Novel synthetic method for polythioamides from aliphatic diamines with element sulfur by oxidative coupling

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Abstract The oxidative polymerization of diamines with element sulfur to provide polythioamides was investigated for the novel synthetic methods of polythioamides. The oxidative polymerization of diamines with 2 equiv. of sulfur in pyridine at 110℃ for 24～48h afforded the polythioamides with higher molecular weights. When one kind of diamines was used, polythioamides contained both symmetrical and unsymmetrical structures. The use of two kinds of diamine monomer, m-xylylenediamine and 1,6-hexamethylenediamine, provided the copolymer containing three structures, such as the unsymmetrical structure prepared from both diamines and two kinds of the symmetrical structure prepared from m-xylylenediamine or 1,6-hexamethylenediamine.

Keywords: Polythioamides / Element sulfur / Aliphatic diamines / Oxidative coupling / Symmetrical structure / Unsymmetrical structure

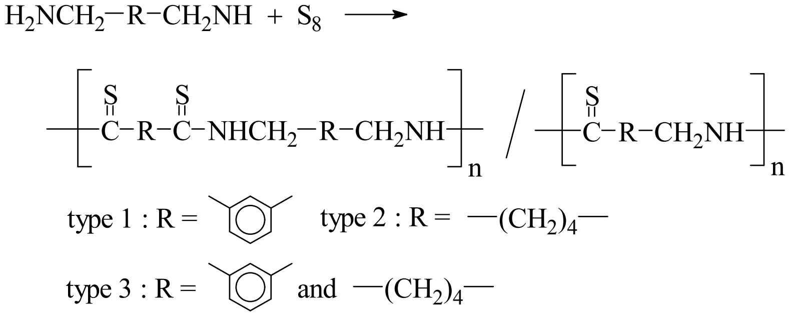
1. INTRODUCTION

While polyamides have been extensively investigated in the field of polymer chemistry, the preparation and characterization of polythioamides, in which the carbonyl oxygen has been replaced by sulfur, have been limited. Typical synthetic methods for polythioamides were polycondensation of bis(thioester)s or bis(dithioester)s with diamines.1,2) However, preparation of monomers such as bis(thioester)s or bis(dithioester)s would be somewhat troublesome. These factors might restrict the usability of polythioamides. As an alternative methods, the chemical modification of polyamides by Lawesson's regent, which is prepared from anisole and P_2O_5, has also been reported.3)

Simple and effective reaction using readily available reagents are seen as key solution for 21st century pollution problems. From the view of above point, the use of element sulfur in organic reaction appears to be highly desirable to maximize atom economy and to avoid expensive complex catalysts.

By the way, compounds containing thioamide functions play an important role in both chemistry and biology. They are also known as building blocks in the synthesis of heterocycles and other compounds having nitrogen and sulfur within their backbones. The Willgerodt-Kindler reaction, starting from aryl alkyl ketones, element sulfur, and secondary amines, is well known as practical and environmentally benign method to synthesize thioamides.4) Because sulfur is nontoxic, stable under ambient condition, easy to handle, and readily available. Using this reaction, the preparation of polythioamides has been reported. The reactions of element sulfur with amines have been the subject of several studies. McMillan reported the formation of N-benzylthiobenzamide from benzylamine and sulfur by only heating.6) Nguyen et al. reported the effective and selective oxidative coupling of two different aliphatic amines by sulfur to give thioamides.7) To Our knowledge, there is no applied study of these reactions to polymer synthesis.

Herein, we show a novel method for the synthesis of polythioamides from element sulfur and aliphatic diamines (Scheme 1). Type 1 and type 2 are the use of only one kind of aliphatic diamines such as m-xylylenediamine and 1,6-hexamethylenediamine. In type 3, the mixture of two kinds of aliphatic diamine, m-xylylenediamine and 1,6-hexamethylenediamine, was used as monomers.



