

Polydisulfide with Variable Molecular Weight

Haruhisa Akiyama, Jun'ichi Nagasawa, Fusae Nakanishi and Takashi Tamaki

National Institute of Materials and Chemical Research, 1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan
Tel: 81-54-4672, Fax: 81-298-54-4673, e-mail: h.akiyama@nimc.go.jp

A conventional method to control molecular weight of polydisulfide is presented. This polymer was obtained by reaction of 1,3-bis(6-bromohexyloxy)benzene with sodium disulfide. The reaction gave a polymer with high molecular weight in high yield, by the replacement of bromide to disulfide. Addition of dihexyl disulfide to the polydisulfides caused decrease in the molecular weight, on heating of the mixture of the polymer and dihexyl disulfide. This means dihexyl disulfide is inserted into polymer chains as terminal groups, due to the exchange of S-S bonds of polymer chains with those of dihexyl disulfide.

Key words: polymer, disulfide, molecular weight

1. INTRODUCTION

These days, many kinds of self-assembly materials have been widely investigated, and interesting findings such as organic sulfide self assembled films on gold substrates¹⁾, supramolecular liquid crystalline materials²⁾ and organic micro-tubes³⁾ have been reported. In such systems, weak non-covalent bonds like hydrogen bonds play a very important role to bring organized structures of assembled molecules, because this kind of bonds need only small energy for rearrangement during self-assembling. On the other hand, there is relatively stable and weak covalent bonds. One of those is a disulfide bond which is well known for utilization in the biological process. In an ordinary dialkyl disulfide compound, a bond between a sulfur and a sulfur is not so strong and not so weak. The energy to cleave the S-S bond is 60-70 kcal/mol⁴⁾ so that a disulfide has potential to be applied in a self-assembly system. Actually, it was known that mixing two kinds of dialkyl disulfides brings about disproportionation, resulting from exchange of disulfide bonds⁵⁾, indicating ability of rearrangement of S-S bonds. Here we have tried to investigate such ability of S-S bonds in the one dimensional system, that is a polymer chain.

Molecular weight of the polymer is closely related to the properties like glass transition temperature, viscosity and so on. That is one of the most important parameters, for application of polymers as functional materials. Regulation of molecular weight is usually achieved by control of the amount of the added initiator for polymerization, or by separation of polymers with a gel permeation chromatography (GPC) method or fractional reprecipitation. In this work, a more conventional method to control of molecular weight is proposed. As mentioned above, polymers having bonds with adequate bonding energy may show rearrangement of the weak bonds with reagents terminals. The exchange of S-S bonds in terminal and those in the polymer results in decrease of the molecular weight, as shown in Figure 1. For this purpose, we have synthesized a polymer which has disulfide bonds periodically in the polymer chains. As shown in Scheme 1, the polymer consists of disulfide bonds attached to benzene rings through hexyloxy spacers, and it is named polydisulfide here. Such

polymers as polyethylenedisulfide have been known in 1931 were reported⁶⁾, and after that further studies on the preparation⁷⁾ and the stability⁸⁾ of other polymers were reported. Dihexyl disulfide is selected as a terminal group in this study, since it has the same reactivity of S-S bonds as that of the polymer

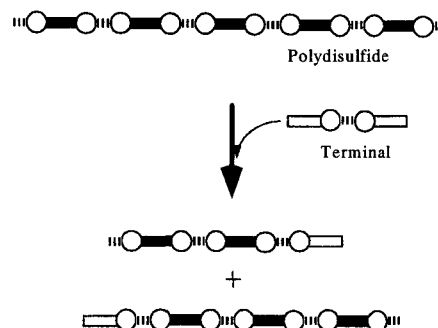


Figure 1. Illustration for exchanging of bonds in polymer chains with terminal groups. Black rectangles, vertical stripes and circles represent polymer chains, bonds of disulfides and sulfur atoms, respectively.

2. EXPERIMENTAL

2.1 Physical measurements

¹H-NMR spectra were measured with a Varian 300BB spectrometer. GPC studies were conducted on Shimadzu LC-5A equipped with Shodex KF 803 and 805 columns at a flow rate of 1 ml/min with tetrahydrofuran as an eluent, with monitoring the absorption at 275 nm. A differential scanning calorimetry (DSC) curve is measured by using a Seiko DSC200/SSC5000 system as the temperature increasing at a rate of 10°C/min.

2.2 1,3-Bis(6-bromohexyloxy)benzene.

