One-Pot Formation of a Reactive Polymer Possessing Anion Sites along the Polymer Backbone and Its Application to Graft Polymerization of ϵ-Caprolactone

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Introduction. Rodlike aromatic polyamides are high-performance polymers, having thermal stability, mechanical strength, and chemical resistance due to their rigid aromatic amide backbones and strong hydrogen bonds. However, these structural characteristics are also responsible for the low solubility and poor processability of these polymers, which are limiting factors for their wide application. Therefore, modification of these polymers is important not only for improving their inherent properties but also for providing new functionalities.

In general, there are two different approaches for improving the solubility and molding properties of aromatic polyamides. One is the introduction of proper groups into the aromatic ring of the monomers or using comonomers with flexible structures, which preserves the secondary amide groups. The other is *N*-substitution of the amide groups in the polymer chains, which takes advantage of the reactivity of the N−H sites.[1] However, by this way, the deprotonation is inevitable for forming the polymeric anions before introducing the side chains, and in some instances cleavage of the polymer backbone may occur.

Recently, we reported a new synthetic procedure for poly(oxamide)s, a kind of polyamide, by reductive coupling polymerization of aromatic diisocyanates via one-electron transfer promoted by SmI_2.[2] The probable polymerization process is illustrated in Scheme 1. The anion-radical species (**1**) is first formed by the electron transfer of SmI_2, and subsequent coupling of **1** gives the samarium poly(oxamide) polyanion (**2**). Then, the poly(oxamide) (**3**) can be obtained quantitatively after quenching the polymerization with 3% HCl aqueous solution.[3]

This mechanism suggests that the obtained polyanion (**2**) could be regarded as a kind of reactive nucleophilic reagent, which provides an opportunity for continuous modifications in the same system. Thus, the polyanion generated *in situ* could be expected to be a new type of reactive polymer, and its reaction with appropriate electrophiles would give a new synthetic route for grafting of pendant side or polymeric chains on the polymer backbone in one pot (Scheme 2). To our knowledge, there are few reports concerning direct formation of reactive polymers bearing anion sites along the polymer backbone. In the present paper, the graft polymerization of an electrophilic monomer with this polyanion is reported. Research on the scope and limitations of its reactivity will be published elsewhere.

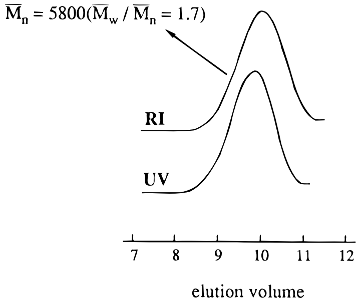
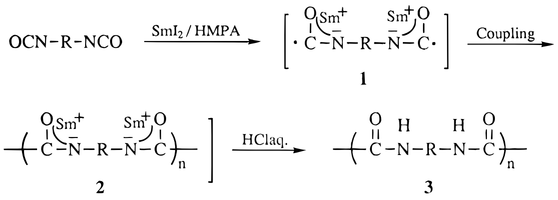
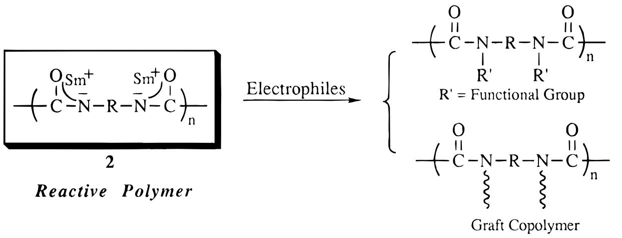


Figure 1. GPC profile of polymer **5** obtained after 7 h of polymerization.

