

One-pot reactions of samarium poly(oxamide) polyanion with various electrophilic reagents

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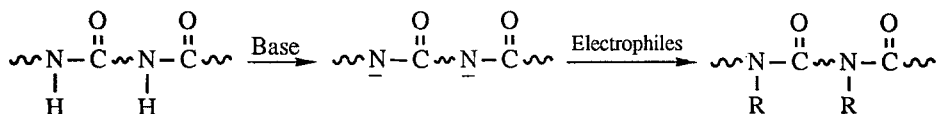
Summary

Samarium poly(oxamide) polyanion generated *in situ* by the reductive coupling polymerization of tolylene 2,6-diisocyanate with samarium(II) iodide was found to be a new type of reactive polymer bearing anion sites along the backbone. Its reactions with various electrophilic reagents, including methyl trifluoromethanesulfonate, acetyl chloride, *n*-butyl isocyanate, *n*-octyl isocyanate, benzyl and allyl bromide, 1,2-epoxy-3-phenoxypropane, isobutyraldehyde, and 1-iodobutane produced the corresponding *N*-substituted poly(oxamide)s in one-pot in good yields. The extents of substitution of the resulting polymers were 6-81%, depending on the electrophiles or conditions. In some cases, the resulting *N*-substituted poly(oxamide)s were much more soluble than the parent polymer. Thus, by this way, not only the poor solubility of the aromatic poly(oxamide) could be improved, but the introduced pendent moieties may provide opportunity for further modification of the polymer.

Introduction

The introduction of pendant substituents into the backbone of organic polymers by chemical modification is an important technique which has been used extensively both to prepare various functional polymers and to improve the inherent properties. For an example, the limited processability of rigid-rod aromatic polyamides has triggered various modifications of these polymers into fusible or soluble analogues [1]. As indicated in Scheme 1, polyamides are generally modified by grafting electrophilic moieties into the polymer backbone. However, the required deprotonation is a burden process, and risks the cleavage of the polymer backbone in some cases.

Scheme 1

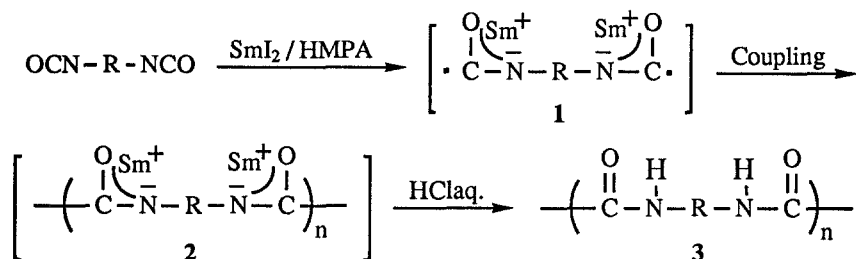


We have already reported a novel synthetic procedure of aromatic poly(oxamide), a kind of polyamide, by the reductive coupling polymerization of diisocyanate with samarium(II) iodide [2]. The probable polymerization mechanism is illustrated in Scheme 2. At first, the anion-radical species (1) are formed by the one-electron transfer of SmI_2 , and the subsequent coupling of 1 gives the samarium poly(oxamide) polyanion (2). The

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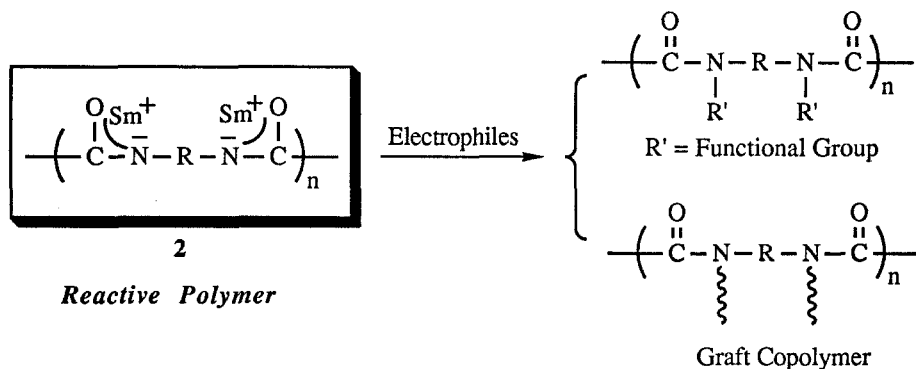
poly(oxamide) (3) can be obtained quantitatively after quenching 2 with 3% HCl aqueous solution.