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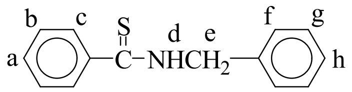
2. EXPERIMENTAL

Model reaction : The mixture of 0.5358g (5mmol) of benzylamine, 0.2405g (7.5mmol) of sulfur, and pyridine (10mL) was stirred at 110℃ for 24 h under nitrogen. The reaction solution was poured into 400mL of water. Product was filtered and dried under reduced pressure. Yield : 0.4056g (71%). IR (KBr) : 3240 cm^{-1} (N-H) and 1620 cm^{-1} (C=S). ^{1}H-NMR ($CDCl_3$) : δ7.76(t, H_a), 7.73(t, H_h),7.69(s, H_d) 7.45(t, $2H_c$), 7.43(s, $2H_b$), 7.37(t, $2H_f$), 7.35(t, $2H_g$)4.99 (d, $2H_e$) ppm.



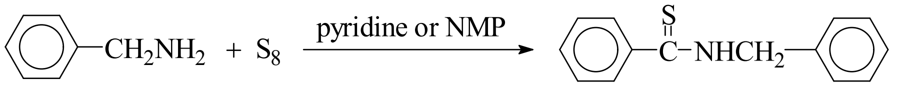
Polymerization (Type 1 and Type 3) : A typical polymerization procedure is as follows. The mixture of 1.3619g (10mmol) of m-xylylenediamine, 0.6418g (20mmol) of sulfur (20 mmol), and pyridine (2.5 mL) was stirred at 110℃ for 24 h under nitrogen. After cooling to room temperature, the solution was poured into water (400mL). Viscous precipitate was separated by decantation. The crude product was dissolved in DMF, and the residual sulfur was removed by filtration. Reprecipitation from the organic filtrate with water gave a pure polymer. Yield : 1.4525 g (98%), η inh : 0.24 dLg-1 (DMF, 30℃). IR (KBr) : 3229 cm^{-1} (N-H) and 1655 cm^{-1} (C=S). ^{1}H-NMR(DMSO-d_6) : δ10.79(s, 2H), 8.10-7.21(m, 8H), 5.93 (d, 4H) ppm.

Polymerization (Type 2) : A typical polymerization procedure is as follows. The mixture of 1.1621 g (10 mmol) of 1,6-hexamethylenediamine, 0.6413g (20mmol) of sulfur, and pyridine (2.5 mL) was stirred at 110°C for 48 h under nitrogen. During the polymerization, some precipitations on the flask occurred. Only reaction solution was poured into water (300mL) and stirred for a few hours. Filtrated product was dried at room temperature under reduced pressure. Crude polythioamide was washed with xylene to remove the residual sulfur. Obtained polythioamide was dried at room temperature under reduced pressure. Yield : 0.3717 g (49%), ηinh : 0.23 dLg^{-1} (H_2SO_4, 30℃), IR (KBr) : 1507 cm^{-1} (C=S).

3. RESULTS AND DISCUSSION

Model reaction

Sulfur is soluble in pyridine at room temperature, partially soluble in NMP on heating, and insoluble in DMF. In an initial approach, the reactions of benzylamine with sulfur in pyridine or NMP were carried out as the model reaction (Scheme 2), as reported procedure was no use of any solvents.



(2)

N-benzylthiobenzamide as coupling products could be prepared in 71% without any purification by the use of pyridine. the use of NMP gave no product. Therefore, pyridine could be used as reaction medium in the formation of thioamides.

Type 1 : the synthesis of polythioamide from m-xylylenediamine and sulfur

After conforming that the formation of thioamide bonds from amine and element sulfur in pyridine, the oxidative polymerization of m-xylylenediamine with various amount of sulfur was carried out at 110 ℃ close to the boiling temperature of pyridine. Theoretically, equimolar amount of sulfur based on amino group is necessary in this reaction according to plausible mechanism. As shown in Figure 1, the polymerization proceeded smoothly in the presence of 2 equivalent of element sulfur based on diamine monomers to give the corresponding polythioamide with the highest molecular weight. A small excess amount of sulfur suppressed the polymerization to decrease the yield and inherent viscosity of obtained polymer.

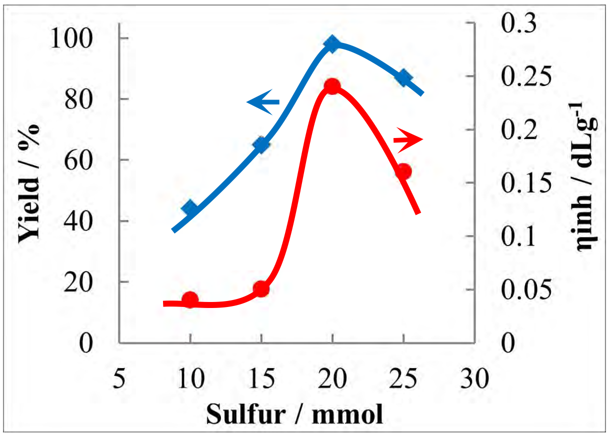


Figure 1 Effect of amount of sulfur on polymerization of m-xylylenediamine (10mmol) in pyridine at 110℃ for 24 h.

