COMMUNICATION

ChemComm www.rsc.org/chemcomm

Characterization of sulfur exchange reaction between polysulfides and elemental sulfur using a ^{35}S radioisotope tracer method

Shigeru Yamada,[b] Danhong Wang,[a] Songri Li,[a] Megumi Nishikawa,[a] Eika Weihua Qian,[a] Atsushi Ishihara[a] and Toshiaki Kabe*[a]

[a] *Department of Chemical Engineering, Tokyo University of Agriculture and Technology, 2-24-16 Nakacho, Koganei, Tokyo 184-8588, Japan. E-mail: kabe@cc.tuat.ac.jp*

[b] *Dainippon Ink & Chemicals, Inc, 18 Higashifukashiba, Kamisu-machi, Kashima-gun, Ibaraki 314-0193, Japan*

Received (in Cambridge, UK) 8th January 2003, Accepted 12th February 2003
First published as an Advance Article on the web 28th February 2003

A sulfur exchange reaction between di-*tert*-butylpolysulfides and elemental sulfur was examined using a ^{35}S tracer method and the reaction mechanism was discussed.

Both dialkyl disulfide and a mixture of diaryl disulfides (aryl = tolyl, xylyl, and simple alkyl aromatics) are in commercial use.[1] In the presence of hydrogen sulfide and basic catalysts, organic disulfides dissolve elemental sulfur leading to the formation of a mixture of liquid polysulfides: $RSSR + S_8 \rightarrow RS_xR$. The value of x is dependent on the amount of elemental sulfur present and the temperature of the system.[2] This reaction is applied commercially to synthesize organic polysulfides which are now used widely as sulfiding agents, lubricant additives, and coke preventives *etc*.[3,4] In the presence of excess sulfur, organic polysulfides are in equilibrium with elemental sulfur, but if individual polysulfides are isolated, they disproportionate to a smaller polysulfide and elemental sulfur. It has been proposed that disproportionation of organic polysulfides occurs *via* radical species resulting from S–S bond homolysis.[5] It is expected that such radical species would have an important role in sulfur exchange reactions between polysulfides and elemental sulfur. However, there is no report in the literature on sulfur exchange reactions between polysulfides and elemental sulfur, but one study on the sulfur exchange reaction between disulfide and ^{35}S labeled elemental sulfur indicates that sulfur exchange reaction between disulfide and elemental sulfur almost did not occur.[6] The object of this study is to examine whether sulfur exchange reaction between polysulfides and elemental sulfur will occur or not and further to clarify the reaction mechanism of sulfur exchange using a ^{35}S tracer method.

In our recent study,[7] we synthesized di-*tert*-butylpolysulfide (DBPS) using isobutene and sulfur in the presence of hydrogen sulfide and solid base catalysts at 125 °C. The results showed that a mixture of DBPS was formed with an average sulfur loading of *ca.* 5, and the value of x varied from 3 to 8 as confirmed by high performance liquid chromatography (HPLC). A mixture of DBPS so prepared and ^{35}S labeled elemental sulfur were used in this study to investigate the sulfur exchange reaction. Before reaction, the following procedure was conducted to remove elemental sulfur dissolved in the polysulfides. Firstly, the mixture of polysulfides was dissolved in ethanol and the insoluble sulfur was eliminated by filtration. Trace sulfur still remaining in the polysulfides was then removed using a centrifugal separator at −40 °C, and following filtration finally the ethanol was removed from the polysulfides by distillation. After distillation, the composition of the polysulfides was clarified by HPLC and the total amount of sulfur in the polysulfides was measured using a Total Sulfur Analyzer (TS-100). The general procedure for the sulfur exchange reaction was as follows: *ca.* 0.5 g [^{35}S] sulfur and *ca.* 5 g polysulfides, which were weighed by a precision balance to four decimal places, were placed in a 50 mL flask fitted with a magnetic stirrer. The system was placed in a bath heater thermostated at the desired temperature. A transparent solution was obtained after reaction. The same procedure was conducted to separate elemental sulfur from polysulfides after reaction as that before reaction. Elemental sulfur and polysulfides were recovered separately, and the weights and radioactivities of elemental sulfur and polysulfides were measured, respectively. The radioactivity was measured using a liquid scintillation counter (Beckman LS-6500). The recovery of total weight and total radioactivity for each experiment is above 90%, indicating that it is possible to clarify the sulfur exchange reaction using the ^{35}S tracer method.