Scheme 2



The above-mentioned mechanism promoted us to consider that whether the polyanions generated *in situ* could be regarded as one of reactive polymer. According to this proposition, reactions with appropriate electrophilic reagents would give a new synthetic route for grafting of pendant side or polymeric chains onto the polymer backbone in one-pot (Scheme 3) [3]. In other word, the polyanion 2 might function as polymeric nucleophile and provide the potential opportunity for the continuous modifications in the same system. As far as we know, the report concerning with direct formation of the reactive polymers bearing anion sites along the polymer backbone is quite few.

Scheme 3



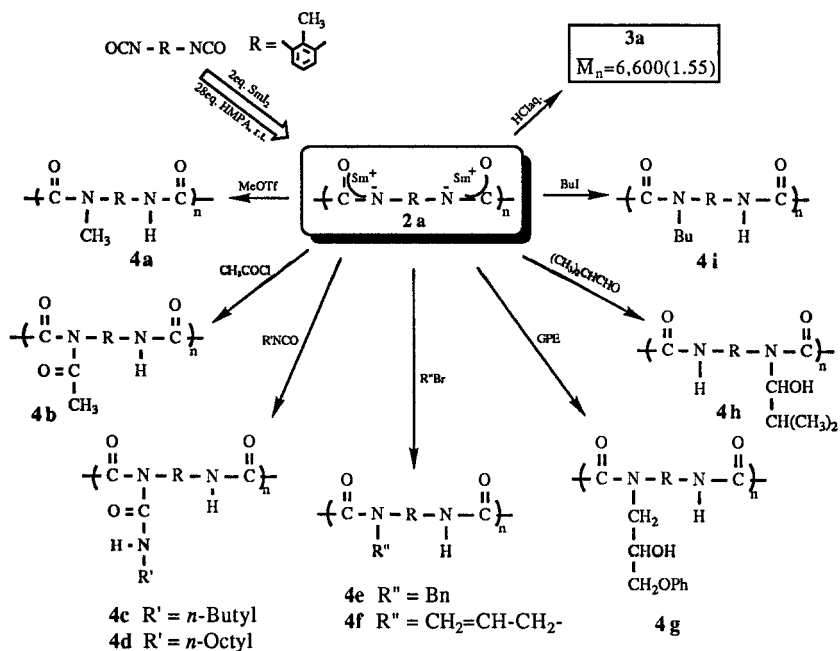
Very recently, the polyanion 2 has been confirmed to be a polymeric initiator, and the corresponding graft copolymers with ϵ -caprolactone were obtained quantitatively under proper conditions [4]. Herein, the reactions of polyanion 2 with various electrophiles were carried out to investigate the scopes and limitations of its reactivities. The electrophilic reagents included methyl trifluoromethanesulfonate (MeOTf), acetyl chloride, *n*-butyl isocyanate (BuNCO), *n*-octyl isocyanate (OctNCO), benzyl (Bn) and allyl bromide, 1,2-epoxy-3-phenoxypropane (GPE), isobutyraldehyde, and 1-iodobutane (BuI). Additionally, the solubility of the resulting polymers were also examined.

Results and Discussion

Reactivity of Samarium Poly(oxamide) Polyanion. In our previous work [2], HMPA was found to be an important factor for the reductive coupling polymerization of aromatic

diisocyanates, and both the yield and molecular weight of the poly(oxamide) showed the highest values when the molar ratio of HMPA to SmI_2 was about 12-14. Therefore, the amount of HMPA was fixed at 14 equivalent to SmI_2 in this work, and the samarium poly(2-methyl-1,3-phenylene oxamide) polyanion (**2a**) was obtained according to the earlier report [2]. After the polymerization proceeded completely, the polyanion generated *in situ* was treated with several electrophilic reagents for introducing the corresponding pendant groups. The reactions with various electrophiles were carried out via the process indicated in Scheme 4 to obtain the corresponding *N*-substituted poly(oxamide)s in one-pot. The structures **4a-4i** given in Scheme 4 intend to show the presence of both substituted and protonated nitrogen atoms but not strict alternation, and the side chains are randomly distributed along the polymer backbone [5].

