c$
none	0	–	40	1000	0	–	5	800	0	–	8	700
$CH_2{=}CH{-}CH_2{-}$	25	1000	43	1600	30	1500	75	3400	25	8800	55	4000
iPr–	25	1400	51	2700	28	1600	50	2450	20	2500	50	3000
tBu–	28	1200	46	1750	32	1250	59	2050	30	5000	40	2500
$EtOCH_2CH_2{-}$	30	900	49	1450	30	1050	63	1900	30	5400	60	3600
$Et(OCH_2CH_2)_2{-}$	40	2000	35	1600	34	2000	84	4600	52	14560	75	7500
$Et(OCH_2CH_2)_3{-}$	36	1600	43	1500	35	1750	80	3750	45	9000	65	3900
$Et(OCH_2CH_2)_6{-}$	30	1200	35	1200	30	1350	70	2400	35	6300	60	2950
$MeOCH_2CH_2{-}$	30	1350	30	1100	25	750	60	3200	35	5250	50	2000
$Bu(OCH_2CH_2)_2{-}$	27	1600	40	1450	20	1200	75	4100	30	9400	60	6950
$Bu(OCH_2CH_2)_3{-}$	30	1500	28	1200	25	1200	60	3500	35	7950	70	4750
Furfuryl–	40	1400	30	1900	20	1400	65	4100	30	9100	50	6300

[a] Temperature, 35°C;
[b] Temperature, 40°C;
[c] Measured by v.p.o. at 37°C in toluene

Table 2 Polymerization of butadiene (100 mM) by complex bases MNH_2 (16.7 mM)–ROM (8.3 mM) at 35°C for 3 h

Solvent (ml)	THF (20)				$PhCH_3$ (20)				–			
Amide	$NaNH_2$		KNH_2		$NaNH_2$		KNH_2		$NaNH_2$		KNH_2	
Activating agent R–	Yield (%)	$\bar{M}_n{}^a$	Yield (%)	$\bar{M}_n{}^a$	Yield (%)	$\bar{M}_n{}^a$	Yield (%)	$\bar{M}_n{}^a$	Yield (%)	$\bar{M}_n{}^a$	Yield (%)	$\bar{M}_n{}^a$
None	0	–	20	900	0	–	10	1100	0	–	0	–
$CH_2{=}CH{-}CH_2{-}$	45	1150	40	1500	35	1500	70	2750	30	4100	65	5250
iPr–	60	1500	50	1700	30	1800	75	3100	20	3950	40	4300
tBu–	65	1950	60	2100	35	2000	65	2500	25	5000	35	2950
$EtOCH_2CH_2{-}$	60	1200	65	1800	30	1000	70	3250	40	4700	60	5200
$Et(OCH_2CH_2)_2{-}$	80	2500	85	3700	45	2000	85	4900	65	20000	80	15000
$Et(OCH_2CH_2)_3{-}$	40	1200	50	2900	40	1600	70	3500	30	13000	60	10200
$Et(OCH_2CH_2)_6{-}$	40	800	50	1500	35	900	60	3400	45	7400	50	5400
$MeOCH_2CH_2{-}$	50	1000	60	1700	40	1400	55	2750	50	4500	40	7100
$Bu(OCH_2CH_2)_2{-}$	40	1450	70	2000	42	2000	65	3100	60	15300	55	12300
$Bu(OCH_2CH_2)_3{-}$	50	1500	35	1450	35	1600	60	2100	20	7100	35	4000
Furfuryl–	60	1000	40	1850	39	1800	55	1500	30	8200	30	6000

[a] Measured by v.p.o. at 37°C in toluene

vinyl monomers. The rates and yields of diene polymerizations were lower than those found for vinyl monomers and only oligomers could be obtained even in bulk polymerization.

The rather low weights obtained with butadiene may be explained as follows. We established[11,12] that polymerizations were initiated by the NH_2 part of the CB or SCB. Thus the oligomers formed contain the NH_2 group, and it is well established[13] that such a group leads to transfer reactions which terminate the propagation reactions.

With isoprene, the reactions are more complicated. The i.r. and ^1H n.m.r. spectra of the oligomers showed low NH_2 group absorption. It must be concluded that initiation of the polymerization was due mainly to the allylic carbanion formed by abstraction of the proton of the methyl group of the isoprene molecule.

Finally, when experiments were conducted in toluene, in some cases (polymerization of isoprene by KNH_2–ROK) we noted the presence of an aromatic ring in the oligomers. It may be concluded that benzylic anions were formed in these reactions, and acted, at least partly, as initiator. Under the same conditions, but using benzene as solvent, aromatic insertion was not observed. Experiments conducted under the same conditions with $LiNH_2$ led to lower yields and the corresponding results are not reported here.

Another interesting point was the structure of the oligomers. It is expected that ratio of 1,4, 1,2 and possibly 3,4 addition pathways vary with the nature of the activating agent. The structures of the oligomers were determined from ^1H n.m.r. spectra (see Experimental) and the results obtained have been briefly summarized in *Table 3*.

From these data it appears that for a given cation, the nature of the activating agent does not influence the structure of the oligomer. The nature of the cation has a more important influence: curiously[3], the 1,4 addition pathway decreases when the cation radius increases, but this phenomenon is still obscure.

