Effect of Thiophenol on Thermal Fragmentation of Polyisoprene

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ABSTRACT: As a fundamental study for chemical recycle of waste vulcanized rubber to reproduce functional polymers, polyisoprene (PI) was thermally fragmented to obtain low molecular weight PI in the presence of thiophenol (PhSH). PI ($M_w = 51,000$) was heated at 140°C under air atmosphere to give low molecular weight PI. The fragmentation in the presence of PhSH effectively decreased the molecular weight ($M_w = 7400$), which is significantly lower than that in the fragmentation in the absence of PhSH. The fragmented PI contained phenyl sulfide moieties based on the addition of phenyl thiyl radical to the hydrogen abstracted methylene or the double bond moieties. T_gs of the fragmented polymers were higher than that of the original PI, despite the lower molecular weights, probably because of the introduction of the rigid phenyl sulfide moieties and the terminal polar carbonyl groups formed by oxidation. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 106: 3051–3057, 2007

Key words: degradation; rubber; recycling

INTRODUCTION

Natural rubber is one of the most important and widely used natural polymers for industrial usage. The major component in natural rubber is *cis*-polyisoprene (PI). Principal use of PI rubber is for tires, which generally require vulcanization of PI by sulfur to acquire effective stiffness. Because vulcanized rubbers are consumable supplies, plenty of waste vulcanized rubbers are put out. Recent global warning on future drain of oil resources calls our attention to the recycling of waste vulcanized rubber.

Present typical approach for recycling of used vulcanized rubber is thermal recycle as fuel,[1–5] because calorific value of vulcanized rubber is higher than top grade coal. However, the thermal recycle emits numerous amounts of carbon dioxide and sulfur dioxide, which are responsible for green house effect and acid rain.

More substantial approaches to recycle waste vulcanized rubber are material and chemical recycles to produce tire and hosepipe, although they have been difficult because of the chemically modified structure of vulcanized rubber.[6–9] Efficient material and chemical recycles of waste vulcanized rubber require scission of crosslinked structure, which is accompanied by side reactions including scission of main chain. For material recycle, considerable efforts must be made to reproduce high performance vulcanized rubbers, which should keep the inherent structure of raw rubber, in spite of their promising aspect. Meanwhile, requirements for products differ in producing substances other than the original materials, namely chemical recycle is advantageous by its cost effectiveness. For example, mild fragmentation of vulcanized rubber will produce low molecular weight rubber, which can be easily utilized as ingredients for adhesives, networked polymers, and so forth. However, only fragmentation of PI under reverse conditions has been reported.[10–15] Thermal fragmentation of PI at 300°C produces an isoprene dimer (limonene) and oligoisoprene ($1000 > M_n$).[16] However, limonene that causes sick house syndrome seems to be a less appropriate recycle product.

As a fragmentation at milder conditions, we focused on researches on plasticization of synthetic rubber at milder conditions by addition of thiols.[16–21] However, the chemical structure of the products, which inherently should rule properties of products, was less studied in spite of the well-evaluated mechanical properties. The number–average molecular weights (M_n) decreased with the increase of sulfide structure, while the viscosity increased. This will mean that the addition of thiol accompanies molecular weight increase by some side reactions. We accordingly investigated thermal fragmentation mechanism of PI in the presence of PhSH (PhSH), and report herein the fragmentation acceleration ability of PhSH to control the thermal fragmentation behavior.

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Materials and instruments

Polyisoprene (PI; $M_w = 51,000$, $M_w/M_n = 3.71$, cis-1,4-unit : trans-1,4-unit : 3,4-unit = 79 : 14 : 7) was obtained from Sigma-Aldrich, (^{1}H NMR (CDCl$_3$, δ): 1.66–1.74 (3H, —CH$_2$—C(—CH$_3$)=CH—CH$_2$—), 1.82–2.12 (4H, —CH$_2$—C(—CH$_3$)=CH—CH$_2$—), 4.96–5.24 (1H, —CH$_2$—C(—CH$_3$)=CH—CH$_2$—)). Thiophenol (PhSH) and methanol were obtained from Kanto Kagaku. All reagents were used as received.

^{1}H and ^{13}C NMR spectra (270 and 67.5 MHz, respectively) were recorded with a JEOL EX-270 spectrometer with tetramethylsilane as an internal standard; the δ values are given in ppm. IR spectra were recorded with a Jasco FT/IR-470 Plus spectrometer and the wavenumbers are given in per centimeter. M_n and weight–average molecular weights (M_w) and molecular weight distribution (M_w/M_n) were estimated by size exclusion chromatography on a Tosoh SC-8020 instrument (columns: TSK gel, TSH-G$_{MH}$HXL, G4000HXL, G3000HXL, and G2500HXL tandem columns, eluent: THF at 40°C) after calibration with polystyrene standards.

