Polymer Bulletin 38, 125–132 (1997)

Polymer Bulletin

One-pot syntheses of water-soluble poly(oxamide)s

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Received: 18 October 1996/Revised version: 8 November 1996/Accepted: 15 November 1996

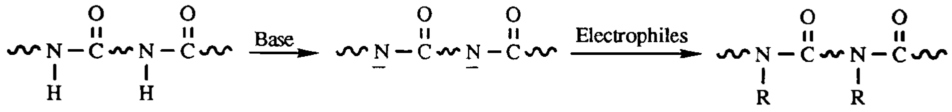
Summary

Two kinds of water-soluble polymers were synthesized by using the poly(oxamide) polyanion generated *in situ* from the reductive coupling polymerization of diisocyanates induced by SmI_2. One is a nonionic polymer bearing oligo(ethylene oxide) pendants, which was obtained by treating the polyanion with α-methyl-ω-(4-bromomethyl)phenylmethyl oligo(ethylene oxide). The other is an ion-containing polymer having sulfonate moieties in the side chains, which was prepared by the reaction of the polyanion with 1,3-propane sultone or sodium 4-(bromomethyl)-benzenesulfonate. In both cases, the corresponding polymers were provided in good yields, and their solubilities were found to be dependent on the structure as well as the substitution degree. The poly(oxamide) with oligo(ethylene oxide) exhibited good solubilities in common organic solvents and was soluble in aqueous system at high level of substitution. On the other hand, the poly(oxamide) with propane-sulfonic acid showed high solubility in both acidic and basic water but was insoluble in organic solvents, while the poly(oxamide) having benzylsulfonate was soluble only in DMF and DMSO.

Introduction

Water-soluble polymers, which are often divided into nonionic and ion-containing types, have been extensively studied for both theoretical interest and practical applications [1]. For example, poly(ethylene oxide)s are well known as a kind of nonionic water-soluble polymer, and they own unique properties such as high solubility, biocompatibility, and complexing ability with alkali metal ions [2]. In general, the water solubility for a polymer is conferred through a balance between the hydrophilic nature of the polar or ionic portion and the hydrophobic property of the nonpolar portion, typically the backbone. Therefore, the introduction of pendent polar or ionic substituents onto polymer backbones can induce water solubility into polymers whose skeletal structures are incompatible with aqueous system such as aromatic polyamides. Usually, as indicated in Scheme 1, in order to modify polyamides by grafting electrophilic moieties onto the backbone, the deprotonation with strong base is necessary, which may risk the cleavage of the polymer backbone in some cases.

Scheme 1



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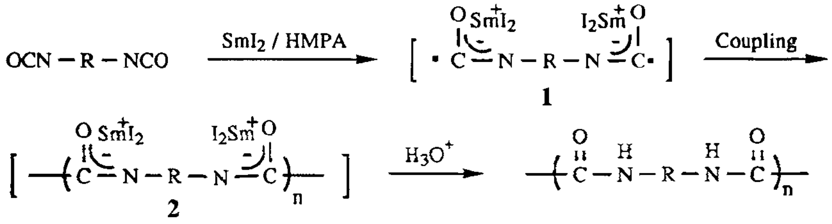
Scheme 2



Recently, we have reported that the reductive coupling polymerization of aromatic diisocyanates under the SmI_2 / HMPA system could provide the corresponding poly(oxamide), a kind of polyamide, quantitatively [3]. The probable polymerization mechanism illustrated in Scheme 2 suggests that the poly(oxamide) polyanion (2), which can be regarded as a new type of reactive polymer bearing anion sites along the backbone, is generated *in situ* by the coupling of the anion radical (1) formed by the electron transfer from SmI_2. In our previous work, the scope and limitation of the reactivities of 2 were surveyed by the reactions of 2 with various electrophiles, and the corresponding *N*-substituted poly(oxamide)s were directly provided under appropriate conditions in high yields [4]. Therefore, it is expected that the desirable functional poly(oxamide) can be obtained by using 2 as the reactive precursor and the designed electrophilic reagents. Herein, introduction of the hydrophilic groups onto 2 was carried out to prepare the poly(oxamide)-based water-soluble polymer. The success of this work might give a facile synthetic procedure for water-soluble poly(oxamide), which have unique features and applications due to their rigid skeletons.