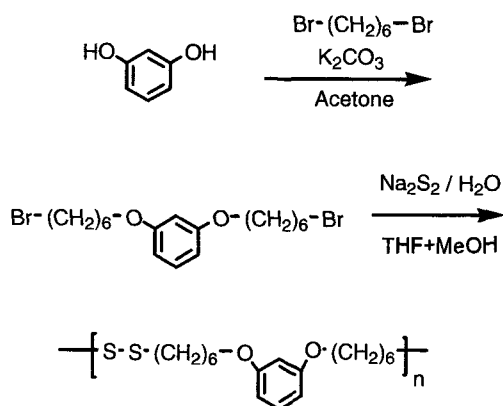
17.8 g of 1,6-dibromohexane and 2.0 g of resorcinol were dissolved in 60 ml of acetone. 12 g of potassium carbonate anhydride was added to the solution. After

stirring for 15 hr at 60°C, the mixture was diluted with ethyl ether and it was filtrated to remove potassium carbonates. The solvent was removed at a reduced pressure. The residual solution was purified by silica gel column chromatography with a mixture of hexane and ethyl acetate (9:1) to give 2.2 g of transparent liquid. The liquid was changed to crystals of mp 36–39°C, after being kept overnight at room temperature.

$^1\text{H-NMR}$ (CDCl_3); δ = 1.4–1.6 (8H, m, $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 1.79 (4H, t, t, Ar-O- $\text{CH}_2\text{-CH}_2$), 1.90 (4H, t, t, Br- $\text{CH}_2\text{-CH}_2$), 3.43 (8H, t, Br- CH_2), 3.94 (4H, t, Ar-O- CH_2), 6.4–6.5 (3H, m, Ar-H), 7.16 (1H, t, Ar-H). Calcd. for $\text{C}_{18}\text{H}_{28}\text{Br}_2\text{O}_2$: C, 49.56; H, 6.47. Found: C, 49.94; H, 6.39.

2.3 Polydisulfide

1.0 g of the monomer was dissolved in the mixture of 6.6 ml of tetrahydrofuran and 3.3 ml of methanol. 0.278 g of sodium disulfide (which was purchased from Wako pure chemical industries LTD.) in water (0.2 ml) was added to the solution. After stirring for 12 hr at 75°C, the solid mass appeared. The mixture was diluted with chloroform and washed with water 3 times. After drying over with sodium sulfate, the solvent was removed at a reduced pressure. The solid mass was dissolved in a small amount of tetrahydrofuran and the solution was poured into hexane. Precipitations were filtrated to separate 0.62 g of a polymeric material: $^1\text{H-NMR}$ (CDCl_3); δ 1.4–1.6 (8H, m, $\text{CH}_2\text{-CH}_2\text{-CH}_2$), 1.6–1.9 (8H, m, Ar-O- $\text{CH}_2\text{-CH}_2$, S-S- $\text{CH}_2\text{-CH}_2$), 2.53, 2.67, 2.88 (See the paragraph of structure of poly disulfide in results and discussion), 3.92 (4H, t, Ar-O- CH_2), 6.4–6.5 (3H, m, Ar-H), 7.14 (1H, t, Ar-H).



Scheme 1. Reaction scheme for the synthesis of polydisulfide

2.4 Dihexyl disulfide.

3.7 g of sodium disulfide in 1ml of water was added to the ethanol solution (20ml) of 5.0 g of 1-bromohexane. After stirring at 75°C for 8 hr, the solution was diluted with hexane and dried with magnesium sulfate. The solution was distilled under a reduced pressure (bp 120°C / 4 mmHg) to give 1.54 g of liquid.

2.5 Molecular weight change

The polymer was put into two micro tubes; one sample was mixed with dihexyl disulfide at 1/5 molar

equivalent to monomer units of polymer. They were covered with polypropylene caps on the top and heated at 160°C with an oil bath. After heating for 4 hr, the molecular weight of polymers was measured by GPC according to polystyrene standard samples.