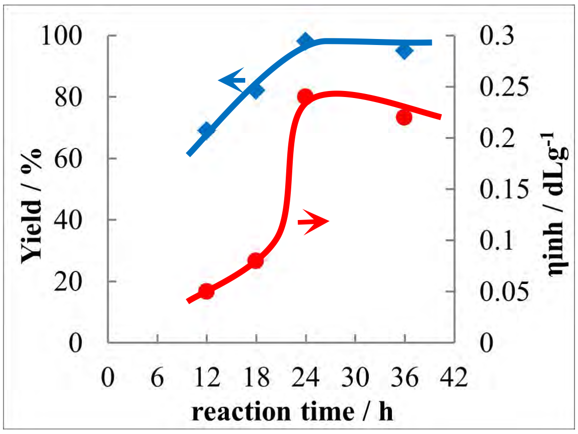


Figure 2 Effect of time on polymerization of m-xylylenediamine (10mmol) and sulfur (20mmol) in pyridine at 110℃.

The influence of polymerization time on the preparation of polythioamides was examined (Figure 2). With increasing polymerization time from 12 h to 24 h, the yields and inherent viscosities became larger and larger. The highest molecular weight was acquired as the polymerization time was 24 h. When the polymerization was prolonged, the inherent viscosity decreased slightly.

From above study, the optimum polymerization condition for the synthesis of polythioamides from m-xylylenediamine was achieved in pyridine, ratio of sulfur to diamines : 2 equiv., and polymerization time : 24 h.

The structure of polythioamide prepared from m-xylylenediamine and element sulfur was confirmed by IR and NMR spectroscopy. In IR spectrum of obtained polymer, the absorption peak attributed to the C=S bond was observed at 1655 cm^{-1}. Figure 3 shows the ^{1}H NMR spectrum of polythioamide prepared from m-xylylenediamine and element sulfur in DMSO-d$_6$. It has found that the polythioamide obtained has two structures, as shown in Figure 3. One is the symmetrical structure concerning with benzene ring and other is the unsymmetrical structure. The composition of symmetrical and unsymmetrical structures is about 40 : 60, calculated from the relative area of peaks of protons (a, b, and j) of phenyl moiety.

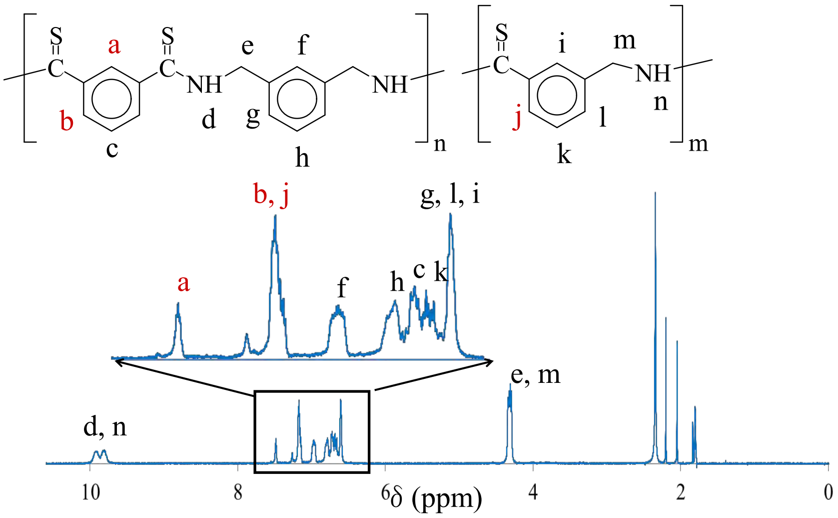


Figure 3 ^{1}H-NMR spectrum (DMSO-d_6) of polythioamide prepared from m-xylylenediamine and element sulfur in pyridine at 110℃ for 24 h.

