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THE IONIC CHARACTER OF ORGANOLITHIUM COMPOUNDS IN THE PRESENCE OF LITHIUM METHOXYETHOXIDE: "COORDINATION-AGENT-SEPARATED" ION PAIRS

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SUMMARY

Small amounts of the lithium salts of methoxyethanol or 2-(dimethylamino)-ethanol have been found to have an enormous effect on the ionic character of alkyl-(or aryl-)lithium. Measurements of the electronic spectra of 1,1-diphenyl-n-hexyllithium coupled with these additives have indicated that the organolithium system possesses a species with the composition $RLi\cdot 2XCH_2CH_2OLi$ [where $X=CH_3O$ or $(CH_3)_2N$]. No peak assignable to such a contact ion pair was observed in the 9-fluorenyllithium–$CH_3OCH_2CH_2OLi$ system at a one to two mole ratio, the only peak observed here being in accordance with that expected for the solvent-separated ion pair. The term "coordination-agent-separated" ion pair is proposed to distinguish such species from "solvent-separated" ion pairs.

INTRODUCTION

In the course of studies on the copolymerization of styrene and 1,3-butadiene by n-butyllithium–poly(propylene oxide) catalyst system, a series of new catalyst systems has been found which produce copolymers containing more styrene units than the initial feed monomer ratios[1]. In the n-butyllithium–poly(ethylene oxide) catalyst system one of the active species was found to be composed of alkyl- (or aryl-)lithium and $ROCH_2CH_2OLi$[2]. The partial results of these copolymerization reactions are given in Table 1.

The analytical data relating to the n-butyllithium–$(CH_3)_2NCH_2CH_2OLi$ system indicate that the active species of this catalyst system consists of RLi ($R=$ $n\text{-}C_4H_9$ or $C_6H_5CH_2$) and $(CH_3)_2NCH_2CH_2OLi$ in a one to two mole ratio. The composition of the active species may also be arrived at from a study of the catalytic behavior of the binary system, $RLi–XCH_2CH_2OLi$ [$X=CH_3O$ or $(CH_3)_2N$], during styrene–butadiene copolymerization.

The increased reactivity of styrene during the copolymerization reaction is presumably related to the change in ionic character of RLi on complexing with CH_3-OCH_2CH_2OLi or $(CH_3)_2NCH_2CH_2OLi$. This paper deals with the effect of CH_3-OCH_2CH_2OLi and $(CH_3)_2NCH_2CH_2OLi$ upon the ionic character of 1,1-diphenyl-n-hexyllithium and 9-fluorenyllithium, and describes the use of electronic spectra to

TABLE I[2,3]

THE COPOLYMERIZATION OF STYRENE AND BUTADIENE IN CYCLOHEXANE IN THE PRESENCE OF THE n-C_4H_9Li–XCH_2CH_2OLi SYSTEM[a]

X	[OLi]/[CLi]	Conversion (mole%)	Styrene content in copolymer (mole%)
CH_3O	0	46.2	7.7
	0.5	52.9	9.8
	1.0	40.3	33.6
	2.0	39.6	69.6
$(CH_3)_2N$	0.5	31.1	13.5
	1.0	52.6	14.2
	2.0	35.1	54.7
	3.0	39.1	47.7

[a] Styrene/butadiene in feed 30/70. Polymerization temperature, 40°.

allow an explanation for the increased reactivity of styrene in the copolymerization reaction mentioned above.

RESULTS

Electronic spectra of the 1,1-diphenyl-n-hexyllithium–XCH_2CH_2OLi system

Waack and Doran have reported that the absorption maxima of 1,1-diphenyl-n-hexyllithium (DPHLi) solutions shifted in accordance with the polarity of solvents used[4,5], with large bathochromic shifts being noticeable in tetrahydrofuran (THF) and 1,2-dimethoxyethane (DME).

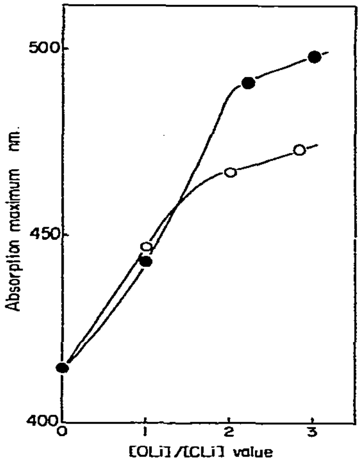
The electronic spectra of DPHLi–XCH_2CH_2OLi system were measured in an attempt to provide information on the "polarity" of XCH_2CH_2OLi through the application of the known relation between the shift in the absorption maximum and the solvent polarity.

