Variation of Pyrolysis Pattern of Polyisoprene Depending on Temperature

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The use of pyrolysis-gas chromatography (pyrolysis-GC) for the characterization and analysis of polymers has been used since the development of the technique in 1959.[1-3] A number of different pyrolyzer designs are currently in general use, each with its own advantages and disadvantages. The major types are resistive filament, Curie point, and furnace pyrolyzers.[4] Pyrolysis-GC, pyrolysis-mass spectrometry (MS), and pyrolysis-GC/MS have been used for decades to elucidate the structures of rubbers.[5-11] The mechanism for the pyrolysis of polyisoprene has been studied by several groups.[11-13] The main volatile products formed from polyisoprene by pyrolysis are isoprene and isoprene dimer species.[11,12] Chien and Kiang[11] identified and quantitatively analyzed volatile products obtained from polyisoprene by pyrolysis at 315-384 °C using pyrolysis GC. Matheson and coworkers[13] studied the effect of carbon black filling on the pyrolysis behavior of natural and synthetic rubbers at 850 °C. Ghebrehiwet and coworkers[10] studied analysis of rubber blends using pyrolysis technique coupled with GC/MS at 600 °C. Amounts of volatile products formed from a novolak rein by pyrolysis and their pyrolysis patterns depend on pyrolysis temperatures.[14] Pyrolysis pattern of polyisoprene will also varies depending on the pyrolysis temperature. However, detail studies about this have not been performed. In the present work, the influence of the pyrolysis temperature on the pyrolysis pattern of polyisoprene (the kinds and the relative abundances of the volatile products) was studied using pyrolysis-GC.

Figure 1 gives the pyrolysis-GC chromatograms of polyisoprene. Figures 1(a), (b), and (c) are the chromatograms obtained at 445, 590, and 764 °C of the pyrolysis temperatures, respectively. The major peaks in the pyrolysis-GC chromatograms are at 2.4, 9.6, 10.9, and 11.4 min of the retention time. The pyrolyzed products at 9.6, 10.9, and 11.4 min of the retention time are isoprene dimer species. The peaks at 2.4, 9.6, 10.9, and 11.4 min are assigned to isoprene, 1,4-dimethyl-4-vinylcyclohexene, 1-methyl-5-(1-methylethenyl)-cyclohexene, and 1-methyl-4-(1-methylethenyl)-cyclohexene, respectively, by pyrolysis-GC/MS analysis. The 1-methyl-4-(1-methylethenyl)-cyclohexene is formed from the head-to-tail sequence of polyisoprene by cyclization, while the 1,4-dimethyl-4-vinylcyclohexene and 1-methyl-5-(1-methylethenyl)-cyclohexene are formed from the head-to-head and tail-to-tail sequences of polyisoprene by cyclization.[12] The number of the volatile products increases and the pyrolysis pattern becomes complex by increasing the pyrolysis temperature. By increasing the pyrolysis temperature, the amount of the volatile products increases and the pyrolyzed products smaller than the isoprene dimer species such as butenes, isoprene, 2,3-dimethylcyclopentene, octene, and *m*-xylene[11] also increase. There are only some isoprene dimer species and no isoprene monomer in the pyrolysis-GC chromatogram at 358 °C. This means that the thermal energy of 358 °C is not enough to form the isoprene monomer from polyisoprene.

By increasing the temperature, the relative abundances of the isoprene dimer species of 1,4-dimethyl-4-vinylcyclohexene, 1-methyl-5-(1-methylethenyl)-cyclohexene, and 1-methyl-4-(1-methylethenyl)-cyclohexene decrease while that of the isoprene monomer increases. Figure 2 gives the variation of the relative abundance ratio of the isoprene dimer species including the pyrolyzed products at 9.6, 10.9, and 11.4 min of the retention time to the isoprene monomer as a function of the 1/T (1/K). The relative abundance ratio decreases by increasing the temperature. The solid line in Figure 2 results from the curve fitting and has the eq. (1),