Results and Discussion

Preparation of Poly(oxamide)-based Water-soluble Polymers. Oligo(ethylene oxide) and sulfonate were selected as hydrophilic moieties to prepare nonionic and ion-containing water-soluble polymers, respectively (Scheme 3). For the introduction of oligo(ethylene oxide) α-methyl-ω-(4-bromomethyl)phenylmethyl oligo(ethylene oxide) was used, and for the alkyl and arenesulfonate derivatives 1,3-propane sultone and sodium 4-(bromomethyl) benzenesulfonate were used, respectively. In this work, tolylene 2,6-diisocyanate (TDI) was polymerized to provide the corresponding poly(oxamide) polyanion according to the earlier report [3], and then the polyanion suspension was treated with the appropriate electrophile to introduce the water soluble structures onto poly(oxamide) backbone [5].

Scheme 3

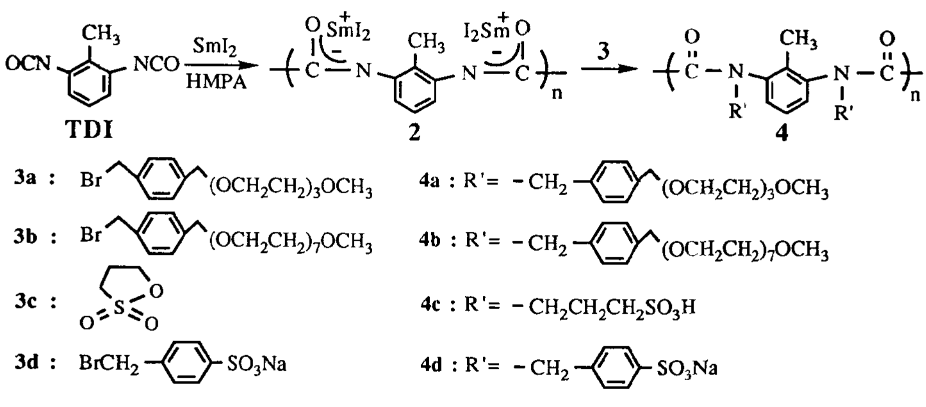


Table 1. Introduction of Hydrophilic Substituents onto Poly(oxamide) Polyanion[a]

Run	Polymer	Electrophile (E)	Molar Ratio (E / TDI)	Time(h)	Sub%[b]	Yield(%)	$\overline{M}_n$(MWD)[d]
1	**4a**	**3a**	3.6	48	32[c]	85	10,900(1.51)
2	**4b**	**3b**	3.5	48	50[c]	93	16,500(1.42)
3	**4c**	**3c**	2.2	24	60	66	—[e]
4	"	"	4.6	6	70	78	—
5	"	"	4.4	24	85	67	—
6	"	"	8.7	24	86	76	—
7	**4d**	**3d**	4.0	30	75	55	6,500(1.54)

[a]Reactions were carried out at room temperature. [b]Calculated from element analysis. [c]Calculated from ^1H NMR spectra. [d]Estimated by GPC based on polystyrene standard, DMF eluent. [e]Not determined.

The reaction conditions and the results are given in Table 1. In every case, the corresponding polymer was obtained in good yield [6], and the substitution degree of the side groups varied with the electrophiles and the reaction conditions. When oligo(ethylene oxide) derivatives with different repeating unit number, **3a** and **3b**, were employed (Runs 1 and 2) [7], a tendency that the introduction of oligo(ethylene oxide) proceeded more smoothly with the increase in the unit number of ethylene oxide was observed. In the cases of alkyl sulfonate derivatives, higher substitution level was obtained when the amount of **3c** was increased (Runs 3 and 5), but no further improvement was found even using excess **3c** (Run 6). Meanwhile, the longer reaction period resulted in improving the substitution extent (Runs 4 and 5), and after 24 h reaction the substitution degree as high as 85% could be achieved when the molar ratio of **3c** to TDI was about 4.4 (Run 5). With the introduction of arenesulfonate, 75% of the *N*-anion could be grafted by methylbenzenesulfonate under the proper conditions (Run 7). For each case, no effective increase in the substitution degree was obtained when the reaction was carried out at 70°C.

