Alkylated 2,2'-Bithiophenes and 2-Phenylthiophenes in the Composition of Pyrolysis Products of High-Sulfur Kerogen

D. A. Bushnev

Institute of Geology, Komi Scientific Center, Ural Division, Russian Academy of Sciences,
Pervomaiskaya ul. 54, Syktyvkar, 167610 Russia
e-mail: boushnev@geo.komisc.ru
Received July 6, 2006

Abstract—Compounds from the 5-*n*-alkyl-2,2'-bithiophene, 5-*n*-alkyl-5'-methyl-2,2'-bithiophene, 5-*n*-alkyl-2-phenylthiophene, and 5-*n*-alkyl-2-*o*-tolylthiophene homologous series were synthesized to prove their presence in the pyrolysis products of sulfur-rich kerogen. A study of the pyrolysis products of sulfur-vulcanized polybutadiene confirmed that these compounds can be formed via the thermal transformation of *n*-alkyl polysulfur-bound fragments of sulfur-rich kerogen. The earlier proposed scheme that assumes the dependence of the composition of the pyrolysis products of sulfur-rich kerogen on its saturation with sulfide bridges was experimentally corroborated.

The presence of alkylated bithiophene and phenylthiophene derivatives was first detected in the pyrolysis products of kerogen from a quarry near Orbagnoux (France) [1], which is extremely enriched in organic sulfur and has an S/C atomic ratio of 0.24. Several homologous series of these organic sulfur compounds were identified in [1] only on the basis of mass spectral data and the analysis of products of reductive desulfurization of the aromatic fraction of the pyrolysis products. Later, these bicyclic sulfur compounds were found in the pyrolysis products of kerogen from oil shale of the Kashpirskoe deposit [2] for which the S/C value is 0.063.

Our studies on the material of Upper Jurassic oil shales from the Sysola deposit showed that the yield of bithiophenes and phenylthiophenes during kerogen pyrolysis depends on the concentration of S_{org} in the kerogen [3]. We proposed an ingenious scheme to explain the dependence of the composition of the sulfur-containing products of kerogen pyrolysis on the amount of bound organic sulfur in the kerogen [3].

Since the identification of alkylated bithiophenes and phenylthiophenes in pyrolysis products has been based to date only on their mass spectra and results of analysis of desulfurization products, one of the aims of the present work was the synthesis of authentic compounds. Another objective of the study was to find experimental evidence for the feasibility of the formation of bithiophenes and phenylthiophenes during the pyrolysis of a polymer consisting of long *n*-alkyl chains crosslinked by sulfur atoms.