Type 2 : the synthesis of polythioamide from 1,6-hexamethylenediamine and sulfur

Instead of m-xylylenediamine, 1,6-hexamethylenediamine was used as monomers. The oxidative polymerization of 1,6-hexamethylenediamine and element sulfur was attempted under various conditions. Figure 4 shows the yields and inherent viscosities of polythioamides prepared from equimolar amount of both diamines with various amounts of sulfur. 2 equiv. of element sulfur based on diamine monomers is also necessary for this polymerization. A small excess amount of sulfur suppressed the polymerization to decrease the yield and inherent viscosity of obtained polymer as same as type 1.

The influence of reaction time was investigated at 110°C, which is near to the boiling point of pyridine (Figure 5). When reaction time increased from 24 h to 36 h, yields of polythioamides increased even slightly. For longer polymerization time than 36 hours, yields became constant in about 50%. On the other hands, inherent viscosity of polythioamide prepared for 48 hours is highest (0.23 dLg^{-1}). Even for longer time, inherent viscosity decreased to 0.12 dLg^{-1}.

From above study, the optimum polymerization condition for the synthesis of polythioamides from 1,6-hexamethylenediamine was achieved in pyridine, ratio of sulfur to diamines : 2 equiv., and polymerization time : 48 h.

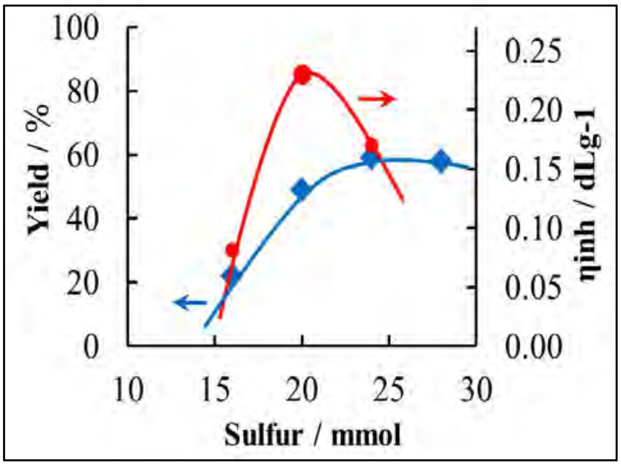


Figure 4 Effect of amount of sulfur on polymerization of 1,6-hexamethylenediamine (10mmol) in pyridine at 110℃ for 24 h.

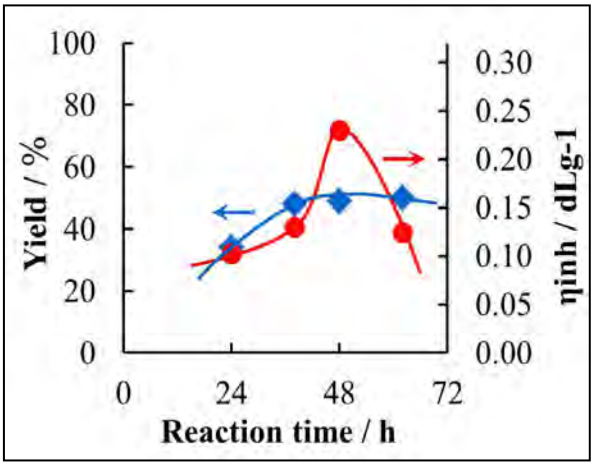


Figure 5 Effect of time on polymerization of 1,6-hexamethylenediamine (10mmol) and sulfur (20mmol) in pyridine at 110℃.

The structure of polythioamide prepared from 1,6-hexamethylenediamine and element sulfur was confirmed by IR. In IR spectrum of obtained polymer, the absorption peak attributed to the C=S bond was observed at 1507 cm^{-1}.

Type 3 : the synthesis of polythioamide from the mixture of m-xylylenediamine and 1,6-hexamethylenediamine with element sulfur

To determine the appropriate copolymerization conditions for equimolar mixture of m-xylylenediamine and 1,6-hexamethylenediamine as diamine monomers, the oxidative copolymerization with element sulfur in pyridine was carried out under various conditions. Figure 6 shows the yields and inherent viscosities of polythioamides prepared from equimolar amount of both diamines with various amounts of sulfur. 2 equiv. of element sulfur based on diamine monomers is also necessary for this copolymerization as same as type 1. However, a small excess amount of sulfur did not affect the yield and molecular weight of obtained copolymers.