Differential scanning calorimetry (DSC) was performed using a Seiko DSC6200 instrument. Samples ($\sim$ 5 mg) were put in aluminum open pans and measurements were carried out from -80 to 150°C at a heating rate of 10°C min^{-1} in nitrogen flow. Glass transition temperatures (T_gs) were determined from endothermic shifts of baselines in DSC curves.[22]

Typical procedure of thermal fragmentation of PI

PI (2.00 g, 29.4 mmol/U) was dissolved in PhSH (1.00 equiv to the C=C moieties, 3.20 g) at room temperature, and the mixture was stirred at the same temperature for 10 min. The solution was stirred at 140°C for 10 h under air atmosphere. The mixture diluted with dichloromethane was poured into methanol. The resulting methanol insoluble precipitate adhered conical flask was collected by filtration and was purified by decantation. The precipitate was dried under vacuum to obtain yellow viscous polymer ($M_w = 7400$, $M_w/M_n = 1.85$). The PhSH introduction ratio was calculated from ^{1}H NMR spectroscopy.

^{1}H NMR (CDCl$_3$, δ): 0.70–1.08 (3 × 0.26H, —CH$_2$—CH(—CH$_3$)—CH(—SPh)—CH$_2$—, —CH$_2$—(PhS—)C(—CH$_3$)—CH$_2$—CH$_2$—), 1.08–1.41 (4 × 0.17H, —CH$_2$—CH(—CH$_3$)—CH(—SPh)—CH$_2$— and 6 × 0.19H, —CH$_2$—(PhS—)C(—CH$_3$)—CH$_2$—CH$_2$—), 1.47–1.62 (3H × 0.7, —CH$_2$—C(—CH$_3$)=CH—CH$_2$—, —CH$_2$—C(—CH$_3$)=CH—CH(—SPh) —: trans), 1.62–1.71 (3H × 0.30, —CH$_2$—C(—CH$_3$)=CH—CH$_2$—, —CH$_2$—C(—CH$_3$)=CH—CH(—SPh)—: cis), 1.82–2.12 (4H, —CH$_2$—C(—CH$_3$)=CH—CH$_2$—), 2.84–3.20 (1 × 0.17H, —CH$_2$—CH(—CH$_3$)—CH(—SPh)—CH$_2$—), 3.42–3.66

(1 × 0.12H, —CH$_2$—C(—CH$_3$)=CH—CH(—SPh)—), 4.96–5.24 (1H ×1.00, —CH$_2$—C(—CH$_3$)=CH—CH$_2$—, —CH$_2$—C(—CH$_3$)=CH—CH(—SPh)—), 7.02–7.50 (5 × 0.48H, C$_6$H$_5$—) ppm. ^{13}C NMR (CDCl$_3$, δ): 18.0–20.1 (—CH$_3$), 26.0–27.0, 27.9–29.3, and 33.4 (—CH$_2$—C(—CH$_3$)=CH—CH$_2$—), 23.4–24.6, 29.3–30.3, 34.2–35.6, and 36.2–37.5 (—CH$_2$—CH(—CH$_3$)—CH(—SPh)—CH$_2$—, —CH$_2$—(PhS—) C(—CH$_3$)—CH$_2$—CH$_2$—), 38.7–41.1 and 41.1–43.8 (—CH$_2$—CH(—CH$_3$)—CH(—SPh)—CH$_2$—), 57.4–57.7 (—CH$_2$—C(—CH$_3$)=CH—CH(—SPh)—), 58.7–59.4 (—CH$_2$—(PhS—) C(—CH$_3$)—CH$_2$—CH$_2$—), 125.1–127.7, 129.1–130.7, and 131.7–133.0 (C$_6$H$_5$—), 136.1–136.9, 127.0–131.0, and 137.5–139.2 (C=C in 1,4-polymerized unit), 112.3–112.9 and 139.9–141.0 (C=C in 3,4-polymerized unit). IR (NaCl): 3057, 3023, 2927–2826 (—C—H, —CH$_2$—, —CH$_3$), 2000–1700 (Ph), 1642 (C=C of 3,4-polymerized unit), 1583 (C=C of Ph), 1452, and 1377 (C=C of PI), 1156 (—CH$_3$ in cis-1,4-polymerized unit), 1025 (—CH$_3$ of trans-1,4-polymerized unit), 888 (=CH$_2$ in 3,4-polymerized unit), 838 (=C—H in 1,4-polymerized unit).