EXPERIMENTAL

Synthesis of Authentic Compounds

The alkylation of commercially available (Fluka) 2,2'-bithiophene (**I**) through thienyllithium derivatives [4] was used for the synthesis of 5,5'-dimethyl-2,2'-bithiophene (**III**) and 5-butyl-2,2'-bithiophene (**V**). The synthesis scheme is shown below.
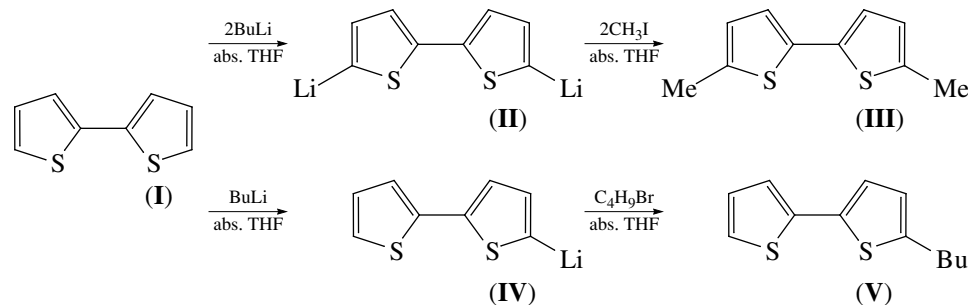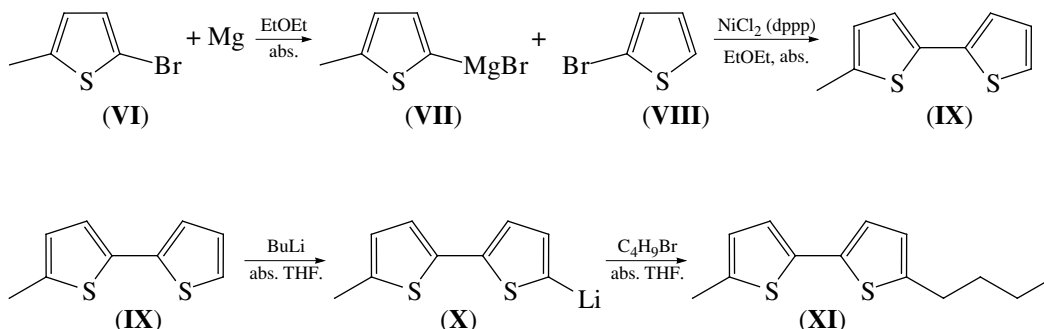
Synthesis of 5,5'-dimethyl-2,2'-bithiophene (III).
Compound **I** (0.5 g, 3 mmol) was dissolved in anhydrous tetrahydrofuran in a nitrogen atmosphere. A 2.5-fold excess of iodomethane was slowly added at −15°C. The mixture was stirred for 2 h. A fourfold excess of iodomethane was added to the resulting solution of **II**. The mixture was refluxed for 2 h. After the addition of water and diethyl ether, the organic phase was separated and successively washed with 2N HCl (*3) and a saturated solution of NaCl (*2). The ethereal solution was dried over MgSO$_4$. After the solvent was distilled off, compound **III** thus formed was purified by column chromatography on silica gel (*n*-hexane). The yield was 75%.

Synthesis of 5-butyl-2,2'-bithiophene (V). Compound **I** (0.5 g, 3 mmol) was dissolved in anhydrous tetrahydrofuran in a nitrogen atmosphere. A 1.2-fold excess of BuLi was slowly added at −15°C. The mixture was stirred for 2 h. A twofold excess of 1-bromobutane was added to the resulting solution of **IV**. The mixture was refluxed for 2 h. After the addition of water and diethyl ether, the organic phase was separated and successively washed with 2N HCl (*3) and a saturated NaCl solution (*2). The ethereal solution was dried over MgSO$_4$. The GC–MS analysis of the reaction mixture showed that it contained the unreacted bithiophene, 5-butyl-2,2'-bithiophene, and 5,5'-dibutyl-2,2'-bithiophene. The desired product (**V**) was isolated via two successive TLC separations of the mixture. The yield was 4%.

5-Methyl-2,2'-bithiophene (**IX**) was synthesized via the Kumada coupling reaction [5]. 5-Butyl-5'-methyl-2,2'-bithiophene (**XI**) was prepared via the butylation of **IX** through the lithium derivative (**X**) as shown in the scheme:
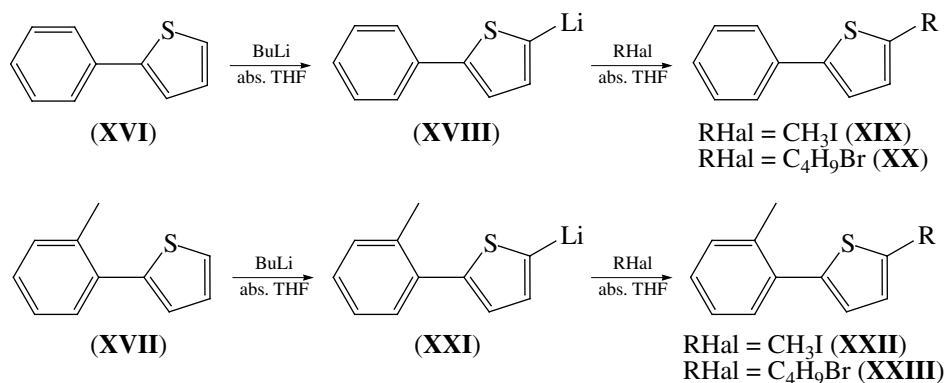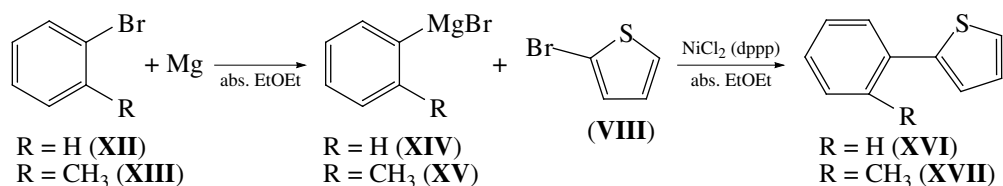