Scheme 4



The detailed conditions and the results are summarized in Table 1. In every case, **2a** is active toward the electrophiles used, and the modified polymers could be obtained in good yields. The extents of substitution of the resulting polymers were estimated by their ^1H NMR spectra. As shown in Table 1, the substitution degree varied with the electrophilic reagents and the reaction conditions. At room temperature, **2a** showed better reactivity for OctNCO than BuNCO (Runs 3 and 4), which might be attributed to the long alkyl chain of octyl group. That is, when the first OctNCO molecular reacts and attaches to the backbone, the solubility of the polyanion might be increased, which would make the continuous reaction proceed smoothly. In the cases of **4a**, **4b**, **4c**, and **4f-1**, the reactions were tried to carry out under reflux condition to increase the extent of substitution, but effective improvement was obtained only for allyl bromide, where the substitution degree was as high as 81% (Run 7). As given in runs 8-10, after 21h reaction (including 8h of reflux), the substitution degrees of GPE [6] and isobutyraldehyde were lower than 20%; whereas, 51% of the reaction sites of the polyanion were grafted by butyl group.

Table 1. Reactions of the Polyanion with Various Electrophiles^a

Run	Polymer	Electrophiles	Molar Ratio to TDI	Time(h)	Sub% ^b	Yield(%)	\bar{M}_n (MWD) ^c
1	4a	MeOTf	8.2	24	22	97	7,400(1.74)
2	4b	CH ₃ COCl	13.3	60	9	90	4,700(1.63)
3	4c	BuNCO	2.5	48	6	85	6,600(1.74)
4	4d	OctNCO	3.7	24	50	90	8,500(1.52)
5	4e	BnBr	3.0	48	20	99	4,400(1.36)
6	4f-1	CH ₂ =CHCH ₂ Br	2.8	48	24	76	4,900(1.42)
7	4f-2		7.0	32 ^d	81	64	4,900(1.37)
8	4g	GPE	6.1	21 ^d	18	89	5,100(1.84)
9	4h	(CH ₃) ₂ CHCHO	6.1	21 ^d	13	98	5,600(1.75)
10	4i	BuI	5.7	21 ^d	51	97	5,000(1.68)

^aReactions were carried out at room temperature. ^bThe extent of substitution of the resulting polymers were calculated from their NMR spectra. ^cEstimated by GPC based on polystyrene standard, THF eluent. ^dIncluding 8h of reflux.

Some factors are considerable for the low introduction degree: (1) The reactions proceeded in the heterogeneous system due to the poor solubility of 2a; (2) The large excess of HMPA, which exists in coordination sites of Sm(III), may hinder the access of the electrophiles to the anion reactive sites; (3) When either anion in the repeated unit of the oxamide dianion is attached by the electrophilic reagent, the reactivity of the rest one may decrease due to the loss of repulsion of the dianion. Meantime, the steric hindrance may be considered as another reason.

Characterization. As a typical example, the ¹H NMR and IR spectra of polymer 4f-2 are shown in Figures 1 and 2, respectively, to illustrate the formation of the *N*-allyl poly(2-methyl-1,3-phenylene oxamide). The peaks in 4.29-5.87ppm can be attributed to allyl moiety, and the proton ratios calculated from the integrated intensity indicated that the *N*-substitution extent is 81% (Figure 1). The obvious decrease in the intensity of the absorption band (1611cm⁻¹) due to the deformation vibration of N-H also supported the proceeding of the *N*-allylation strongly (Figure 2). Additionally, the absence of oligomer peak in the GPC curves and no serious difference in molecular weights between 4f-2 and 3a suggested that no cleavage of the parent polymer occurred under these conditions. Therefore, it is clear that the *N*-allyl poly(oxamide) could be synthesized easily by the present one-pot method. The formations of other *N*-substituted poly(oxamide)s were also verified by the similar studies. The changes in the molecular weights between the *N*-substituted and the parent polymers might result from their different structures.