RESULTS AND DISCUSSIONS

Thermal fragmentation of PI

PI was heated at 140°C for 10 h under air in the presence and absence of PhSH to obtain thermally fragmented PIs (TFPIs). Each reaction decreased M_ws of methanol insoluble products from 51,000 to 7400 and 28,000, respectively. It is of notice that the obvious decrease of M_w was observed in the initial stage of the fragmentation in the presence of PhSH. This result suggests that PhSH acted as a fragmentation accelerator. The M_w/M_ns also decreased from 3.71 to 1.74 and 2.24, respectively (Fig. 1). The slightly decreased M_w/M_ns, which did not depend on addition of PhSH, suggest the random fragmentation (Fig. 1).

PhSH addition and double bond such as Unit A —CH$_2$—C(—CH$_3$)=CH—CH$_2$— and Unit E —CH$_2$—CH<C(—CH$_3$)=CH$_2$ contents were calculated from the ^{1}H NMR spectrum as follows. PhS-content was calculated from integral ration of the signal intensities attributable to the aromatic and all the other protons. The ratio of phenyl sulfide containing units (a) Unit B: —CH$_2$—C(—CH$_3$)=CH—CH(—SPh) — (b) Units C: —CH$_2$—CH(—CH$_3$)—CH(—SPh)—CH$_2$—, and (c) Unit D: —CH$_2$— (PhS—) C (—CH$_3$) —CH$_2$—CH$_2$— was calculated from the integral ratio of signals at 2.84, 3.42–3.66, and 7.00–7.30 ppm, respectively. As shown in Figure 2, phenyl sulfide content increased and the double bond content decreased. This suggests that the fragmentation at the double bond moieties becomes slower as the reaction proceeds (discussed later).

As the reaction proceeded, amounts of methanol insoluble parts decreased especially in the absence of PhSH (Fig. 3). The methanol soluble parts contained
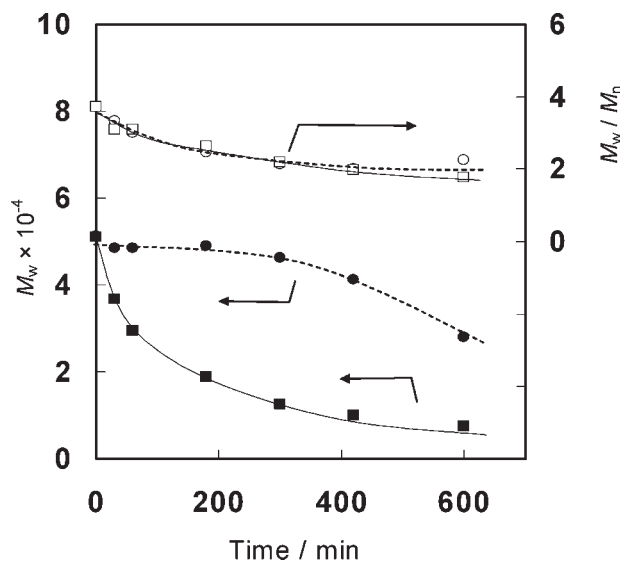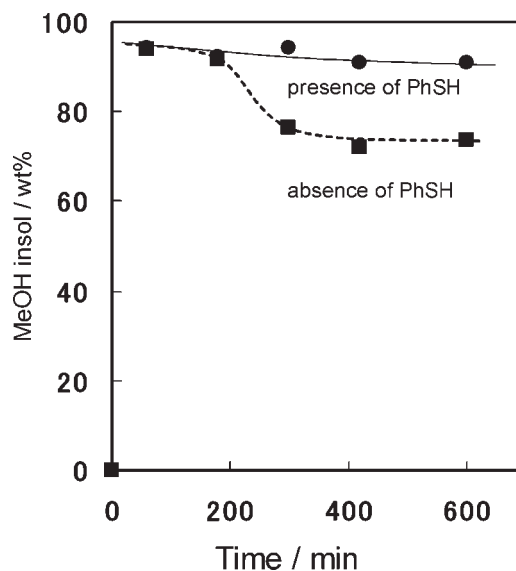
Figure 1 Relationship between M_w, M_w/M_n versus reaction time in thermal fragmentation of PI at 140°C in the presence (plain line) and absence (dotted line) of PhSH. Absence of PhSH M_w ● M_w/M_n ○; presence of PhSH M_w ■ M_w/M_n □.

oligoisoprenes, M_w of which ranged from ∼ 500 to ∼ 2000. ^{1}H NMR spectroscopic analysis revealed that the methanol soluble part obtained in the presence of PhSH contained diphenyl disulfide originated from the oxidization of PhSH under air atmosphere.