$$P_{d/m} = 3.35110^6\,(1/T)^2 - 5.97710^3\,(1/T) + 3.077 \qquad (1)$$

where the $P_{d/m}$ is the relative abundance ratio of the isoprene

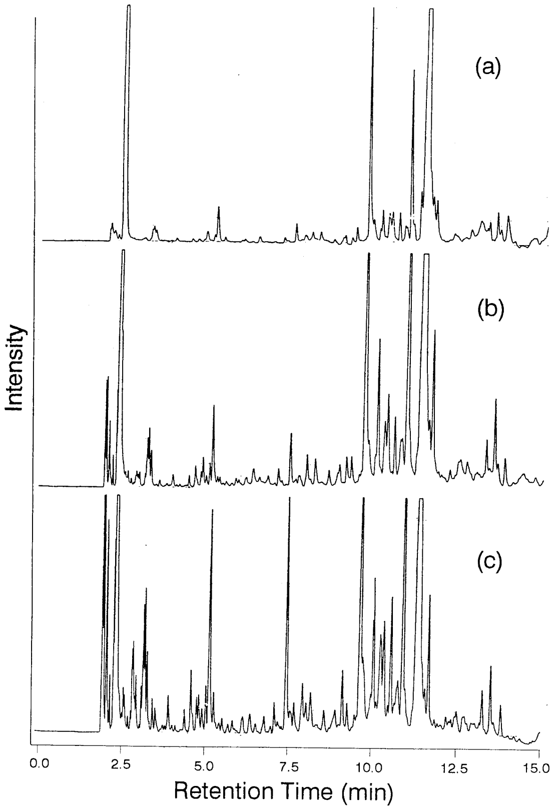

Figure 1. Pyrolysis-GC chromatograms of polyisoprene at 445 (a), 590 (b), and 764 °C (c).

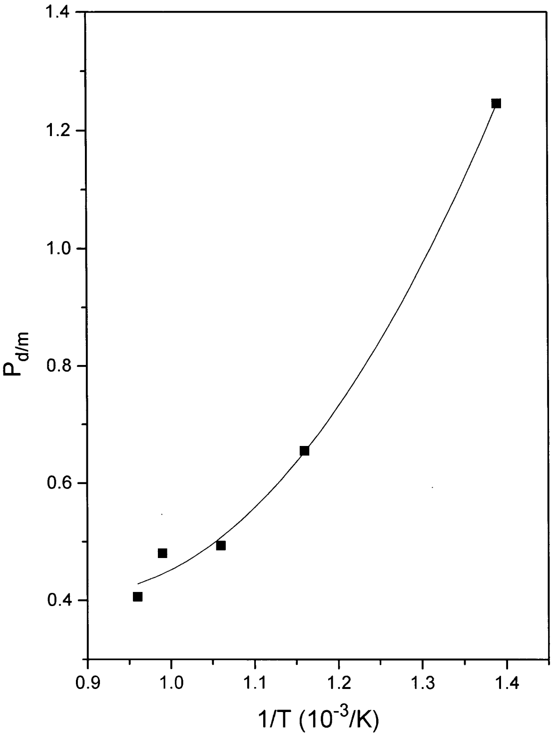

Figure 2. Variation of the relative abundance ratio of the isoprene dimer species to the isoprene monomer, $P_{d/m}$, as a function of 1/T.

dimer species to the isoprene monomer and the 1/T is the inverse temperature in 1/K. The r^2 for the curve fitting is 0.996. The $P_{d/m} = 1.0$ means that probabilities to form the isoprene monomer and the isoprene dimer species by pyrolysis are the same while the $P_{d/m} = 0.5$ means that probability to form the isoprene monomer is higher than that to form the isoprene dimer species by twice. The temperatures having the $P_{d/m}$ of 1.0 and 0.5 are about 490 and 676 °C, respectively.

A homopolymer has a structure of multiple repetition of a single type of repeat unit which may contain one or more species of monomer unit. Sequence of a homopolymer is determined by polymerization types of head-to-tail and head-to-head (or tail-to-tail) when the repeat unit is asymmetric. Since isoprene is asymmetric there are head-to-head and tail-to-tail linkages as well as head-to-tail linkage between 1,4-isoprene units in polyisoprene.[5] The pyrolyzed products at 9.6 and 11.4 min are the isoprene dimer species and are formed from the head-to-head and head-to-tail sequences of polyisoprene. The relative abundances of these species are varied with the pyrolysis temperatures. Their relative abundance ratio depending on the temperature was measured to compare the favorabilities for their formations from polyisoprene by pyrolysis. Figure 3 gives the variation of the relative abundance ratio of 1-methyl-4-(1-methylethenyl)-cyclohexene (11.4 min) to 1,4-dimethyl-4-vinylcyclohexene (9.6 min) as a function of the temperature. The relative abundance ratio decreases by increasing the temperature. The solid line in Figure 3 results from the curve fitting and has the eq. (2),