Characterization. **4a** was used as an example to confirm the formation of the polymer bearing oligo(ethylene oxide) pendants. All the proton signals could be assigned as illustrated in Figure 1, and the proton ratios calculated from the integrated intensity indicated that 32% of the *N*-anion sites were alkylated by the substituted benzyl moieties [8]. Additionally, in its IR spectrum, the success in the introduction of the ethylene oxide group can be supported by the new absorption band at 1103 cm^{-1} due to the stretch vibration of C-O-C and the obvious increase in the intensity of the absorption band at 2872 cm^{-1} attributed to the stretch vibration of C-H (Figure 2). And also, the introduction of propanesulfonic acid side chains onto the poly(oxamide) was confirmed by the IR and NMR spectra of **4c**. As can be seen in Figure 3, the absorption bands at 1213, 1161, 1044 cm^{-1} indicated the existence of the sulfonate group, and the ^{13}C NMR spectrum displayed the expected series of aromatic carbon resonances and the alkyl peaks due to the methyl carbon of TDI as well as the methylene carbons of the pendants (Figure 4). The two carbonyl resonances are resulted from the presence of both the substituted and protonated nitrogen atom. The structure of **4d** was also identified by the similar way [9].

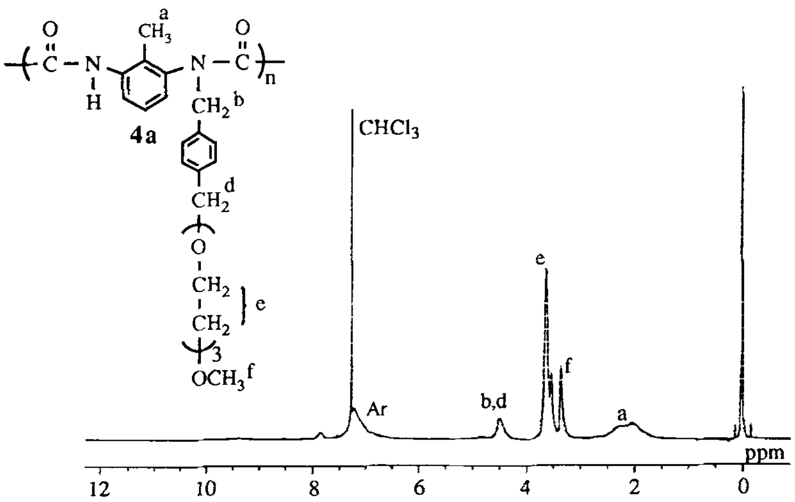


Figure 1. ^{1}H NMR spectra of 4a (28 °C, in $CDCl_3$).

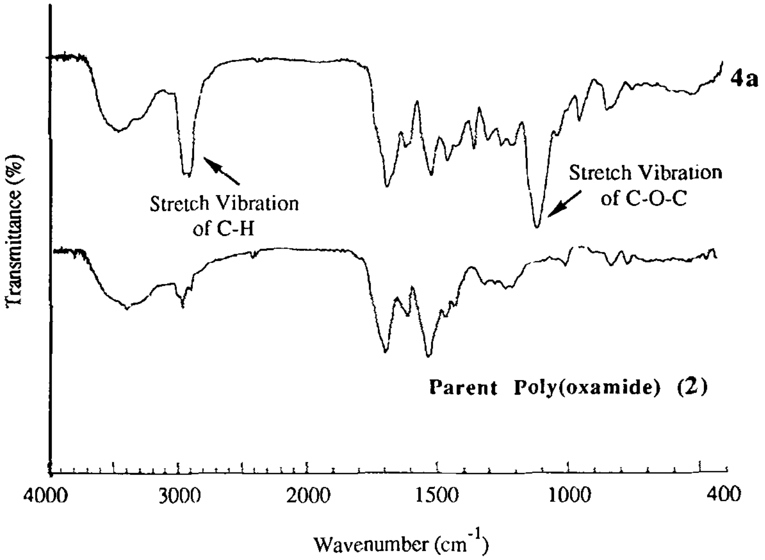


Figure 2. IR spectra of 4a and the parent poly(oxamide) (2) (KBr).