The following observations can be made: KNH_2 initiates the oligomerization, but none of the ROK give this reaction. The structures of the oligomers obtained from KNH_2 and KNH_2–ROK being different, it is clear that, as expected, ROK plays an important role during the polymerization.

Table 3 Structure of polybutadiene and polyisoprene

Polymer	Polybutadiene						Polyisoprene								
Solvent	THF		$PhCH_3$		None		THF			$PhCH_3$			None		
Initiator	1,4	1,2	1,4	1,2	1,4	1,2	1,4	1,2	3,4	1,4	1,2	3,4	1,4	1,2	3,4
$LiNH_2$–ROLi[a]	70	30	75	25	80	20	75	5	20	75	5	20	80	5	15
$NaNH_2$–RONa[a]	60	40	65	35	65	35	50	15	35	55	15	30	60	15	25
KNH_2	75	25	70	30	–	–	80	5	15	65	15	20	60	15	25
KNH_2–ROK[a]	50	50	50	50	50	50	50	15	35	50	15	35	55	15	30

[a] Experiments were performed with all the activating agents given in *Tables 1* and *2*

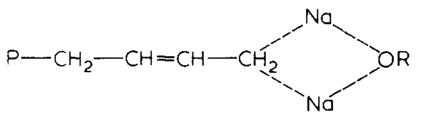
The role taken by the alkoxides with $LiNH_2$ and $NaNH_2$ appears clear since neither amides nor the corresponding alkoxides were able to initiate the oligomerizations.

Finally we established that during the polymerizations of vinyl monomers, the alkoxides form complexes with the carbanion from which the polymerizations propagated. Such complexations have been shown by Cheng[14–17] for the polymerization of butadiene initiated by Na or RNa associated with a sodium alkoxide.

Moreover with CB $NaNH_2$–RONa the oligomers obtained are different from those obtained with R–Na in the same solvent[1–3] but they resemble the oligomer obtained by Cheng.

Thus, alkoxides influence the initiation and the propagation rates but do not influence the nature of the oligomers formed, although they must be complexed with the living carbanion.

This apparent contradiction may be reconciled by the following hypothesis. The aggregates formed in CB or SCB promote the reactivity of $LiNH_2$ and $NaNH_2$ and modulate the reactivity of KNH_2 in the initiating step. During the propagation step, the alkoxides, by complexation of the cations (scheme), maintain a sufficient electron density to propagate the polymerization but they are too far from the active site to have enough steric influence on the pathway of the polymerizations.



CONCLUSION

Aggregate complex bases and solid complex bases promote the reactivity of $LiNH_2$ and $NaNH_2$ allowing the initiation of oligomerization of butadiene and isoprene by these amides. Good results are obtainable only with $NaNH_2$ activated by the best activating agents, as shown in the vinyl polymerization study[11,12]. The presence of ROK with KNH_2 changes the properties of this amide, thus leading to oligomers different from those which may be obtained when potassium amide is used alone.

ACKNOWLEDGEMENTS

We thank Mrs Roques (Université de Nancy I) for fruitful discussions and the SNPE for financial support.

REFERENCES

1 Stavely, F. W. *Ind. Eng. Chem.* 1956, **48**, 778
2 Kuntiz, I. *Polym. Sci. (Polym. Chem. Edn.)* 1962, p. 2827
3 Bywater, S. and Worsfold, D. J. *Can. J. Chem.* 1967, **45**, 1821
4 Schue, F., Worsfold, D. J. and Bywater, S. *J. Polym. Sci. (Polym. Lett. Edn.)* 1969, **7**, 821
5 Schue, F., Worsfold, D. J. and Bywater, S. *Macromolecules* 1970, **3**, 509
6 Sledz, J., Kaempf, B. and Schue, F. *Makromol. Chem.* 1975, **176**, 459
7 Bywater, S., Worsfold, D. J. and Hollingsworth, G. *Macromolecules* 1972, **5**, 389
8 Alev, S., Collet, A., Vignier, M. and Schue, F. *J. Polym. Sci.* 1980, **18**, 1163
9 Coudert, G., Ndebeka, G., Caubere, P., Raynal, S., Lecolier, S. and Boileau, S. *J. Polym. Sci. (Polym. Lett. Edn.)* 1978, **16**, 413
10 Raynal, S., Lecolier, S., Ndebeka, G. and Caubere, P. *J. Polym. Sci. (Polym. Lett. Edn.)* 1980, **18**, 13
11 Ndebeka, G., Caubere, P., Raynal, S. and Lecolier, S. *Polymer* 1981, **22**, 347
12 Raynal, S., Lecolier, S., Ndebeka, G. and Caubere, P. *Polymer*, 1981, **22**, 356
13 French, D. M. *Rubber Chem. Technol.* 1969, **42**, 90
14 Cheng, T. C., Halasa, A. F. and Tate, D. T. *J. Polym. Sci.* 1971, **9**, 2493
15 Cheng, T. C., Halasa, A. F. and Tate, D. T. *J. Polym. Sci.* 1973, **11**, 253
16 Cheng, T. C. and Halasa, A. F. *J. Polym. Sci.* 1976, **14**, 573
17 Halasa, A. F., Cheng, T. C. and Hall, J. E. *J. Polym. Sci.* 1979, **17**, 1771
18 Tanaka, Y., Takenchi, Y. and Lobayashi, M. *J. Polym. Sci.* 1971, **9**, 42
19 Pham, Q. T. *J. Polym. Sci.* 1970, **8**, 723