3. RESULT AND DISCUSSION

3.1 Synthesis of monomer and polymer

The synthesis of a polydisulfide is shown in Scheme 1. The monomer, 1,3-bis(6-bromohexyloxy)benzene, was made from resorcinol and 1,6-dibromohexane by Williamson reaction. The yield was not so high because the reaction also brought about a by-product which was 1,6-bis[3-(6-bromohexyloxy)phenoxy]hexane. The monomer was polymerized with sodium disulfide by replacement of bromide to disulfide. At first, ethanol was used as reaction solvent according to the literature⁹, in which synthesis of diamyldisulfide was reported. But, in our case, no polymerization was observed because of the phase separation of monomers from the reaction solution. Then the reaction solvent was changed to a mixture of tetrahydrofuran and methanol (volume ratio=2:1) to improve the miscibility for monomer and water. As a result, the polymer was formed successfully. The yield of this polymerization was 68%, and the weight average of the molecular weight of the polymer was 16.5×10^4 . The DSC curve of the polymer showed no exothermic and endothermic peaks within the range between the room temperature and 180°C and also no peak corresponding to the glass transition temperature.

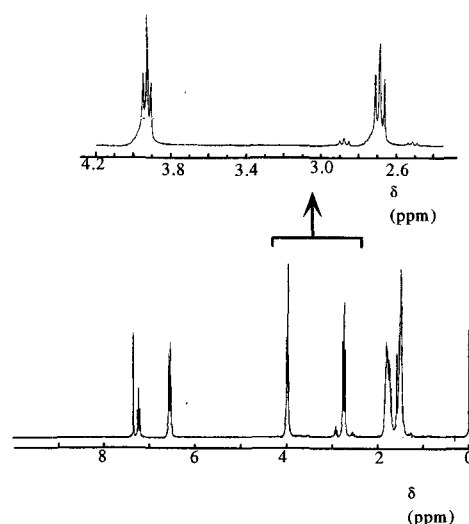


Figure 2. $^1\text{H-NMR}$ spectrum of polydisulfide.

3.2 Structure of polydisulfide

The reaction with sodium disulfide is suitable for synthesis of polydisulfides at the point that it gives a polymer of high molecular weight with a high yield. The structure of the polymer was evaluated by using $^1\text{H-NMR}$ spectra. Figure 2 shows the $^1\text{H-NMR}$ spectra of this polymer. In the spectra, there are the triplet peak at 3.92 ppm, and the three triplet peaks at 2.88, 2.67 and 2.53 ppm corresponding to the protons of methylenes

next to oxygen and sulfur, respectively. The integration of the area of the former peak and a sum of those of the latter peaks were exactly same. The latter three peaks indicate the presence of three kinds of moieties including sulfur atoms which were introduced into polymer chains. According to a handbook of NMR, it was found that the peaks at 2.67 and 2.53 ppm derived from methylene protons next to disulfide and monosulfide residues, respectively. Monosulfide probably comes from the reaction of sodium sulfide because a mixture of sodium sulfide and sulfur was used to obtain the sodium disulfide in the literature⁹. It means that the sodium monosulfide changes to disulfide by reaction with sulfur. In our case, it is thought that sodium disulfide was similarly changed to sodium mono- and trisulfide during the reaction. Then the peak at 2.88 ppm probably corresponds to methylene proton next to the trisulfide. Here, the amount of the mono- and trisulfide included in the polymer chain is less than 10%. Therefore, these bonds will affect little on an experiment for the molecular weight change which is mentioned in the next paragraph.

3.3 Molecular weight change

Figures 3a and 3b show the GPC curves of polymers before and after heating. Figure 3c represents a GPC curve of the polymer which was mixed with dihexyl disulfide and heated. The number average of the molecular weight (M_n) of the polymer heated without addition of dihexyl disulfide is similar to that of the polymer before heating. The difference of 7000 is not so much, so that a small portion of polymers might gel on hard heating. As a number average of molecular weight is proportional to an average of molecular lengths of polymers, this small difference in M_n means that the polymer hardly decomposes and depolymerizes on heating at 160 °C. On the other hand, the dispersity (M_w/M_n) of the polymer became large after heating. It reflects that the distribution of molecular lengths is changed due to the exchange of S-S bonds in polymer chains with those of other polymer chains. Moreover, the heating of the polymer after addition of dihexyl disulfides caused to decreasing in molecular weight. The number average was reduced to about one third of the initial value. This fact suggests the insertion of the terminal groups into polymer chains due to the exchange of S-S bonds in polymer chains with those of dihexyl disulfide. But, in this case, the molecular weight is still high compared as the theoretical value calculated from the amount of the added dihexyl disulfide. If the exchange was completely finished, a value of M_n should be about 2000. The measured value by GPC (Figure 3c, Table 1) is about 15 times larger than that value. It is certainly different from a real value because it was estimated from polystyrene-standard sample. But, 15 times difference is too large to be recognized as a deviation of GPC measurement. One possibility is that a S-S exchange reaction is not completed under this condition. Another one is a contribution of gels which induces the increase of molecular weight.