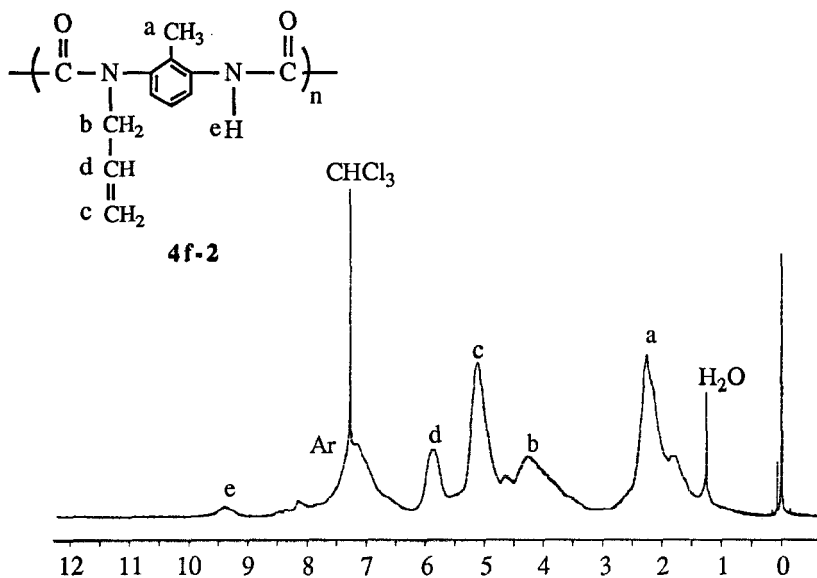


Figure 1. $^1\text{H NMR}$ spectra of 4f-2 (28 °C, in CDCl_3).

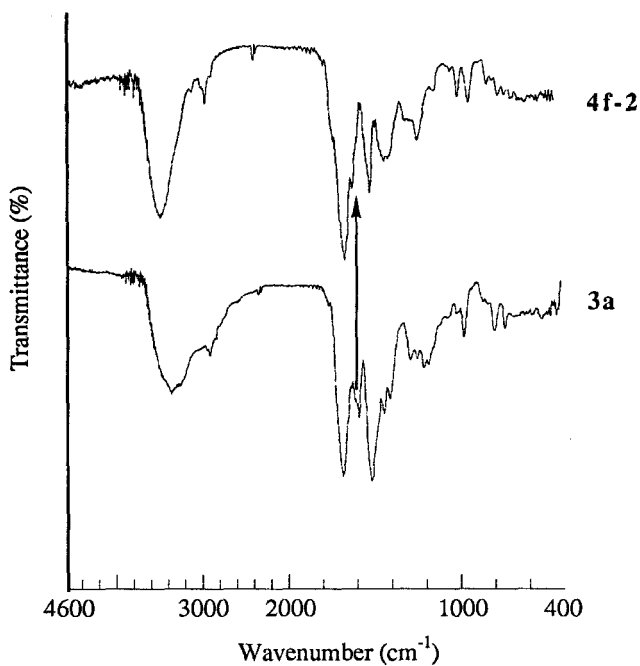


Figure 2. IR spectra of 3a and 4f-2 (KBr).

Solubility. The solubilities of the *N*-substituted poly(oxamide)s were examined, and the results are given in Table 2. The parent poly(oxamide) is soluble only in DMF and DMSO, and in the cases of **4a-4c**, **4f-1**, **4g**, and **4h**, the solubilities of the resulting polymers were not improved. This probably resulted from the low substitution extent and the increased hydrogen concentration due to the introduction of N-H, O-H, or C=O (Run 2, 3, 8, and 9). However, it is interesting to find that although only 20% of the N-H sites in the backbone was substituted by benzyl (Run 5), the modified polymer exhibited good solubility in THF and CHCl₃. The polymers **4d**, **4f-2**, and **4i** were highly soluble in THF and CHCl₃, and the latter two were soluble even in acetone. Therefore, the modification of the poly(oxamide) with appropriate electrophilic reagents could improve the solubility of the parent polymer, which will also provide the opportunity for further application. For instance, the cross-linked polymer will be obtained from the *N*-allylated poly(oxamide), and the functionalized polymer based on poly(oxamide) backbones may be synthesized by using the designed substituted benzyl bromide as the alkylation reagent.