IR spectroscopic analysis revealed that the methanol insoluble products obtained in the absence of PhSH contain ketone and aldehyde structure probably produced by oxidation of double bond moieties in PI. The ^{13}C NMR spectrum also revealed the presence of the carbonyl groups based on the characteristic signals at
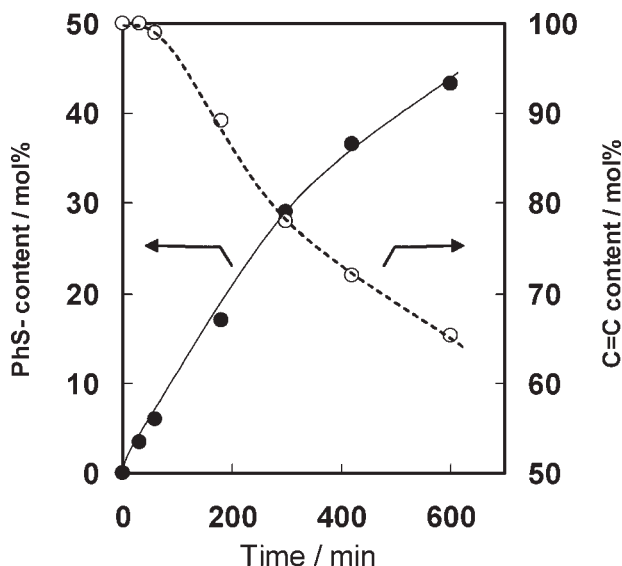
Figure 2 Relationship between reaction time, phenyl sulfide, and double bond content in TFPI obtained in the presence of PhSH.


Figure 3 Relationship between reaction time and yield of methanol insoluble product (wt %) obtained by the thermal fragmentation of PI in the presence (plain line) and absence (dotted line) of PhSH.

197.00 and 210.00 ppm, as well as the ^{1}H NMR spectrum showing a signal at 9.32 ppm assignable to aldehyde group. In contrast, these carbonyl groups were not observable in the methanol insoluble products obtained in the presence of PhSH. The different terminal structure may result in the different yields of the methanol insoluble products. That is, the polar carbonyl groups in oligoisoprene may solubilize in methanol.