And also, the mechanism of disulfide exchange is not clear. It is well known that the mechanism of thiolate/disulfide interchange involves the nucleophilic attack of thiolate anion to the S-S bond¹⁰. Actually

disproportionation of two kinds of dialkyl disulfides⁵ was brought about in ethanol solution by using sodium hydroxide as a catalyst. However, in our case, the exchange reaction was observed under solvent-free and non-polar but hard heating condition. Then an exchange via homolytic cleavage process should be considered because the cleave energy of S-S bonds is not large. Now effects of heating temperature and an amount of terminal groups on change of molecular weight are being investigated, in order to establish the condition for control of molecular weight and to reveal a mechanism of the disulfide exchange.

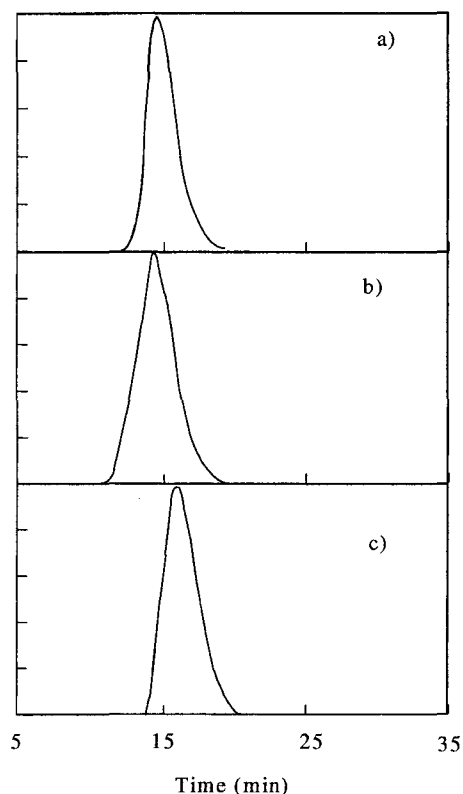


Figure 3. GPC spectra of polymers a) before heating, b) after heating at 160 °C for 4 hr and c) after heating at 160 °C for 4 hr with 1/5 molar equivalent of dihexyl disulfide.

Table 1. Molecular weight of polydisulfide on heating

	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	M_w/M_n
no heating	8.5	16.5	1.9
heating	9.2	28.5	3.1
heating after addition of dihexyl disulfide	3.2	7.0	2.2

4. CONCLUSIONS

A conventional synthesis method was found to prepare polydisulfide with sodium disulfide. The polydisulfide thus prepared underwent significant decrease in the molecular weight in the presence of dihexyl disulfide upon heating.

References

- (1) R. G. Nuzzo, B. R. Zegarski, L. H. Dubois, *J. Am. Chem. Soc.*, **109**, 733 (1987).
- (2) a) T. Kato, O. Ibata, M. Tokita, J. Watanabe, *Macromolecules*, **31**, 3551 (1998). b) T. Kato, "Handbook of Liquid Crystals Vol. 2B", Ed. by D. Demus, J. Goodby, G. W. Gray, H.-W. Spiess, V. Vill, WILEY-VCH, Weinheim (1998) pp. 969-979.
- (3) T. Shimizu, M. Kogiso, M. Matsuda, *Nature*, **383**, 487 (1996).
- (4) a) H. Macle, *Tetrahedron*, **19**, 1159 (1963). b) B. G. Gowenlock, J. Kay, J. R. Majer, *Trans. Faraday Soc.*, **19**, 2463 (1963).
- (5) G. Dalman, J. McDermed, G. Gorin, *J. Org. Chem.*, **29**, 1480-1484 (1963).
- (6) S. M. Martin Jr, J. C. Patric, *Ind. Eng. Chem.*, **28**, 1446 (1931)
- (7) K. Murayama, Y. Kato, S. Morimoto, *Elletin Chem. Soc. Jpn*, **40**, 2645 (1967).
- (8) K. Kishore, K. Ganesh, *Macromolecules*, **26**, 4700 (1993).
- (9) Miller, E.; Crossley, F.S.; Moore, M., *J. Am. Chem. Soc.*, **64**, 2322 (1942).
- (10) R. Singh, G. M. Whitesides, *J. Am. Chem. Soc.*, **112**, 6304 (1990).

(Received December 18, 1998; accepted January 20, 1999)