The total amount of sulfur in polysulfides after reaction and the radioactivities of polysulfides and elemental sulfur after reaction were summarized in Table 1. HPLC analysis of polysulfides confirmed that there was no significant difference in the composition of polysulfides (x = 3–8) before and after reaction. The sulfur exchange degree was used to evaluate the extent of sulfur exchange between polysulfides and elemental sulfur, which was defined as the ratio of exchanged amount of sulfur to total amount of sulfur in polysulfides. Considering that polysulfides are in equilibrium with elemental sulfur in the presence of excess sulfur, the sulfur exchange degree can be calculated from the ratio of radioactivity of polysulfides per gram sulfur to radioactivity of elemental sulfur per gram sulfur after reaction using the equation: $D_{EX} = 100 \times (R_{PS}/(S_{total}/100))/R_S$. The result obtained was also shown in Table 1.

Fig. 1 shows the change in the sulfur exchange degree with reaction time at 120 °C. The result clearly indicates that sulfur exchange reaction between polysulfides and sulfur is occurs very readily and the sulfur exchange degree increased to 44%

Table 1 The total amount of sulfur in polysulfides, and radioactivities of polysulfides and sulfur after sulfur exchange reaction

Time/h	Temp./°C	S_{total}[a] (%)	R_{PS}[b]/10^6 dpm g^{-1}	R_S[c]/10^6 dpm g^{-1}	D_{EX}[d] (%)
1/6	120	56.8	0.795	3.18	44.0
1	120	55.1	0.901	2.72	60.1
3	120	54.0	0.733	2.11	64.3
14	120	57.0	0.854	2.26	66.3
3	100	55.6	0.879	3.61	43.8
3	80	60.9	0.735	3.26	37.0

[a] S_{total}: Total amount of sulfur in polysulfides after reaction. [b] R_{PS}: Radioactivity of polysulfides per gram after reaction. [c] R_S: Radioactivity of sulfur per gram after reaction. [d] D_{EX}: Sulfur exchange degree of polysulfides, $D_{EX} = 100 \times (R_{PS}/(S_{total}/100))/R_S$.

DOI: 10.1039/b212438f

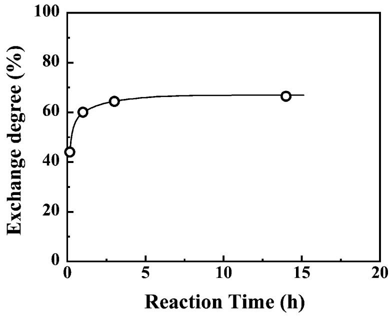
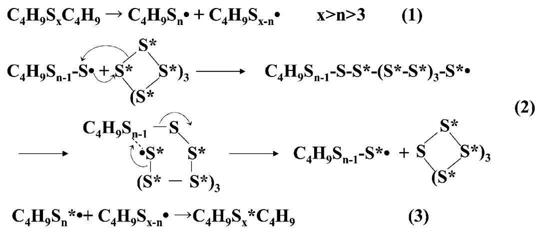


Fig. 1 The change in the sulfur exchange degree of polysulfides with reaction time at 120 °C.

immediately when the reaction was conducted for only 10 min. The exchange degree of sulfur approached a steady state of 64–66% and showed little change with reaction time until 14 h. The results shown in Table 1 also indicated that the sulfur exchange degree increased with reaction temperature when the reaction was conducted at 80, 100, 120 °C for 3 h. In order to understand the exchange reaction mechanism, the exchange reactions of di-*tert*-butylmonosulfide, di-*tert*-butyldisulfide and di-*tert*-butyltrisulfide with [^{35}S] sulfur were also conducted for 3 h at 120 °C. The results show that not only for monosulfide and disulfide but also for trisulfide, the exchange reaction with elemental sulfur almost did not occur, the exchange degrees were only 0.1, 0.2, 0.3% for monosulfide, disulfide and trisulfide, respectively, which were much lower than that for polysulfides. This can be explained by the fact that the scission of the C–S bond in monosulfide, disulfide and trisulfide almost did not occur due to the strong bond energy, and the scission of the S–S bond in trisulfide is considered to be difficult due to the high bond dissociation energies (BDE). From this result, it can be supposed that the sulfur connected to C in polysulfides is also difficult to exchange, similar to the sulfur in disulfide. Taking into account that polysulfides used in this study present an average sulfur loading of *ca.* 5, two of which connected to C are considered to be difficult to exchange, then the other three sulfurs are suggested to be exchanged easily which can be confirmed by the fact that the sulfur exchange degree of polysulfides approached a steady state of 64–66%. The reaction mechanism will now be discussed to give explanations for the trend of the sulfur exchange degree.