Structure of thermally fragmented polyisoprenes

The ^{1}H NMR spectra of TFPIs are shown in Figure 4(b,c) with the signal assignments. The ^{1}H NMR spectrum of TFPI obtained in the absence of PhSH revealed that the chemical structure was not obviously changed. The ^{1}H NMR, ^{13}C NMR, and IR spectroscopic analysis suggested the presence of C=O attributable to ketone or aldehyde moieties [Figs. 4(b), 5, 6(b)], which were also observed in the spectra of the methanol soluble product. The fragmentation termini of the TFPIs probably are aldehyde and ketone moieties originate from oxidation[23,24] [Figs. 4(b), 5, 6(b)]. The double bond content is determined as 80 mol %, suggesting the presence of some side reactions such as radical coupling of double bond moieties.
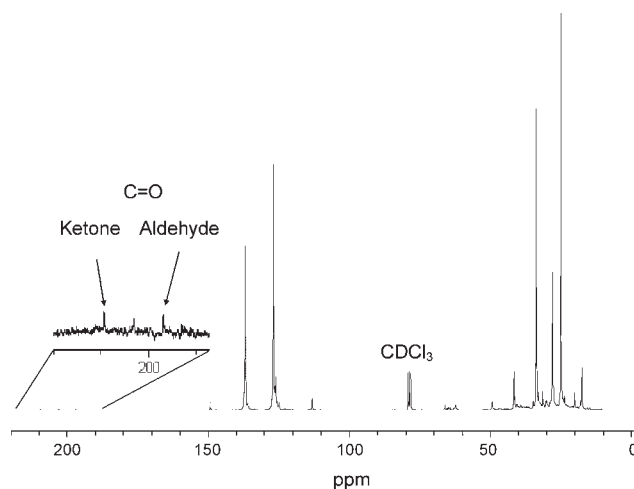
We speculated the structure of TFPI obtained in the presence of PhSH by ^{1}H NMR spectroscopic analysis. The ^{1}H NMR spectrum of the TFPI obtained in the presence of PhSH exhibited relatively broad and obviously increased aliphatic proton peaks (0.70–3.80 ppm), compared with the spectrum of original PI [Fig. 4(a)], in which signals assignable to saturated
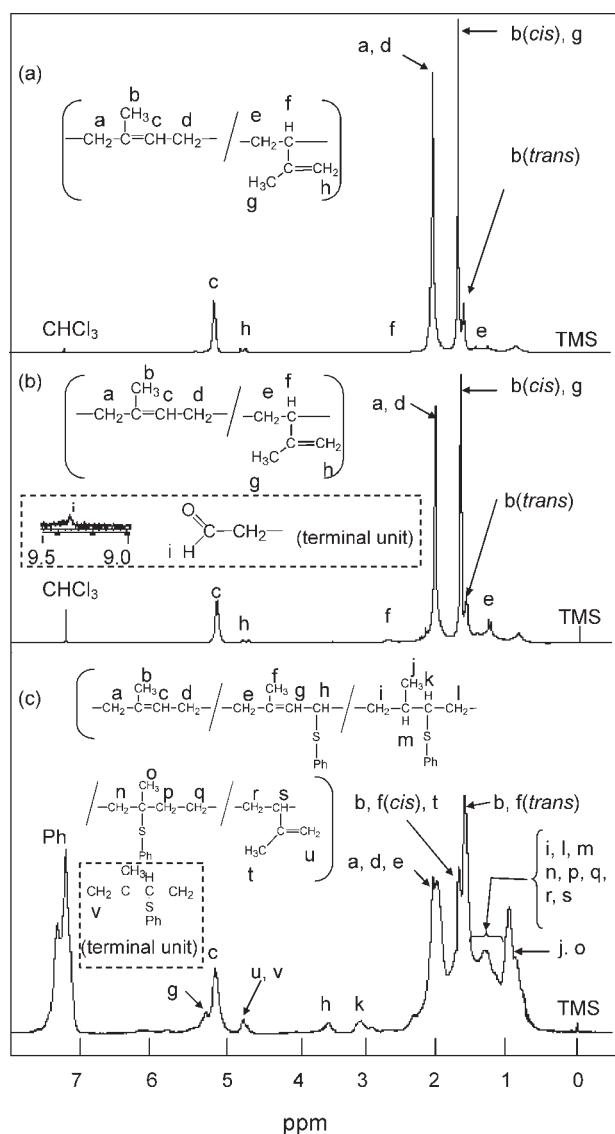
Figure 4 ^{1}H NMR spectra of PI (a), TFPI in the absence (b), and presence of PhSH (c).

aliphatic moieties are observed at 0.70–2.50 ppm [Fig. 4(c)]. The increased aliphatic signals is ascribable to the addition of phenyl thiyl radical to consume double bond moieties, which also resulted in increasing peaks at 2.84 and 3.42–3.66 ppm assignable to the methine groups connected with the phenyl sulfide groups and peaks at 1538 (C=C in Ph) and 1667–2000 cm^{-1} (Ph) to phenyl moiety [Figs. 4(c) and 6(c)]. The incorporation molar ratio of phenyl sulfide moieties was calculated as 43.00% from the integral ratios of the aliphatic and aromatic protons. The addition of PhSH took place onto both the allylic methylene and the double bond moieties, whose ratios were determined as 23.00 and 77.00%, respectively.

The addition of phenyl sulfide moiety also differed from the spectral pattern of olefinic protons. The 3,4-unit increased in the TFPI obtained in the presence of PhSH, which was not observed for the TFPI obtained

Figure 5 ^{13}C NMR spectrum of TFPI obtained in the absence of PhSH.