$$P_{h\text{-}t/h\text{-}h} = -0.01748\,T + 23.48871 \tag{2}$$

where the $P_{h\text{-}t/h\text{-}h}$ is the relative abundance ratio of 1-methyl-4-(1-methylethenyl)-cyclohexene to 1,4-dimethyl-4-vinylcyclohexene and the T is the temperature in K. The correlation coefficient for the curve fitting is 0.997. The eq. (2) means that the $P_{h\text{-}t/h\text{-}h}$ increases by decreasing the temperature. That is, at low temperatures the formation of 1-methyl-4-(1-methylethenyl)-cyclohexene is more favorable than that of 1,4-dimethyl-4-vinylcyclohexene. This may be because the formation of 1-methyl-4-(1-methylethenyl)-cyclohexene from the polyisoprene requires less energy than that of 1,4-dimethyl-4-vinylcyclohexene. Their heats of formation (DH) were calculated using AM1 semi-empirical calculations to explain the variation of the $P_{h\text{-}t/h\text{-}h}$ depending on the pyrolysis temperature. The heats of formation for 1-methyl-4-(1-methylethenyl)-cyclohexene and 1,4-dimethyl-4-vinylcyclohexene are -14.54 and 9.65 kJ/mol, respectively. Therefore, one can say that the formation of 1-methyl-4-(1-methylethenyl)-cyclohexene from polyisoprene is more favorable than that of 1,4-dimethyl-4-vinylcyclohexene. Figure 4 shows the production mechanism of both products. The eq. (2) say that the $P_{h\text{-}t/h\text{-}h}$ decreases by about 2% per 10 K as the pyrolysis temperature increases.

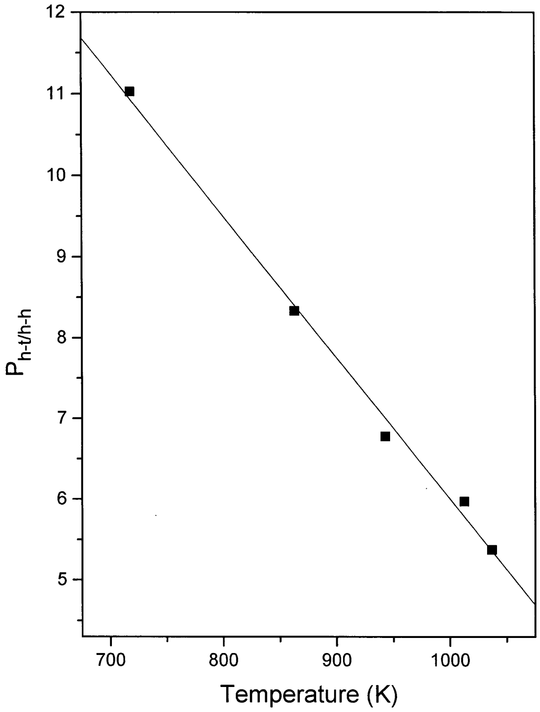

Figure 3. Variation of the relative abundance ratio of 1-methyl-4-(1-methylethenyl)-cyclohexene to 1,4-dimethyl-4-vinylcyclohexene, $P_{h\text{-}t/h\text{-}h}$, as a function of temperature. The 1-methyl-4-(1-methylethenyl)-cyclohexene and 1,4-dimethyl-4-vinylcyclohexene are formed from the head-to-tail and head-to-head sequences, respectively.

Experimental Section

Nipol IR 2200 was employed as polyisoprene. Pyrolysis-GC chromatograms of the samples were acquired with Curie point pyrolyzer (JHP-22) and HP5890 gas chromatography. The sample (0.6 ± 0.1 mg) was pyrolyzed for 5 sec. Temperature of the pyrolyzer was controlled by using various ferro-

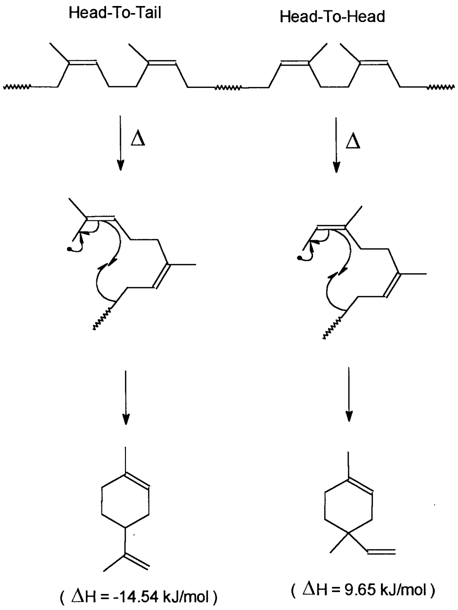

Figure 4. Production mechanism and heats of formation of 1-methyl-4-(1-methylethenyl)-cyclohexene and 1,4-dimethyl-4-vinyl-cyclohexene from the head-to-tail and head-to-head sequences of polyisoprene by pyrolysis.

magnetic foils. The pyrolysis temperatures were 358, 445, 590, 670, 740, and 764 °C. HP-5 capillary column (length 21m) was used. Temperatures of the injector and detector of the GC were 200 °C. The GC oven temperature program was as follows. (1) The initial temperature was 60 °C and keeping for 3 min. (2) Increasing the temperature from 60 °C to 160 °C with a rate of 8 °C/min. GC/MS spectra of principal peaks were acquired with Shimadzu QP-2000. The sample (about 0.5 mg) for the GC/MS analysis was pyrolyzed at 590 °C for 5 sec.

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