Synthesis of 5-methyl-2,2'-bithiophene (IV).
Compound **VI** (5.73 g, 32 mmol) in absolute ether was added dropwise to a 1.05-fold excess of Mg in absolute ether. The formation of **VII** was stimulated by the addition of an iodine crystal. The mixture was refluxed for 0.5 h until the dissolution of magnesium. Bromothiophene **VIII** (5.64 g, 35 mmol) in an ethereal solution containing a suspension of NiCl$_2$(dppp) (0.08 g) was added to the resulting solution at 0°C. The solution was refluxed for 2 h. After cooling, the reaction mixture was washed with 2N HCl. After phase separation, the aqueous layer was repeatedly extracted with ether, and the organic phases were combined. The resulting solution of **IX** was washed with a saturated NaCl solution and dried over MgSO$_4$. The product was purified by column chromatography on silica gel (*n*-hexane). The yield of **IX** was 40%.

Synthesis of 5-butyl-5'-methyl-2,2'-bithiophene (XI). Compound **IX** (0.57 g, 3.16 mmol) was dissolved in anhydrous tetrahydrofuran in a nitrogen atmosphere. A 1.2-fold excess of BuLi was slowly added at −15°C. The mixture was stirred for 2 h. A twofold excess of 1-bromobutane was added to the resulting solution of **X**. After the addition of water and diethyl ether, the organic phase was separated and successively washed with 2N HCl (*3) and a saturated NaCl solution of (*2). The ethereal solution was dried over MgSO$_4$. After solvent removal by distillation, **XI** was purified by column chromatography on silica gel (*n*-hexane). The yield of **XI** was 48%.

Alkylated phenylthiophenes were synthesized by means of Kumada coupling [5] followed by the alkylation of phenylthiophene (**XVI**) and *o*-tolylthiophene (**XVII**) according to the scheme:

R = H (**XII**)
R = CH₃ (**XIII**)
+ Mg →(abs. EtOEt)→
R = H (**XIV**)
R = CH₃ (**XV**)
+ (**VIII**) →(NiCl₂ (dppp), abs. EtOEt)→
R = H (**XVI**)
R = CH₃ (**XVII**)

(**XVI**) →(BuLi, abs. THF)→ (**XVIII**) →(RHal, abs. THF)→
RHal = CH₃I (**XIX**)
RHal = C₄H₉Br (**XX**)

(**XVII**) →(BuLi, abs. THF)→ (**XXI**) →(RHal, abs. THF)→
RHal = CH₃I (**XXII**)
RHal = C₄H₉Br (**XXIII**)