in the absence of PhSH. This agrees with a report described in the thermal fragmentation of PI enriches *trans*-1,4- and 3,4-microstructure.[3] Therefore, it is suggested that PhSH may also isomerize 1,4-units.[16] The slight increase of peak at 4.7 ppm is also ascribable to
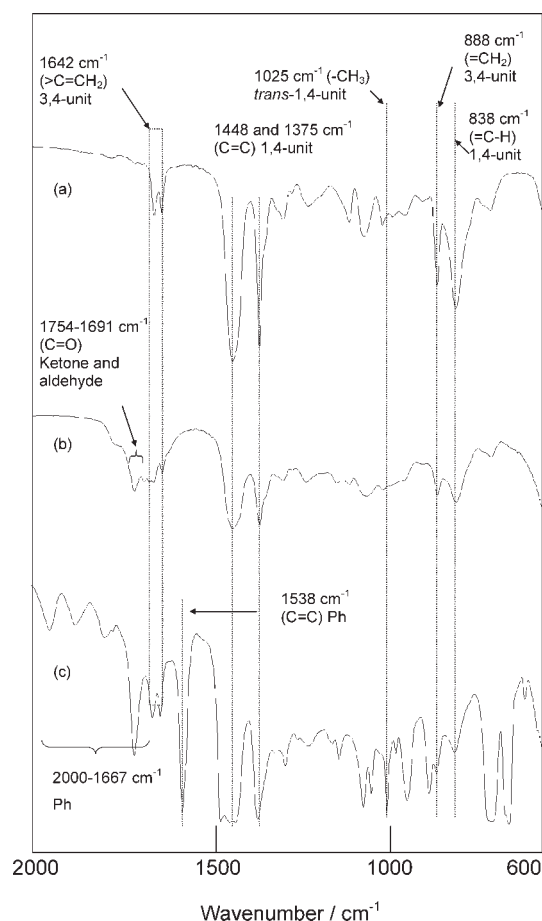
Figure 6 IR spectra of PI (a), TFPI in the absence (b), and presence of PhSH (c).
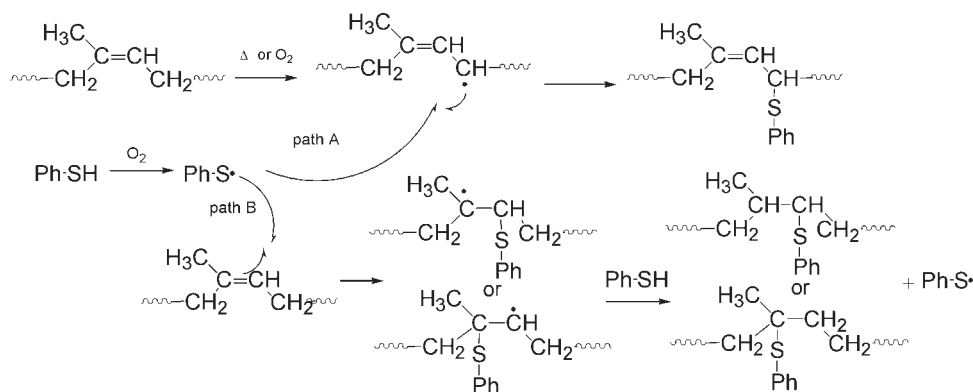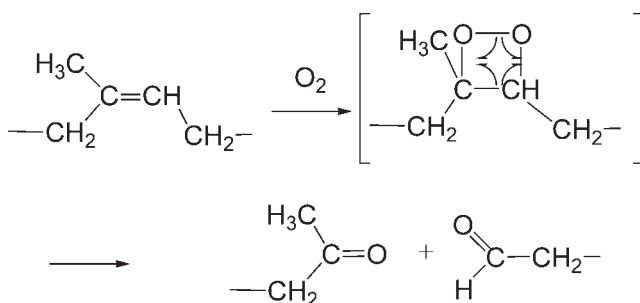
Scheme 1 PhSH addition to polyisoprene.

the terminal vinylidene moieties. The ratios of units containing on reacted and produced double bond moieties were calculated from the integral ratio of the signal intensities attributable to the corresponding double bond moieties and the saturated moieties-reacted PhSH. The double bond content of the TFPI obtained in the presence of PhSH was calculated as 66.5% by ^{1}H NMR spectroscopy.

The slightly broadened signals assignable to the double bond moieties in the main chain [see in Fig. 4(c)] originates from the isomerization of cis-double bonds into thermodynamically favorable trans-double bonds by free radicals.[3,25] The isomerization was clearly confirmed by the increased peak at 1.6 ppm assignable to methyl group attached to the trans-double moiety. The cis-trans ratio was ∼ 30 : 70, which had been 86 : 14 in the original PI. On the basis of the aforementioned peak assignments, the composition of the TFPI obtained in the presence of PhSH was estimated to be A : B : C : D : E = 52.7 : 9.8 : 17.2 : 16.3 : 4.0.

The structural elucidation allowed the authors to suggest the following addition and fragmentation mechanism. Plausible reaction pathways of the thiol addition onto PI is illustrated in Scheme 1. The second pathway is the addition of the thiyl radical that can add to PI through two pathways.[26,27] The first pathway is the radical coupling of the thiyl radical with hydrogen-abstracted PI produced by oxidation (Path

A). The resulting radical makes PhSH to phenyl thiyl radical by the chain transfer mechanism, in which the thiyl radical subsequently reacts in the same manner (Path B).[25,28–31] Thermal fragmentation of PI by oxidation (i.e., fragmentation without PhSH) can proceed via several pathways as already reported.[32,33] The most plausible fragmentation pathway in the absence of PhSH is shown in Scheme 2. That is, oxidation of double bond moieties forms cyclic peroxide as the degradation intermediate, and the subsequent fragmentation of both oxygen–oxygen and carbon–carbon bonds leads to ketone and aldehyde moieties as confirmed in the forementioned spectra.