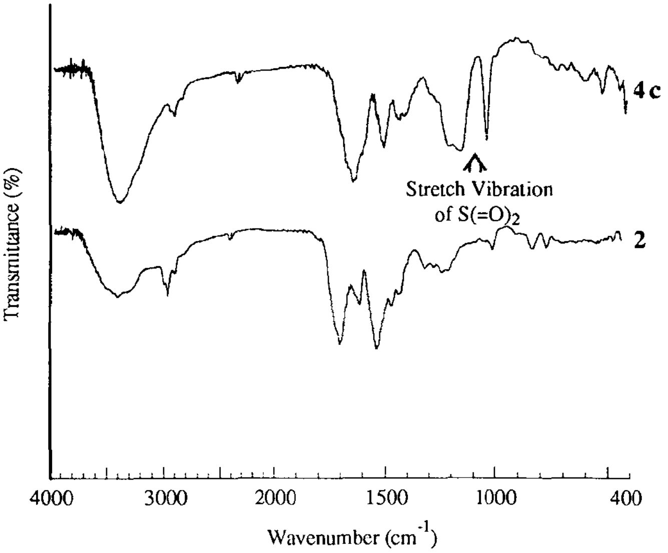


Figure 3. IR spectra of 4c (Run 4 in Table 1) and 2 (KBr).

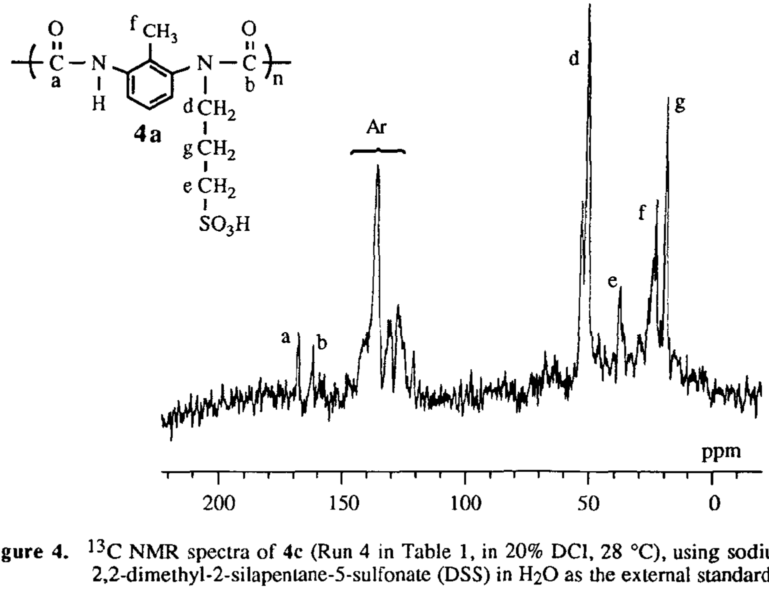


Figure 4. ^{13}C NMR spectra of 4c (Run 4 in Table 1, in 20% DCl, 28 °C), using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) in H_2O as the external standard.

Generally, introduction of ionic groups onto the polymer backbone would offer the characteristics as polyelectrolyte to the existing polymer. Therefore, the resulting polymers **4c** and **4d** could be regarded as new polyelectrolytes based on rigid aromatic poly(oxamide), whereas usual synthetic polyelectrolytes have flexible aliphatic backbones [10]. pH and conductivity of the obtained polymers in deionized water (pH = 7.11) were measured to be 4.88, 169.3 μScm^{-1} for **4c** and 6.24, 59.7 μScm^{-1} for **4d**, respectively, which supports that both **4c** and **4d** can behave as polyelectrolytes exactly.

Table 2. Solubilities of the Resulting Polymers

							Aqueous system[b]		
Polymer	DMF	DMSO	THF	$CHCl_3$	CH_3COCH_3	MeOH	A.	N.	B.
4	+	+	–	–	–	–	–	–	–
4a	+[a]	+	+	+	+	–	–	–	–
4b	+	+	+	+	+	+	+	+	+
4c	–	–	–	–	–	–	+	–	+
4d	+	+	–	–	–	–	–	–	–

[a] "+" and "–" mean good and poor solubility at room temperature, respectively.

[b] A., N., and B. are the abbreviations of acidic, neutral, and basic, respectively.

Solubility. The solubilities of **4a**-**4d** were examined, and the results are shown in Table 2. Although the parent poly(oxamide) (**4**; R'=H) was soluble only in DMF and DMSO because of its rigid structure and the strong hydrogen bonds, both **4a** and **4b** showed high solubilities in common organic solvents due to the introduced oligo(ethylene oxide). Furthermore, **4b** exhibited good solubility in aqueous system due to its longer pendent oligo(ethylene oxide)s and higher substitution degree. With the polymers containing sulfonate derivatives, **4c** was soluble in both acidic and basic water, whereas **4d** showed good solubility in only DMF and DMSO, which might result from the hydrophobic property of the benzyl group in the side chains.