Synthesis of 2-phenylthiophene (XVI) and 2-*o*-tolylthiophene (XVII). Compound **XII** (5.84 g, 37 mmol) (or 5.74 g (29 mmol) of compound **XIII**) in absolute ether was added dropwise to a 1.05-fold excess of Mg in absolute ether. The formation of compound **XIV** (**XV**) was stimulated by the addition of an iodine crystal. The mixture was refluxed for 0.5 h until Mg dissolution. A 6.08-g portion of **VIII** (37 mmol) or 5.51 g (34 mmol) of **VIII** in an ethereal solution containing a suspension of NiCl₂(dppp) (0.09 g) was added to the resulting solution at 0°C. The solution was refluxed for 2 h. After cooling, the mixture was washed with 2N HCl. After phase separation, the aqueous layer was repeatedly extracted with ether, and the organic phases were combined. The resulting solution of **XVI** (**XVII**) was washed with a saturated NaCl solution and dried over MgSO₄. The product was purified by column chromatography on silica gel (*n*-hexane). The yield of **XVI** was 50% and that of **XVII** was 53%.

Synthesis of 5-methyl-2-phenylthiophene (XVIII) and 5-methyl-2-*o*-tolylthiophene (XXII). Compound **XVI** (0.5 g, 3.15 mmol) (or 0.46 g (2.6 mmol) of compound **XVII**) was dissolved in anhydrous tetrahydrofuran in a nitrogen atmosphere. A 1.2-fold excess of BuLi was added slowly at –15°C. The mixture was stirred for 2 h. A twofold excess of iodomethane was added to the resulting solution of compound **XVIII** (**XXI**). After water and diethyl ether were added, the organic phase was separated and successively washed with 2N HCl (*3) and a saturated solution of NaCl (*2). The ethereal solution was dried above MgSO₄. After the solvent was distilled off, com-

pound **XIX** (**XXII**) was purified by column chromatography on silica gel (*n*-hexane). The yields of **XIX** and **XXII** were 86 and 77%, respectively.

Synthesis of 5-butyl-2-phenylthiophene (XX) and 5-butyl-2-*o*-tolylthiophene (XXIII). Compound **XVI** (0.5 g, 3.15 mmol) (or 0.84 g (4.8 mmol) of **XVII**) was dissolved in anhydrous tetrahydrofuran in a nitrogen atmosphere. A 1.2-fold excess of BuLi was slowly added at –15°C. The mixture was stirred for 2 h. A twofold excess of 1-bromobutane was added to the resulting solution of **XVIII** (**XXI**), and the mixture was refluxed for 2 h. After the addition of water and diethyl ether, the organic phase was separated and successively washed with 2N HCl (*3) and a saturated NaCl solution (*2). The ethereal solution was dried over MgSO₄. After solvent removal by distillation, **XX** (**XXIII**) was purified by column chromatography on silica gel (*n*-hexane). The yields of **XX** and **XXIII** were 31 and 85%, respectively.

Synthesis of Sulfur-Vulcanized Polybutadiene (Rubber)

Polybutadiene (1530–2070 g/mol, Aldrich) was mixed with a calculated amount of sulfur. After the dissolution of sulfur, the mixture was heated in a sealed ampule at 170°C for 2 h.

Pyrolysis of Kerogen and Rubber

Kerogen and rubber were pyrolyzed in a quartz reactor with a 15 mm diameter with a product with-

drawal arm placed in a trap (5 ml of chloroform at 0°C). The pyrolysis was carried out in a nitrogen stream for 1 h at 420°C [6]. The pyrolysis products were concentrated in preliminarily weighed weighing bottles (fraction P0).

The pyrolyzate P0 was divided into two fractions by liquid chromatography on a column (10 × 1.5 cm) packed with alumina (Fluka), which was preliminarily activated for 2.5 h at 150°C. Elution with an *n*-hexane–dichloromethane (9 : 1, vol/vol) mixture gave an apolar fraction (P1) containing all aliphatic and aromatic components of P0. With a dichloromethane–ethanol (1 : 1) blend used as an eluent, polar components (P2) were eluted. Then, P1 was separated into the aliphatic (P3) and aromatic (P4) fractions. For this purpose, a column (8 × 0.6 cm) packed with silica gel (Fluka) was used. Fraction P3 was obtained via elution with *n*-hexane, and elution with benzene gave fraction P4.