As already mentioned, M_w of TFPI obtained in the presence of PhSH obviously decreased. This means that PhSH has the fragmentation acceleration effect. The plausible PI fragmentation mechanism in the presence of PhSH under air is as follows[32,33]: upon addition of thiyl radical to double bond in PI, a produced radical in the main to lead the fragmentation of neighboring carbon–carbon bonds (Scheme 3). The cleavage increase vinylidene termini instead of ketone or aldehyde termini, which agrees well with the above-mentioned ^{1}H NMR spectra. The resulting radical probably reacts with PhSH to reproduce thiyl radical again.

Thermal properties of thermally fragmented polyisoprene obtained in the presence of thiophenol

Thermal behavior of the TFPIs was evaluated by DSC measurement. T_gs and M_ws of PI and the TFPI obtained in the presence and absence of PhSH are shown in Table I. Despite the decrease in molecular weights, both the T_gs of TFPI increased. On the contrary, T_g of low molecular weight polymer is generally lower than that of high molecular weight polymer.[34–36] This would be ascribable to the different chemical structure of PI and the TFPIs. That is, the differences include cis-trans content, induction of phenyl sulfide moiety, and polar oxidized terminals. The typical T_g

Scheme 2 Fragmentation of polyisoprene in the presence of oxygen.
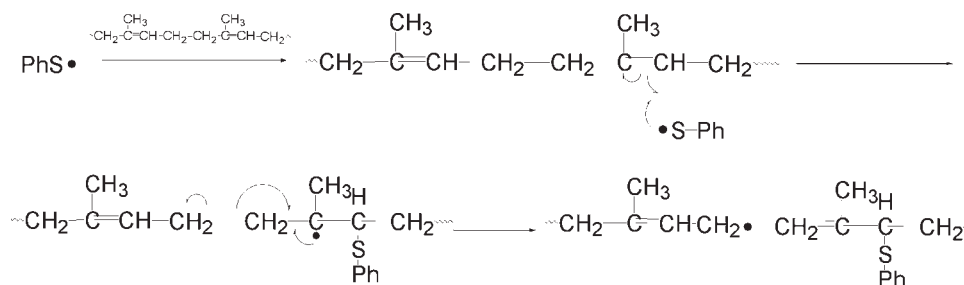
Scheme 3 Fragmentation of polyisoprene in the presence of PhSH.

of *trans*-PI, which is thermoplastic elastomer, is −68°C, indicating that *cis-trans* isomerization is not the main factor of the increased T_gs. Considering that the higher T_g of TFPI obtained in the presence of PhSH, incorporation of phenyl sulfide moiety seems to be the major factor than the presence of ketone and aldehyde moieties in the termini. This presumption may be supported by the obviously lower M_w of the TFPI in the presence of PhSH, which should mean that TFPI obtained in the presence of PhSH contains the more termini than TFPI in the absence of PhSH. This results agree with the thermal behavior of PI obtained in the presence of methane thiol, in which the Gehman T_{100} values (approximately equal to T_g) increased with the increasing methyl sulfide moiety.[17] These sulfide moieties decreased the mobility of the PI chain by the induction of the less flexible structure and the decrease of double bond moieties.

SUMMARY

The above-mentioned results can draw the following summary. PI can be fragmented thermally to low molecular weight PI both in the presence or absence of PhSH at 140°C. PhSH accelerated the fragmentation, which was accompanied by the modification with phenyl sulfide moiety. Because the added phenyl sulfide moieties can cleave during the reaction, isomerization of *cis*-double bond to *trans*-one takes place. On the other hand, *cis-trans* isomerization was not observed in the thermal fragmentation in the absence of PhSH. Despite the decrease in molecular weights, the T_gs increased, probably because of the introduced rigid phenyl sulfide moiety and polar carbonyl group

originated from oxidation. The fragmentation acceleration ability of thiol would develop facile technique to obtain low molecular weight PI.