Table 2. Solubility of Various Modified Polymers^a

Run	Polymer	DMF	DMSO	THF	CHCl ₃	CH ₃ COCH ₃	MeOH
1	4a	+ ^b	+	— ^b	—	—	—
2	4b	+	+	—	—	—	—
3	4c	+	+	—	—	—	—
4	4d	+	+	+	+	—	—
5	4e	+	+	+	+	—	—
6	4f-1	+	+	—	—	—	—
7	4f-2	+	+	+	+	+	—
8	4g	+	+	—	—	—	—
9	4h	+	+	—	—	—	—
10	4i	+	+	+	+	+	—

^aThe parent poly(oxamide) is soluble only in DMSO and DMF.

^b"+" and "—" mean good and poor solubility at room temperature, respectively.

In summary, the samarium poly(oxamide) polyanion generated *in situ* by the coupling polymerization of tolylene 2,6-diisocyanate with SmI₂ was found to be a reactive polymeric nucleophile, and various of *N*-substituted poly(oxamide)s have been facily prepared in one-pot in good yields. The formation of the modified polymers were confirmed by ¹H NMR and IR spectra, and no cleavage of the parent polymer backbone was found by GPC analyses. The substitution degrees were 6-81% depending on the property of the electrophilic reagent as well as the reaction conditions. In some cases, the modified polymers exhibited higher solubility compared to the parent one, which would provide the possibility for further modification and application. The study on this matter is now in progress.

Experimental Section

Materials. All reagents and solvents used in the present work were purified according to the standard methods and stored under nitrogen. A SmI_2 / THF solution was prepared by the reported manner [7].

Measurements. ^1H NMR spectra were recorded on JEOL EX-400 spectrometer using tetramethylsilane (TMS) as an internal standard. FT-IR spectra were obtained with Jasco FT/IR-3 spectrometer. Gel permeation chromatographic analysis was carried out on Toyo Soda HLC 8020 system with SC-8010 data processor equipped with polystyrene gel columns (TSK gel G2500, 4000, and G5000) using *N,N*-dimethylformamide as an eluent after calibration with polystyrene standards.

General procedure. As a typical example, the synthesis of *N*-benzyl poly(2-methyl-1,3-phenylene oxamide) was described as follows: a 0.1 M SmI_2 / THF solution (28 mL) was added to 2,6-tolylene diisocyanate (0.248g, 1.42 mmol) in HMPA (7.1 mL) at room temperature to provide the corresponding samarium poly(oxamide) polyanion [2]. After the polymerization system became yellow, benzyl bromide (0.732g, 4.27 mmol) was added and the stirring was kept for 2 days. THF was removed *in vacuo* and the reaction mixture was poured into 3% HCl aq. The precipitate was collected and dried, and the final polymer was obtained after purifying by high performance liquid chromatography (HPLC) (0.272g, 91%). The other *N*-substituted poly(2-methyl-1,3-phenylene oxamide)s were synthesized by the similar process, and the details were described in the text. In every case, the excess electrophilic reagents can be washed free by appropriate solvent or removed by HPLC.