The analysis by gas chromatography coupled with mass spectrometry (GC–MS) was performed on a QP 5050A instrument (Shimadzu). An SPB-5 column (Supelco) of 60 m length and 0.32 mm inner diameter was used for chromatographic separation (the stationary-phase layer thickness was 0.25 μm). Chromatography was carried out in the temperature-programming mode from 50 to 300°C at a rate of 5°C /min. The injector temperature was 300°C, and the temperature of the ion source was 250°C. A sample was injected in the flow-splitting mode (1 : 30), and the sample volume was 1 μl. A quadrupole mass spectrometer with an ionization energy of 70 eV was used.

Proton NMR spectra were recorded on a Bruker instrument at a frequency of 300 MHz in $CDCl_3$. The chemical shifts were measured relative to tetramethylsilane.

RESULTS AND DISCUSSION

We synthesized eight compounds belonging to the 2,2'-bithiophene and 2-phenylthiophene series. The structures of these compounds were confirmed by synthesis and the mass spectral and ^{1}H NMR data (table). The main pathway of the mass-spectrometric degradation of alkylated aromatic compounds, including thiophenes, is the β-cleavage of the alkyl chain [7]. In the case of methyl-substituted derivatives, the molecular and M-1 ions have the highest abundance. This specific feature of the mass-spectral decomposition is employed for the group identification of bithiophenes and phenylthiophenes in the pyrolysis products of kerogen by means of the GC–MS technique [1].

The synthesized compounds belong to four homologous series, namely, 5-*n*-alkyl-2,2'-bithiophenes, 5-*n*-alkyl-5'-methyl-2,2'-bithiophenes, 5-*n*-alkyl-2-phenylthiophenes, and 5-*n*-alkyl-2-*o*-tolylthiophenes. Two compounds that differ by three methylene units
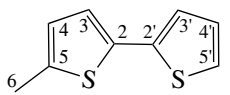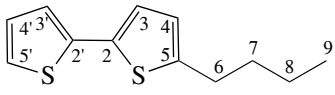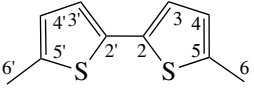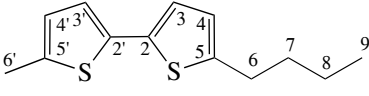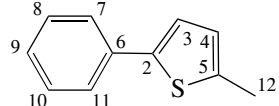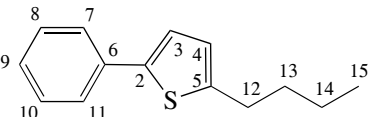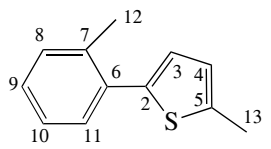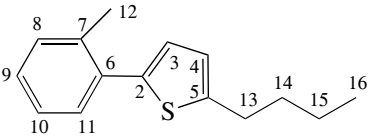
(methyl- and butyl-substituted derivatives) were synthesized for each homologous series. The presence of two members of the homologous series allows the group identification of members of this series to be performed on the basis of the dependence of the retention time on the number of carbon atoms in a homologue molecule [7].

A sample of oil shale KSh-1/5-03 taken from the Kashpirskoe deposit was chosen as a source of high-sulfur kerogen: the organic carbon content was 37.3% and the amount of chloroform-extractable bitumens was 0.36%. The analysis of the unfractionated pyrolyzate of this kerogen showed the presence of low-molecular-mass thiophenes in high concentrations. For example, the thiophene ratio (TR is the ratio of the 2,3-dimethylthiophene content to the sum of 1-nonene and 1,2-dimethylbenzene) used for estimating S_{org} in the kerogen composition is 0.81, which corresponds to an S/C value of 0.05 [8]. The elemental analysis data allow us to attribute this kerogen to the type II-S (H/C = 1.52, S/C = 0.053). According to Orr's classification [9], geopolymer samples with an S/C atomic ratio above 0.04 and H/C atomic ratios characteristic of type II kerogen are categorized with type II-S kerogen.