The results obtained with cyclohexane as a solvent are shown in Fig. 1. With the $CH_3OCH_2CH_2OLi$ system, a considerable bathochromic shift in the absorption maximum is observed until the [OLi]/[CLi] value reaches 2.0; above this value the extent of this shift is not so pronounced. The absorption maxima for [OLi]/[CLi] = 2.0 and 3.0 are very close to the maxima observed in THF (496 nm). It should be noted that the concentration of polar compounds present in this system is extremely small in comparison to that when THF is present as a solvent.

The curve for the $(CH_3)_2NCH_2CH_2OLi$ system also possesses an inflection point at [OLi]/[CLi] = 2.0, although in this case the bathochromic shift is not so pronounced as that observed in the $CH_3OCH_2CH_2OLi$ system. This result is in agreement with the observation that the coordination ability of the ether-oxygen in $CH_3OCH_2CH_2OLi$ is greater than that of the amino-nitrogen in $(CH_3)_2NCH_2CH_2OLi$.

Electronic spectra of the 9-fluorenyllithium–$CH_3OCH_2CH_2OLi$ system

Smid and coworkers have reported that 9-fluorenyllithium (FlLi) in THF exhibits an absorption maximum at 349 and 373 nm, these being assigned as those for contact (or intimate) ion pairs and solvent-separated ion pairs, respectively[6-9]. The fraction of each type of ion pair present in the system was also determined. The absorption peak corresponding to the free ion could not be detected because of its low concentration. Information regarding the nature of the ion pairs involved in the FlLi–$CH_3OCH_2CH_2OLi$ system may be obtained by measuring the electronic spectra of the fluorenyllithium system. This was undertaken in THF since the fluorenyllithium system is insoluble in dioxane in which no solvent-separated ion pair should be observable. The results obtained are shown in Fig. 2.



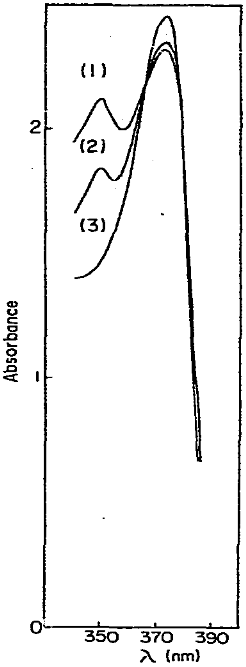


Fig. 1. The variation in the absorption maximum in the electronic spectrum of 1,1-diphenyl-n-hexyllithium in the presence of XCH_2CH_2OLi. ● $CH_3OCH_2CH_2OLi$ system, ○ $(CH_3)_2NCH_2CH_2OLi$ system; [DPHLi] 10^{-2} *M*.

Fig. 2. The electronic spectrum of 9-fluorenyllithium in THF in the presence of $CH_3OCH_2CH_2OLi$. [OLi]/[CLi] value: (1) 0 (2) 1.0 (3) 2.0; [FlLi] 6×10^{-3} *M*.

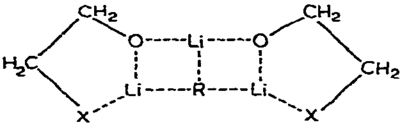
When no additive other than fluorenyllithium is present in THF two absorption peaks are observed at 349 and 373 nm, as reported by Smid *et al.* With the FlLi–$CH_3OCH_2CH_2OLi$ system, the intensity of the peak assignable to the contact ion pair, 349 nm, decreases with increasing concentration of the additive. Contact ion pairs are almost completely absent in the binary system which contains double the molar quantity of the additive compound, $CH_3OCH_2CH_2OLi$, in combination with FlLi.