In summary, two kinds of water-soluble polymers were prepared in one-pot by introducing the designed hydrophilic substituents onto the poly(oxamide) polyanion. One is a nonionic poly(oxamide) bearing oligo(ethylene oxide) pendants, which exhibited high solubilities in both common organic solvents and aqueous system. The other is a poly(oxamide)-based polyelectrolyte containing either alkyl or arenesulfonate side chains. The resulting polymer with propanesulfonic acid moieties showed high solubilities in acidic and basic water, but the polymer with methylbenzene-sulfonate groups was soluble only in DMF and DMSO. The present method could offer a facile synthetic procedure of water-soluble poly(oxamide)s, which might have new characteristics and applications based on their rigid skeletons.

Experimental Section

Materials. THF was purified prior to use by distillation over sodium and benzophenone under nitrogen. Tolylene 2,6-diisocyanate (TDI) was distilled under reduced pressure before use. Hexamethylphosphoramide (HMPA) was distilled over CaH_2 under reduced pressure. A SmI_2 / THF solution was prepared by the reported manner [11]. Triethylene glycol monomethyl ether was dried over CaH_2 and then distilled under reduced pressure. Oligo(ethylene glycol) methyl ether ($\overline{M}_n$ = 350) was used without further purification. *p*-Xylylene dibromide was purified by recrystallization from benzene and dried in vacuum. Dimethyl sulfoxide (DMSO) was dried over CaH_2 and distilled under reduced pressure. 1,3-Propane sultone was used without further purification. Sodium 4-(bromomethyl) ben- zenesulfonate was synthesized according to the reported procedure [12].

Measurements. ^1H NMR spectra were recorded on JEOL EX-400 spectrometer using tetramethylsilane (TMS) as the internal standard or on JEOL JNM-GX 500 FT NMR spectrometer using sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as the external standard. FT-IR spectra were obtained with Jasco FT / IR-3 spectrometer. Gel permeation chromatographic analysis was carried out on a Toyo Soda HLC 8020 (TSK gel G2500, 4000, &5000, DMF) after calibration with polystyrene standards. High performance liquid chromatography (HPLC) analysis was performed on a Nihon Bunseki Kogyo Model LC50.

Synthesis of 3a and 3b. To a suspension of NaH (0.315 g, 13.14 mmol) in THF (10 mL) was added triethylene glycol monomethyl ether (1.635 g, 9.95 mmol) at 0°C. The mixture was allowed to warm to room temperature and treated with *p*-xylylene dibromide (3.075 g, 11.65 mmol) in THF (25 mL). After stirring for 12 h, the reaction suspension was poured into $CHCl_3$, and the filtrate was collected. After evaporation of the solvents, the residue was purified by column chromatography on silica gel to obtain **3a** (2.218 g, 64%, yellow liquid). ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.37 (s, 3H), 3.54-3.67 (m, 12H), 4.49 (s, 2H), 4.56 (s, 2H), 7.27-7.37 (m, 4H). IR (KBr) 3511, 2870, 1458, 1350, 1298, 1248, 1107, 1038, 949, 853, 610 cm^{-1}. **3b** was similarly synthesized from oligo(ethylene glycol) methyl ether ($\overline{M}_n$ = 350, 4.837 g) and *p*-xylylene dibromide (5.274 g, 19.98 mmol) in 79% yield (5.810 g, bright yellow liquid). The spectral data are almost the same as those of **3a**.

Introduction of Oligo(ethylene oxide) onto Poly(oxamide). As a typical method, a 0.1 M SmI_2 / THF solution (11 mL) was added to tolylene 2, 6-diisocyanate (0.100 g, 0.57 mmol) in HMPA (2.8 mL) at room temperature to generate the corresponding poly(oxamide) polyanion (**2**). After the reaction mixture changed yellow, **3a** was added to the suspension of **2** with stirring for 3 days at room temperature. Then the reaction mixture was poured into 3% HClaq. solution, and the organic part was extracted with chloroform. After evaporation of the solvent, the residue was purified by HPLC to give **4a** (0.127 g, 85%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.12 (bs, 3H), 3.35 (s, 1.9H), 3.53-3.65 (m, 7.6H), 4.50 (bs, 2.5H), 7.27 (bs, 5.5H). IR (KBr) 3424, 2872, 1678, 1611, 1510, 1453, 1352, 1300, 1248, 1202, 1103, 951, 849 cm^{-1}.