References

1. Brazier, D. W.; Schwartz, N. V. Rubber Chem Technol 1978, 51, 1061.
2. Nishimura, K. Kautsch Gummi Kunstst 1993, 46, 989.
3. Mouri, M. Nippon Gomu Kyokaishi 2000, 73, 621.
4. Adhikari, B.; De, D.; Maiti, S. Prog Polym Sci 2000, 25, 909.
5. Joung, S. N.; Park, S. W.; Kim, S. Y.; Yoo, K.; Bae, S. Y. J Chem Eng Jpn 2001, 34, 132.
6. Dhawan, J. C.; Bencsath, A. F.; Legendre, R. C. ACS Symp Ser 1993, 514, 380.
7. Akiba, M. Nippon Gomu Kyokaishi 1997, 70, 597.
8. Kojima, M.; Ogawa, K.; Mizoshima, H.; Tosaka, M.; Kohjiya, S.; Ikeda, Y. Rubber Chem Technol 2003, 76, 957.
9. Usukura, S.; Ikeda, Y.; Kouzai, H. Koubunshi Ronbunshu 2004, 61, 95.
10. Lemayev, N. V.; Kurbatov, V. A.; Liakumovich, A. G. Polym Sci USSR 1981, 23, 419.
11. Pchelintsev, V. V.; Denisov, Y. T. Polym Sci USSR 1983, 25, 909.
12. Chiantore, O.; Guaita, M.; Lazzari, M.; Hadjichristidis, N.; Pitsikalis, M. Polym Degrad Stab 1995, 49, 385.
13. Anachkov, M. P.; Rakovski, S. K.; Stefanova, R. V. Polym Degrad Stab 2000, 67, 355.
14. Bussière, P.-O.; Gardette, J.-L.; Lacoste, J.; Baba, M. Polym Degrad Stab 2005, 88, 182.
15. Asano, Y.; Yamazaki, H.; Nagasawa, T.; Choi, W.; Endo, T. J Network Polym Jpn 2005, 26, 81.
16. Cataldo, F. J Anal Appl Pyrolysis 1998, 44, 121.
17. Pierson, R. M.; Gibbs, W. E.; Meyer, G. E.; Naples, F. J.; Saltman, W. M.; Schrock, R. W.; Tewksbury, L. B.; Trick, G. S. Rubber Chem Technol 1958, 31, 213.
18. Swaney, M. W.; Serinuk, G. E. (to Standard Oil Development Company). U.S. Pat. 2,481,257 (1949).
19. Swaney, M. W.; Banes, F. W. (to Standard Oil Development Company). U.S. Pat. 2,556,856 (1951).
20. Fryling, C. F. (to Philips Petroleum Company). U.S. Pat. 2,543,844 (1951).
21. Pritchard, J. E. (to Philips Petroleum Company). U.S. Pat. 2,543,867 (1951).
22. Hatakeyama, T.; Quinn, F. X., Eds. Thermal Analysis: Fundamentals and Applications to Polymer Science, 2nd ed.; Wiley: New York, 1999.
23. Rodrigues, J. F.; Bezerra, C. C. Polym Bull 1996, 36, 347.
24. Li, G. Y.; Koeing, J. L. Appl Spectrosc 2002, 56, 1390.

TABLE I
T_g and M_w of TFPIs and the Original PI

Polymer	T_g (°C)[a]	M_w^b
TFPI in the absence of PhSH	−54.6	28,000
TFPI in the presence of PhSH	−26.4	7400
Original PI	−62.5	51,000

[a] Determined from endothermic shifts of the baselines in DSC curves.
[b] Estimated by SEC analysis (eluent: THF, polystyrene standards).

25. Chen, F. Z.; Qian, J. L. Fuel 2002, 81, 2071.
26. Oswald, A. A.; Griesbaum, K.; Hudson, B. E., Jr. J Org Chem 1963, 28, 2351.
27. Oswald, A. A.; Griesbaum, K.; Hudson, B. E., Jr. J Org Chem 1963, 28, 2355.
28. Midgley, T.; Henne, A. L. J Am Chem Soc 1929, 51, 1215.
29. Bevilacqua, E. M. J Am Chem Soc. 1955, 77, 5396.
30. Hrivikova, J.; Blazkova, A.; Lapcik, L. J Appl Polym Sci 1980, 25, 761.

31. Tamura, S.; Murakami, K. Nippon Gomu Kyokaishi 1980, 53, 649.
32. Wallace, T. J.; Schriesheim, A. J Org Chem 1962, 27, 1514.
33. Walling, C.; Helmreich, W. J Am Chem Soc 1958, 81, 1144.
34. Fos, T. G.; Flory, P. J. J Appl Phys 1958, 21, 581.
35. Rudin, A.; Burgin, D. Polymer 1975, 16, 291.
36. O'Driscoll, K.; Sanayei, R. A. Macromolecules 1991, 24, 4479.