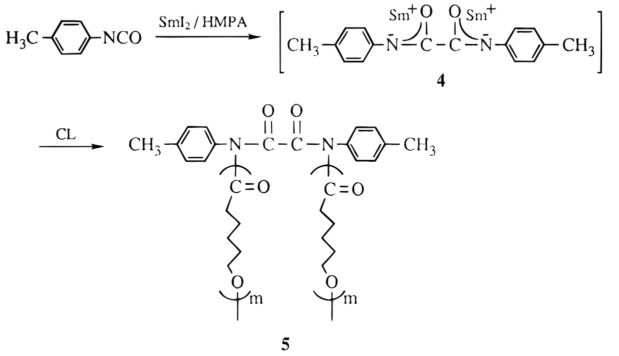
Scheme 1



Scheme 2



Scheme 3



Results and Discussion. ϵ-Caprolactone (CL) was utilized here as an electrophilic monomer because it can be easily polymerized by typical anionic initiators. The initiating ability of the oxamide dianion unit was first examined by using samarium oxamide dianions which were derived from the coupling reaction of the monoisocyanate (Scheme 3).[4] The coupling reaction of *p*-tolyl isocyanate induced by SmI_2 was carried out at room temperature, and the model polymerization was performed by adding CL to the reaction mixture after the coupling reaction was completed.[5]

As an example, the GPC chromatogram of the polymer obtained after 7 h of polymerization is illustrated in Figure 1. Usually, UV absorption cannot be observed in poly(CL); however, the polymer synthesized by the present method showed a UV absorption at 254 nm, which was attributed to the aromatic ring in the polymer chain. This strongly supported that the ring-opening polymerization of CL was initiated by the dianions, which was also confirmed by the results of IR and ^{1}H NMR spectra. Thus, it can be concluded that the oxamide dianions (**4**), which can be considered as the repeating unit of poly(oxamide) polyanions (**2**), have an initiating ability for polymerization of CL.

Next, the graft polymerization of CL with the samarium poly(oxamide) polyanions formed *in situ* from the reductive coupling polymerization of tolylene 2,6-diisocyanate (TDI) was attempted. The polymerization of TDI was carried out at room temperature according

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Scheme 4

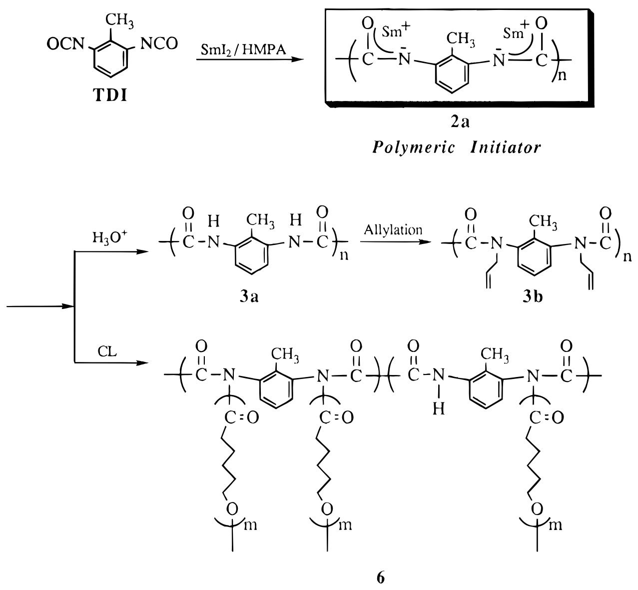


Table 1. Graft Copolymerization under Various Conditions[a]

run	HMPA equiv to SmI$_2$	CL equiv to TDI	yield (%)[b]	$\bar{M}_n$ (MWD)[c]
1	7.1	85.8	75	21 700 (1.92)
2	14.0	91.6	80	44 500 (1.47)
3	29.8	99.8	31	31 700 (1.57)
4	13.7	41.6	55	14 600 (2.06)
5[d]	14.0	90.0	99	32 200 (1.81)

[a] The graft copolymerization was carried out at room temperature for 7 h. [b] Methanol-insoluble part. [c] Estimated by GPC based on polystyrene standards, THF effluent. [d] Polymerization time was 24 h.

to the previous report,[2] and then the graft polymerization with CL was performed by adding CL to the reaction mixture when the coupling polymerization proceeded completely (Scheme 4). A portion of **2a** was quenched with 3% HCl aqueous solution when the homopolymer resulting from the polymerization of diisocyanate was needed for comparison.

The results of the graft polymerization conducted under various conditions are summarized in Table 1. Both the molecular weight and the yield of the resulting copolymer increased as the amount of HMPA increased (run 2), which might result from the improved nucleophilicity of the polyanions due to the strong coordination effect of HMPA toward Sm(III). Furthermore, polymerization for 24 h gave the corresponding polymer quantitatively (run 5). On the other hand, a large excess of HMPA decreased both the molecular weight and the yield of the polymer (run 3), which might be because the coordination sites of Sm(III) were preferentially occupied by the excess HMPA. The decrease in both the molecular weight and the yield of the polymer was also observed as the amount of CL decreased (run 4).