Introduction of Sulfonic Acid Moiety onto Poly(oxamide). As a typical procedure, a 0.1 M SmI_2 / THF solution (17.4 mL) was added to tolylene 2, 6-diisocyanate (0.152 g, 0.87 mmol) in HMPA (3.7 mL) at room temperature to provide the corresponding poly(oxamide) polyanion (**2**). After the reaction mixture changed yellow, the side chains were introduced by adding 1,3-propane sultone (0.473 g, 3.88 mmol) to the suspension of **2** with stirring for 24 h at room temperature. Then the reaction mixture was poured into a large excess of ethyl ether to remove HMPA and the unreacted 1, 3-propane sultone. The precipitate was dissolved in 3% HClaq. solution and reprecipitated with methanol to remove the Sm (III) complexes, and the methanol-insoluble part was collected and dried in vacuum at 50°C to obtain **4c** (0.224 g, 67%). IR (KBr) 3414, 2926, 1655, 1510, 1439, 1213, 1161, 1044, 610, 529 cm^{-1}.

Introduction of Methylbenzenesulfonate Moiety onto Poly(oxamide). As a typical procedure, a 0.1 M SmI_2 / THF solution (17.4 mL) was added to tolylene 2,6-diisocyanate (0.152 g, 0.87 mmol) in HMPA (3.7 mL) at room temperature to provide the corresponding poly(oxamide) polyanion (**2**). After the polymerization proceeded completely, THF was removed under vacuum and dry-DMSO was added to the residue. Then **5b** (0.950 g, 4.0 mmol) was added to the suspension of **2**, and the reaction mixture was poured into a large excess of methanol after 24 h stirring at room temperature. The insoluble part was collected and washed with H_2O, then dried in vacuum at 50°C to obtain **4d** (0.220 g, 55%). ^{1}H NMR (400 MHz, DMSO-d_6) δ 2.18 (bs, 3H), 4.59 (m, 0.3H), 7.21-7.55 (m, 6.2H), 10.25-10.79 (d, 0.67H); ^{13}C NMR (400 MHz, DMSO-d_6) δ 34.46, 54.47, 123.67, 124.07, 125.92, 127.35, 128.32, 133.66, 137.27, 144.55, 150.91, 156.53; IR (KBr) 3382, 2926, 1655, 1522, 1451, 1412, 1221, 1179, 1125, 1038, 1011, 818, 694 cm^{-1}.

References and Notes

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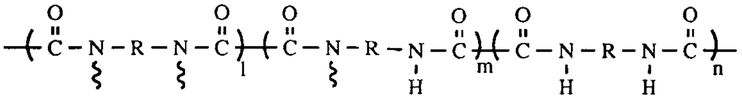
4) J. Wang, R. Nomura, T. Endo, *Polym. Bull.*, in press.
5) Number of ethylene oxide unit of **3b** was calculated from the molecular weight of the PEO used ($\overline{M}_n$ =350).
6) In the purification, water was used to remove the unreacted **3d**, where the partial solubility of **4d** in H_2O resulted in its moderate yield.
7) Based on the previous work, the molar ratio of the substituted benzyl bromide to TDI should be over 3.
8) The structures of **4** were used only for simplicity, and the possible form is:



$$\left(\overset{O}{\overset{\|}{C}}-\underset{\wr}{N}-R-\underset{\wr}{N}-\overset{O}{\overset{\|}{C}}\right)_{l}\left(\overset{O}{\overset{\|}{C}}-\underset{\wr}{N}-R-\underset{\underset{H}{|}}{N}-\overset{O}{\overset{\|}{C}}\right)_{m}\left(\overset{O}{\overset{\|}{C}}-\underset{\underset{H}{|}}{N}-R-\underset{\underset{H}{|}}{N}-\overset{O}{\overset{\|}{C}}\right)_{n}$$

9) It was suggested that no cleavage of the parent polymer backbone took place during all these reactions, because neither new oligmer peaks nor obvious changes in molecular weight distribution were observed in the GPC charts of the obtained polymers comparing with that of the parent poly(oxamide) prepared by quenching the coupling polymerization of TDI by H_3O^+.
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