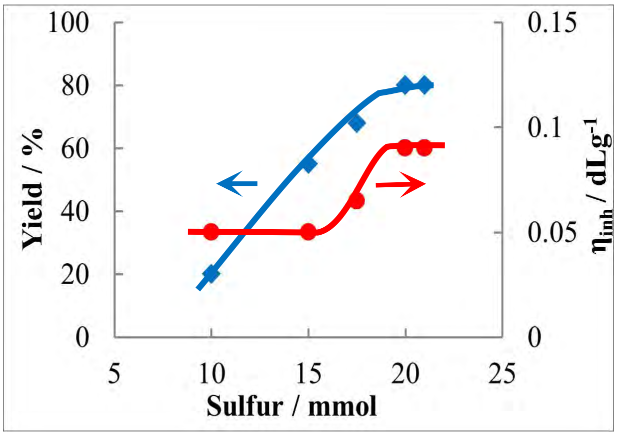


Figure 6 Effect of amount of sulfur on polymeri -zation of m-xylylenediamine (5mmol) and 1,6-hexamethylenediamine (5mmol) in pyridine at 110℃ for 24 h.

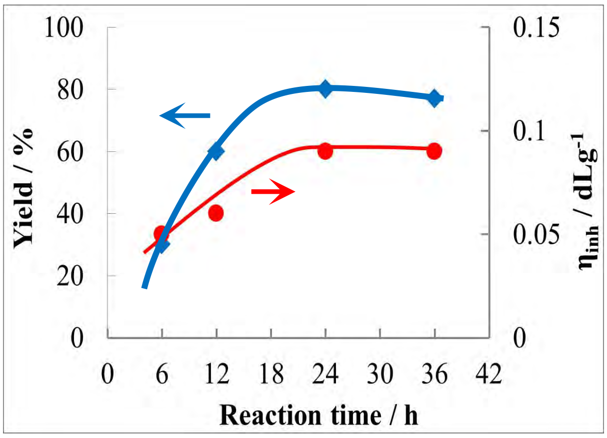


Figure 7 Effect of time on polymerization of m-xylylenediamine (5mmol), ,6-hexamethyl enediamine (5mmol), and sulfur (20mmol) in pyridine at 110℃.

The influence of copolymerization time on the preparation of polythioamides was examined (Figure 7). With increasing polymerization time from 6 h to 24 h, the yields and inherent viscosities became larger and larger. The highest molecular weight was acquired as the polymerization time was 24 h, as same as type 1 and type 2. When the polymerization was prolonged, the yield decreased slightly.

The behavior of the oxidative copolymerization of the mixture of diamines is not changed compored with the oxidative homopolymerization.

The structure of polythioamide prepared from m-xylylenediamine, 1,6-hexamethlenediamine, and element sulfur was also confirmed by IR and NMR spectroscopy. In IR spectrum of obtained polymer, the absorption peak attributed to the C=S bond was observed at 1644 cm^{-1}. Figure 6 shows the ^{1}H NMR spectrum of polythioamide prepared from m-xylylenediamine, 1,6-hexamethylenediamine, and element sulfur in DMSO-d_6. It has found that the polythioamide obtained has three structures, as shown in Figure 8. First is the unsymmetrical structure prepared from both diamines, second is the symmetrical structure prepared from only m-xylylenediamine, and third is the symmetrical structure prepared from only 1,6-hexamethylenediamine. The composition of these structures could be calculated from three equations shown below.

$$\begin{cases} \mathrm{H(aromatic)} : \mathrm{H(benzyl)} = 4l + 8m : 4m = x : y \\ \mathrm{H(aromatic)} : \mathrm{H(aliphatic)} = 4l + 4m : 4n = x : z \\ l + m + n = 1 \end{cases}$$

Here, l, m, and n represent the proportions of each structure in the copolymer, mentioned above, respectively. x, y, and z are the relative areas of each protons such as phenyl (a, b, c, h, i, j, m, n, o), benzyl (l), and methylene (p) adjusted to C=S in ^{1}H-NMR spectrum of polythioamides, respectively. It has been found that l : m: n is 74 : 24 :1 in the case of polythioamide prepared from 1:1 mixture of m-xylylenediamine and 1,6-hexamethylenediamine with sulfur.

