Effect of Samarium Iodide on Isocyanate-Polymerization by Alkyllithiums

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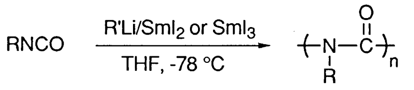
An addition of samarium iodide (SmI_2 or SmI_3) drastically suppressed the trimerization of isocyanates during the polymerization with alkyllithiums, providing the polymer with high molecular weight in good yield.

In these two decades, much attention has been paid to lanthanide salts-promoted reactions because of their superior selectivity and efficiency to the traditional synthetic methods.[1] Especially, organolanthanides prepared by the reaction of lanthanide halides with alkyllithiums or Grignard reagents have been established as excellent alkylation agents of carbonyl compounds.[1a,2] In spite of a numerous number of synthetic applications of these reagents in the field of organic chemistry, their use in polymer synthesis has been quite limited. In this paper, we demonstrate a new polymerization system of isocyanates by using organosamariums prepared by the reaction of samarium (II) or (III) iodide in which back biting reaction was dramatically suppressed to give high molecular weight polymers.[3]



The anionic polymerization of isocyanates with alkyllithium in toluene is reported to give poly(1-nylon) only in a low yield.[4] Especially, the use of polar solvents such as THF led to a low conversion of monomers. Indeed, the polymerization of butyl isocyanate (BuNCO) by BuLi in THF at -78 °C for 7 h led to the quantitative production of the cyclic trimer which was formed by the back biting reaction (Run 1, Table 1).[5] On the other hand, the polymerization of BuNCO with BuLi in the presence of SmI_2 resulted in the rapid increase in the viscosity of the system, indicating the formation of the polymer (Run 3).[6] It should be noted that the formation of the cyclic trimer was restrained and that the high molecular weight polymer was obtained in good yield. Reaction run in the absence of BuLi gave only a trace yield of the polymer (Run 2), meaning that both SmI_2 and *n*-BuLi are essential for this polymerization system in order to obtain the polymer. The use of SmI_3 was also effective whereas other lanthanide halides such as $SmCl_3$, CeI_3 YbI_2, $LaCl_3$, and $NdCl_3$ exhibited extremely poor effect on the BuNCO-polymerization (Runs 4 - 8).

Both the molecular weights and the yields of the polymers were greatly dependent on the molar ratio of BuLi to SmI_2 (Table 2); the highest values were obtained when the ratio (SmI_2:BuLi) was 1:1 or 1:2. This result excludes the possibility that SmI_2 serves only as a Lewis acid. The polymerization produced only the cyclic trimer when the ratio of SmI_2 to BuLi was above 1:3, which might be due to the faster polymerization and sequential back biting induced by BuLi than the polymerization promoted by the organosamarium.

Imamoto has reported that organocerium(III) can be generated by the transmetalation of cerium(III) halides with alkyllithiums and demonstrated their nucleophilic addition reactions with carbonyl compounds.[1a,2] Considering their results, an organosamarium with the structure of $RSmI_2Li$ or R_2Sm seems to be generated by the reaction of alkyllithium with SmI_2 and works as an initiator.[7] ^1H NMR analysis of the oligomer formed by the reaction of BuNCO with a small excess of methyllithium revealed the origin of methyl group (Scheme 1); *ie*, the methyl group of **1** contributes to the initiation reaction. In other words, the initiation reaction involves the attack of alkyl group of the organosamarium toward the carbonyl carbon of isocyanate.

Table 1. Effect of lanthanide salts on the polymerization of BuNCO by BuLi [a]

Run	LnX_n	BuNCO : LnX_2	Yield (%)[b]	$\overline{M}_n$ (MWD)[c]	Yield of MeOH-soluble part (%)[d]		
					trimer	urethane[e]	urea[f]
1	—	53.7 : 1	0	——	100	0	0
2[g]	SmI_2	54.8 : 1	8	24000 (1.95)	0	91	0
3	SmI_2	56.0 : 1	70	57500 (2.90)	3	24	3
4	$SmCl_3$	50.0 : 1	0	——	100	0	0
5	CeI_3	52.6 : 1	0	——	——	——	——
6	YbI_2	59.8 : 1	3	17600 (1.45)	——	——	——
7	$LaCl_3$	60.2 : 1	6	44800 (6.34)	——	——	——
8	$NdCl_3$	58.8 : 1	1	31100 (8.62)	——	——	——
9	SmI_3	57.1 : 1	32	68700 (4.52)	——	——	——

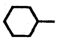
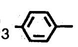
[a] BuLi:LnX_n = 1:1 [b] MeOH-insoluble part. [c] Estimated by GPC($CHCl_3$, PSt standards). [d] Determined by GC. [e] Resulted by the reaction of the unreacted BuNCO with MeOH. [f] Resulted by the reaction of BuNCO with H_2O. [g] Without BuLi.