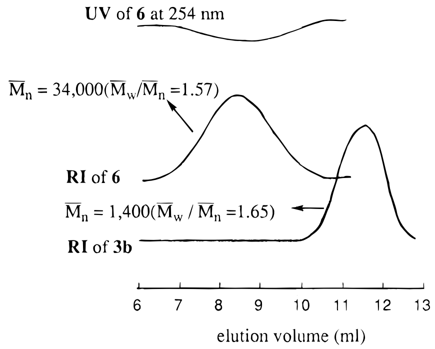


Figure 2. GPC profiles of (a) **3b** and (b) **6**.

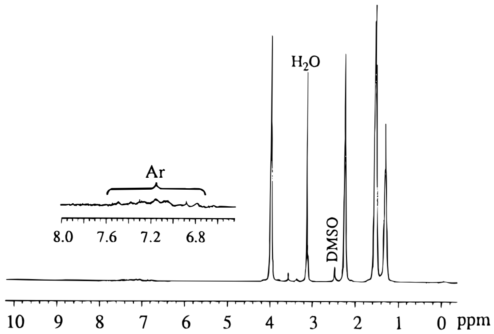


Figure 3. ^{1}H NMR spectrum of **6** (run 4, purified by HPLC) (25 °C, DMSO-d_6).

The formation of the graft polymer could be confirmed by the process illustrated in Scheme 4. Because **3a** was insoluble in THF, the GPC profile of its *N*-allylated form (**3b**) is shown in Figure 2 compared with that of the copolymer (**6**). As can be seen, the GPC curve of **3b** shifted to a high molecular weight region after the graft polymerization, and the UV absorption of the resulting polymer could be found in the high molecular weight region while poly(CL) usually does not show UV absorption. Furthermore, in the ^{1}H NMR spectrum of **6** (run 4, purified by HPLC), the proton signal of the aromatic ring could be found at 7.55−6.75 ppm (Figure 3). These results supported that the samarium poly(oxamide) polyanions (**2a**) worked as polymeric initiators, and the corresponding graft polymer could be formed in one pot under mild conditions.

In summary, the samarium poly(oxamide) polyanions (**2**) generated *in situ* by the reductive coupling polymerization of the aromatic diisocyanate have been proven to be a new type of reactive polymer. The graft polymers could be prepared facilely in one pot by using **2** as the polymeric initiator. Further investigations are being continued into the details of the present system, including the preparation of other graft polymers.

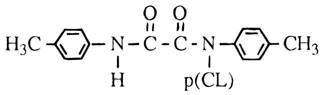
References and Notes

(1) (a) Takayanagi, M.; Katayose, T. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 1133. (b) Takayanagi, M.; Ueta, S.; Koga, K. *Polym. J.* **1988**, *20*, 639. (c) Kim, Y. H.; Calabrese, J. C. *Macromolecules* **1991**, *24*, 2951. (d) Gieselman, M. B.; Reynolds, J. R. *Macromolecules* **1993**, *26*, 5633.

(2) Wang, J.; Nomura, R.; Endo, T. *J. Polym. Sci., Polym. Chem. Ed.* **1995**, *33*, 869.

(3) Although the formation of the *O*-anion could not be denied, the *N*-anion was found to be the main form probably due to the strong oxophilicity of Sm(II) complexes.

(4) The structure of **5** shown in Scheme 3 is given only for simplicity. The resulting polymers might be a mixture with the following structure, and further research on this matter is in progress.



$$H_3C\text{-}C_6H_4\text{-}\underset{H}{N}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{p(CL)}{N}\text{-}C_6H_4\text{-}CH_3$$

(5) A typical procedure was as follows: A 0.1 M SmI$_2$/THF solution (1.2 mL) was added to *p*-tolyl isocyanate (16.0 mg, 0.12 mmol) in HMPA (0.1 mL) at room temperature to provide the corresponding samarium oxamide dianion. After the reaction mixture became yellow, CL (0.684 g, 5.99 mmol) was added to the system and the mixture was stirred for 14 h. The resulting polymer was obtained as the methanol-insoluble part (0.643 g, 94%). The graft polymerization was conducted according to a similar method.

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