The associated kinetics of exchange reaction is possible by consideration of the mechanisms summarized in Scheme 1. These mechanisms are based on radical species which have been described in the literature to explain the disproportionation of organic polysulfides and the thermal decomposition of dimethyldisulfide (DMDS).[8–10] Equation (1) describes the homolytic cleavage of S–S bonds in a DBPS molecule. Polysulfides containing large numbers of sulfur atoms are expected to undergo internal S–S bond cleavage most readily to produce radical species $C_4H_9S_n^{\cdot}$, $C_4H_9S_{x-n}^{\cdot}$, with $x > n > 3$. Equation (2), which is described in detail, is of particular significance since it suggests the exchange reaction between sulfur in $C_4H_9S_n^{\cdot}$ and elemental sulfur (S_8) by the scission of S–S bond. The activation energy for the exchange reaction of polysulfides should be small (calculated to be 8.3 kJ mol^{-1}) since it involves the exchange reaction by a radical species. At low sulfur loadings (x = 3–4), S–S bond dissociation energies are relatively high and low populations of radicals are present. At higher sulfur loadings, the average BDE is expected to be somewhat lower[11–13] and the increased number of radicals would result in an increase in the sulfur exchange degree.



Scheme 1 Mechanism of sulfur exchange reaction between polysulfides and elemental sulfur.

In conclusion, when a mixture of polysulfides with an average sulfur loading of *ca.* 5 was exposed to excess [^{35}S] sulfur, sulfur exchange reaction between polysulfides and sulfur occurs very readily; and sulfur exchange degrees of 64–66% can be obtained.

Notes and references

1 R. J. Voorhees, E. R. Thomas and K. J. Kennelley, *Oil Gas J.*, 1991, Sept 2, , 85.
2 P. D. Clark, J. B. Hyne and K. L. Lesage, *Alberta Sulfur Res. Ltd. Quart. Bull.*, 1984, **20**, 1.
3 S. Yamada, W. Qian, A. Ishihara, G. Wang, L. Li and T. Kabe, *J. Jpn. Petr. Inst.*, 2001, **44**(4), 217.
4 W. Qian, S. Yamada, A. Ishihara, M. Ichinoiseki and T. Kabe, *J. Jpn. Petr. Inst.*, 2001, **44**(4), 225.
5 T. L. Pickering, K. J. Saunders and A. V. Tobolsky, *J. Am. Chem. Soc.*, 1967, **89**, 2364.
6 E. N. Gur'yanoava, *Vulkanizatsiya Rezin Sb.*, 1954, 101.
7 S. Yamada, S. Hirasawa, G. Awano, K. Hirabayashi, E. W. Qian, A. Ishihara and T. Kabe., *J. Jpn. Petr. Inst.*, 2003, **46**(1), 34.
8 T. Hirabayashi, S. Mohamad and H. Bock, *Chem. Ber.*, 1982, **115**, 483.
9 J. A. R. Coope and W. A. Bryce, *Can. J. Chem.*, 1954, **32**, 768.
10 J. E. Wajon, R. Alexander and R. I. Kagi, *J. Chromatogr.*, 1985, **319**, 187.
11 T. L. Pickering and A. V. Tobolsky, *Inorganic and Organic Polysulfides*, , in *Organic and Inorganic Sulfur Chemistry*, ed. S. Senning, Marcel Dekker, NewYork, 1972, vol. 111, p. 19.
12 L. Field, *Disulfides and Polysulfides*, , in *Organic Chemistry of Sulfur*, ed. S. Oae, Plenum Press, New York, 1977, p. 303.
13 R. Steudel, *Angew. Chem., Int. Ed. Engl.*, 1975, **14**, 655.