Table 2. Influence of the ratio of SmI_2 to BuLi on the polymerization of BuNCO

Run	SmI_2 : BuLi	BuNCO : SmI_2	Yield (%)^a	$\overline{M}_n$ (MWD)^b
1	1 : 0.25	52.2 : 1	19	39600 (2.04)
2	1 : 0.5	57.1 : 1	40	55800 (2.39)
3	1 : 1	56.0 : 1	70	57500 (2.90)
4	1 : 2	56.6 : 1	75	70200 (2.84)
5	1 : 3	57.6 : 1	0	——
6	1 : 4	52.8 : 1	0	——

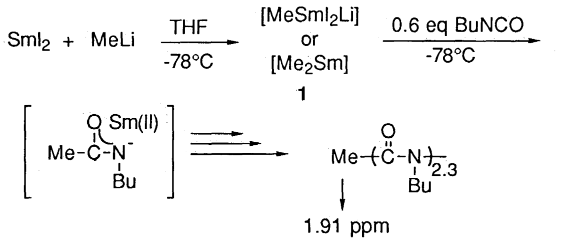
^{a} MeOH-insoluble part. ^{b} Estimated by GPC($CHCl_3$, PSt standards).

Table 3. Polymerization of other isocyanates by the SmI_2/BuLi system

Run	R	SmI_2 : BuLi	Yield (%)^a	$\overline{M}_n$ (MWD)^b
1	*n*-Oct.	1 : 1	42	84900 (3.42)
2		1 : 2	71	77200 (3.47)
3		1 : 1	0	—
4		1 : 2	0	—
5	CH_3-	1 : 1	20	10600 (1.12)
6		1 : 2	24	18700 (1.26)

^{a} MeOH-insoluble part. ^{b} Estimated by GPC ($CHCl_3$, PSt standards).

Scheme 1.



The present system is available for the polymerization of primary alkyl isocyanates (Table 3). For example, the polymerization of *n*-octyl isocyanate gave the high molecular weight polymer in good yield when the ratio of SmI_2 to BuLi was 1:2. In the cases of *p*-tolyl isocyanate and cyclohexyl isocyanate, satisfactory yield was not obtained similarly to the conventional isocyanate-polymerizations.

In summary, we have demonstrated a dramatic effect of the addition of SmI_2 or SmI_3 on isocyanate-polymerization by BuLi to suppress the formation of cyclic trimer. The simple procedure of the present polymerization system would provide a new method for preparing poly(1-nylon)s.

References and Notes

1 For recent reviews, a) G. A. Molander and C. R. Harris, *Chem. Rev.*, **96**, 307 (1996). b) T. Imamoto, *Lanthanides in Organic Synthesis*, Academic Press, London, Great Britain (1994). c) G. A. Molander, *Chem. Rev.*, **92**, 29 (1992). d) G. A. Molander, *Comprehensive Organic Synthesis*; ed by B. M. Trost, I. Fleming, Pergamon Press: Oxford, Great Britain (1991), Vol 1, Chapter 1.9, p 251.

2 a) T. Imamoto, *Pure Appl. Chem.*, **62**, 747 (1990). b) T. Imamoto, *Comprehensive Organic Synthesis*; ed by B. M. Trost, I. Fleming, Pergamon Press: Oxford, Great Britain (1991), Vol 1, Chapter 1.8, p 231.

3 Quite recently, lanthanide alkoxides were reported as effective catalysts of isocyanates-polymerization. See, N. Fukuwatari, H. Sugimoto, and S. Inoue, *Macromol. Rapid Commun.*, **17**, 1 (1996).

4 G. Natta, J. DiPietro, and M. Cambini, *Macromol. Chem.*, **56**, 200 (1962).

5 Natta et al. reported that the polymerization of BuNCO with ethyllithium in THF at -78 °C gave the polymer in 27 % yield, which was inconsistent with our results.

6 A typical procedure was as follows; BuNCO (55 equiv. to BuLi) was added to the mixture of BuLi (1.8 M in hexane) and 1 equiv. of a 0.1 M SmI_2/THF solution at -78 °C under nitrogen.[8] After 7h stirring, The polymerization was quenched by methanol, and poly(*N*-butyl 1-nylon) was obtained by the reprecipitation with methanol.

7 This formulation might be the most possible form of the organosamarium reagent. However, some other species such as a weakly associated complex (RLi·SmI_2) or dialkylsamarium (R_2Sm) may be also present in equilibrium. In this paper, the organosamariums are represented as $RSmI_2Li$ for convenience.

8 An immediate color change was observed after the addition of BuLi to a solution of SmI_2 in THF.