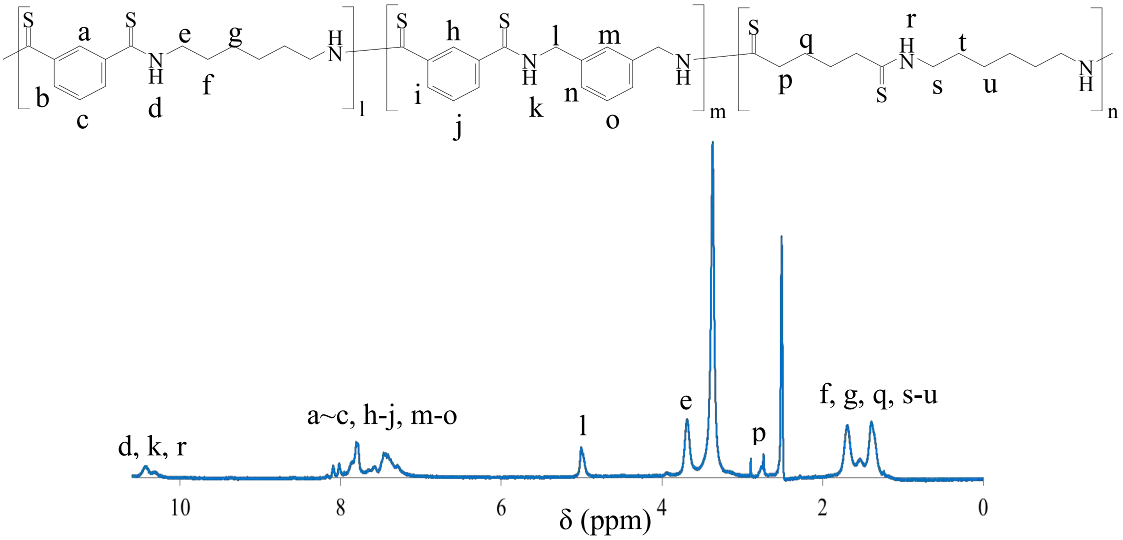


Figure 8 ^{1}H-NMR spectrum (DMSO-d_6) of polythioamide prepared from m-xylylenediamine, 1,6-hexamethylenediamine, and element sulfur in pyridine at 110℃ for 24 h.

The oxidative polymerizations of sulfur with various feed ratio (5/5 to 5/15) of m-xylylenediamine and 1,6-hexamethylenediamine were carried out under optimum condition obtained above (Table1). It is noted from Table 1 that the composition (l) of the unsymmetrical structure prepared from both diamines are constant, about 75%, even though the feed ratio of diamines changed. Increasing the content of 1,6-hexamethylenediamine, the composition (n) of symmetrical structure prepared from only 1,6-hexamethylenediamine gradually increased from 1% to 21%.

Table 1 Synthesis of polythioamides from m-xylylenediamine, 1,6-hexamethylenediamine, and sulfur[a)]

m-Xylylenediamine (mmol)	1,6-Hexamethylenediamine (mmol))	Sulfur (mmol)	Yield (%)	η inh[b)] (dLg^{-1})	l : m : n[c)]
5	5	20	68	0.12	74:25:1
5	7.5	25	66	0.06	75:11:14
5	10	30	64	0.06	75:8:18
5	15	40	99	0.06	75:4:21

a) pyridine (2.5mL) at 110℃ for 24h under nitrogen.

b) b) Measured at a concentration of 0.5 gdL^{-1} in DMF at 30℃

c) Calculated from the ^{1}H-NMR spectra of polythioamides.

4. CONCLUSIONS

In this study, three types of the oxidative polymerization of diamines and sulfur to provide polythioamides were investigated in detail. Pyridine is suitable polymerization solvent for all type of the oxidative polymerization, because of good solvent for sulfur and diamines. 2 equivalent of sulfur based on diamines is necessary to provide the polythioamides with higher molecular weights. Polythioamides prepared from one kind of diamines such as m-xylylenediamine and sulfur contained both symmetrical and unsymmetrical structures. When the use of two kinds of diamine monomers such as m-xylylenediamine and 1,6-hexamethylenediamine with element sulfur cause the three structures in copolymers, such as the unsymmetrical structure prepared from both diamines and two kinds of the symmetrical structure prepared from m-xylylenediamine or 1,6-hexamethylenediamine.

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