DISCUSSION

In a preceding paper[3] the composition of the chemical species which is responsible for the unique behavior of the active species was assumed to the $RLi \cdot 2XCH_2CH_2OLi$ [$X = CH_3O$, $(CH_3)_2N$]. The results quoted in Figs. 1 and 2 apparently strongly support the above assumption. The spectra of both DPHLi systems in Fig. 1 possess inflection points at $[OLi]/[CLi] = 2.0$, the bathochromic shift being less pronounced above this value. From Fig. 2 it is also seen that the peak assignable to the contact ion pair has virtually disappeared in the one to two $FlLi-CH_3OCH_2CH_2OLi$ system. In agreement with this observation, the yield of 1,1-diphenylpentene in the reaction between diphenylmethane and butadiene has recently been found to increase markedly when a $n\text{-}C_4H_9Li-CH_3OCH_2CH_2OLi$ catalyst system was used at a one to two mole ratio[10].

According to Smid contact ion pair formation is still observable after the addition of as much as a 17-fold excess of tri(ethylene glycol) dimethyl ether to FlLi in dioxane. In the $CH_3OCH_2CH_2OLi$ system, on the other hand, only twice as many moles of $CH_3OCH_2CH_2OLi$ to FlLi is required to convert the contact ion pair completely into the "solvent-separated" ion pair. This type of ion pairs may preferably be referred to as "coordination-agent-separated" ion pairs in order to distinguish them from solvent-separated ion pairs. "Coordination-agent-separated" ion pairs may be considered as producing local polar conditions in the vicinity of organolithium species even in non-polar solvents, this being the reason for the unique behavior of the lithium catalyst in styrene–butadiene copolymerizations.

Although the structure of $RLi-XCH_2CH_2OLi$ system has not been clearly elucidated, we wish to propose the structure shown below from the basis of NMR data[3], electronic spectra and compositional analysis:



EXPERIMENTAL

Most of the experiments were carried out in a purified nitrogen atmosphere in order to exclude oxygen and atmospheric moisture.

The 1,1-diphenyl-n-hexyllithium–XCH_2CH_2OLi system was prepared from stoichiometric amounts of 1,1-diphenylethylene, XCH_2CH_2OH and $n\text{-}C_4H_9Li$ in cyclohexane at room temperature[2]. The 9-fluorenyllithium–$CH_3OCH_2CH_2OLi$ system was prepared from fluorene, ethylene glycol monomethyl ether and $n\text{-}C_4H_9Li$ in THF at room temperature[2,7].

1,1-Diphenylethylene was synthesized by the usual method[11], $n\text{-}C_4H_9Li$ was prepared from $n\text{-}C_4H_9Cl$ and Li metal in purified petroleum ether, and fluorene was recrystallized from ethanol. Ethylene glycol monomethyl ether and 2-(dimethylamino)ethanol were refluxed over CaH_2 and distilled, while cyclohexane and THF were carefully purified by the usual method.

The electronic spectra were recorded by means of a Shimadzu Multipurpose Recording Photoelectric Spectrometer, Type MPS-50L, using 0.1-cm quartz cell.

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REFERENCES

1 T. Narita, N. Imai and T. Tsuruta, *Kogyo Kagaku Zasshi (J. Chem. Soc. Jap., Ind. Chem. Sect.)*, 72 (1969) 994.
2 T. Narita, A. Masaki and T. Tsuruta, *J. Macromol. Sci., Chem.*, 4 (1970) 277.
3 T. Narita, M. Kazato and T. Tsuruta, *J. Macromol. Sci., Chem.*, 4 (1970) 885.
4 R. Waack and M. A. Doran, *J. Phys. Chem.*, 67 (1963) 148.
5 R. Waack and M. A. Doran, *J. Amer. Chem. Soc.*, 88 (1966) 2109.
6 T. H. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 87 (1965) 669.
7 T. H. Hogen-Esch and J. Smid, *J. Amer. Chem. Soc.*, 88 (1966) 307.
8 L. L. Chan and J. Smid, *J. Amer. Chem. Soc.*, 89 (1967) 4547.
9 L. L. Chan and J. Smid, *J. Amer. Chem. Soc.*, 90 (1968) 4654.
10 T. Yamaguchi, T. Narita and T. Tsuruta, to be published.
11 H. Gilman (Ed.), *Organic Syntheses, Coll. Vol. 1*, Wiley, New York, 1941, p. 226.