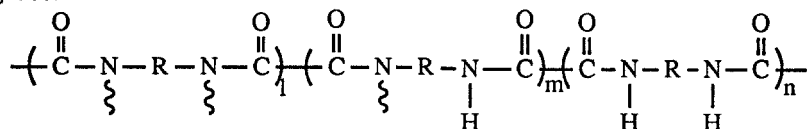
Spectrum data. ^1H NMR spectrum(400 MHz) data of the produced *N*-substituted poly(2-methyl-1,3-phenylene oxamide)s are as follows. **4a:** (DMSO- d_6) δ 2.19 (bs, 3H), 3.09 (bs, 0.65H), 3.22 (bs, 0.65H), 7.17-7.76 (m, 3H), 10.26 (bs, 0.15H), 10.85 (bs, 0.15H). **4b:** (DMSO- d_6) δ 1.91-2.04 (m, 0.5H), 2.18 (bs, 3H), 7.20-7.78 (m, 3H), 9.20-10.78 (m, 1H). **4c:** (DMSO- d_6) δ 0.89 (bs, 0.4H), 1.33 (bs, 0.3H), 1.60 (bs, 0.3H), 2.21 (bs, 3H), 3.64 (bs, 0.3H), 7.18-7.78 (m, 3H), 9.40-10.62 (m, 0.4H). **4d:** (CDCl_3) δ 0.88 (bs, 3H), 1.27 (m, 12H), 2.33 (bs, 3H), 3.67 (bs, 1H), 3.74 (bs, 1H), 7.17-7.76 (m, 3H), 9.35 (bs, 0.5H). **4e:** (CDCl_3) δ 2.05 (bs, 3H), 4.85 (bs, 0.8H), 6.17-7.26 (bs, 3H), 9.22 (bs, 0.6H). **4f-2:** (DMSO- d_6) δ 2.26 (bs, 3H), 4.29 (bs, 3.2H), 5.11 (bs, 3.2H), 5.87 (bs, 1.6H), 6.50-7.70 (bs, 3H), 9.38 (bs, 0.2H). **4g:** (DMSO- d_6) δ 2.21 (bs, 3H), 3.88 (bs, 0.71H), 6.87 (bs, 2H), 7.24 (bs, 2H), 10.17 (bs, 0.25H), 10.72 (bs 0.25H) [8]. **4h:** (DMSO- d_6) δ 0.95 (bs, 0.8H), 1.14 (bs, 0.8H), 2.21 (bs, 3H), 2.60 (bs, 0.27H), 3.67 (bs, 0.13H), 3.87 (bs, 0.13H), 7.19-7.83 (m, 3H), 9.00-10.62 (m, 1.3H). **4i:** (CDCl_3) δ 0.90 (bs, 3H), 1.07-1.74 (m, 4H), 2.27 (bs, 3H), 3.69 (bs, 2H), 7.26 (bs, 3H), 9.65 (bs, 0.5H).

IR spectrum data (KBr) of the resulted *N*-substituted poly(2-methyl-1,3-phenylene oxamide)s are as follows. **4a:** 3289, 2926, 2809, 1680, 1611, 1510, 1453, 1292, 1260, 1194, 1161, 1100, 1032, 988, 883, 808, 750, 639, 519 cm^{-1} . **4b:** 3366, 2928, 1686, 1595, 1510, 1449, 1412, 1372, 1217, 988, 820, 754, 635 cm^{-1} . **4c:** 3358, 2959, 1707, 1595, 1510, 1449, 1231, 1069, 1003, 882, 818, 758, 546 cm^{-1} . **4d:** 3362, 2928, 2857, 1686, 1595, 1522, 1452, 1302, 1223, 1069, 1036, 992, 816, 758 cm^{-1} . **4e:** 3366, 3063, 3030, 2926, 1676, 1610, 1510, 1453, 1298, 1204, 1080, 1030, 990, 820, 729, 700, 525 cm^{-1} . **4f-2:** 3449, 2926, 1655, 1611, 1561, 1508, 1422, 1229, 993, 928, 758, 610, 469 cm^{-1} . **4g:** 3366, 2926, 1684, 1597, 1518, 1451, 1414, 1240, 1040, 885, 816, 756, 693 cm^{-1} . **4h:** 3360, 2967, 1686, 1597, 1522, 1451, 1414, 1302, 1221, 1067, 992, 816, 752,

683 cm⁻¹. 4i: 3366, 2959, 2932, 2872, 1680, 1611, 1510, 1451, 1300, 1262, 1215, 1115, 992, 810, 752 cm⁻¹.

References and Notes

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- Although the formation of *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.
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- The structures in Scheme 4 were used only for simplicity. Actually, the probable form might be:



- The methine of GPE might not react with the polyanion because of its steric hindrance.
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- The other proton peaks of the polymer were covered by the proton of water existed in DMSO-d₆ solvent.