The analysis of the aromatic fraction of the pyrolysis products of Kashpirskii kerogen showed the presence of a wide variety of sulfur-containing compounds. To reveal bithiophene and phenylthiophene derivatives in the composition of the P4 fraction, we constructed mass fragmentograms by the following *m/z* sums: 179 + 180 for 5-*n*-alkyl-2,2'-bithiophenes, 193 + 194 for 5-*n*-alkyl-5'-methyl-2,2'-bithiophenes, 173 + 174 for 2-*n*-alkyl-5-phenylthiophenes, and 187 + 188 for and 2-*n*-alkyl-5-*o*-tolylthiophenes (Fig. 1). The P4 fraction with added authentic standards was chromatographed to confirm the presence of these compounds in the kerogen pyrolysis products (Fig. 2). The heights of the corresponding peaks increased, thus confirming the validity of the identification. Taking into account that we synthesized two members for each of the test homologous series, the retention times of the intermediate members of the homologous series were determined by the interpolation method.

The kerogen represented a geopolymer of an irregular structure containing the *n*-alkyl, isoprenoid, and polycyclic, aromatic, and heteroatomic moieties bridged to one other by different linkages: ester, ether, sulfide, and polysulfide bridges [10]. Type II kerogen is characterized by a higher S_{org} content, in which organic sulfur appears in heterocycles and forms bridges between its local carbonaceous structures, thus determining the special properties of sulfur-rich kerogen [11]. Sulfur is inserted into the kerogen at the diagenesis stage as a result of the interaction of functionally saturated lipids of the original organic matter with reduced forms of sulfur [4]. In addition, under certain

Spectral characteristics of the synthesized compounds

| No.	Compound	^{1}H NMR	Mass spectrum
1	5-methyl-2,2'-bithiophene	d 1H, 7.19 (5') d 1H, 7.12 (3') m 2H, 7.00 (3, 4') d 1H, 6.69 (4) s 3H, 2.51 (6)	M$^{+\bullet}$ (100), 179 (86) 147 (41)
2	5-butyl-2,2'-bithiophene	d 1H, 7.19 (5') d 1H, 7.12 (3') m 2H, 7.00 (3, 4') d 1H, 6.69 (4) t 2H, 2.82 (6) m 2H, 1.70 (7) m 2H, 1.45 (8) t 3H, 0.97 (9)	M$^{+\bullet}$ (22), 179 (100)
3	5,5'-dimethyl-2,2'-bithiophene	d 1H, 6.90 (3, 3') d 1H, 6.65 (4, 4') s 3H, 2.49 (6, 6')	M$^{+\bullet}$ (100), 193 (72) 161 (44), 179 (11)
4	5-butyl-5'-methyl-2,2'-bithiophene	m 2H, 6.91 (3, 3') d 2H, 6.66 (4, 4') s 3H, 2.49 (6') t 2H, 2.81 (6) m 2H, 1.69 (7) m 2H, 1.45 (8) t 3H, 0.97 (9)	M$^{+\bullet}$ (27), 193 (100)
5	5-methyl-2-phenylthiophene	d 2H, 7.58 (7, 11) t 2H, 7.37 (8, 10) t 1H, 7.27 (9) d 1H, 7.13 (3) d 1H, 6.75 (4) s 3H, 2.53 (12)	M$^{+\bullet}$ (100), 173 (99) 141 (17)
6	5-butyl-2-phenylthiophene	d 2H, 7.59 (7, 11) t 2H, 7.37 (8, 10) t 1H, 7.27 (9) d 1H, 7.15 (3) d 1H, 6.77 (4) t 2H, 2.85 (12) m 2H, 1.72 (13) m 2H, 1.46 (14) t 3H, 0.98 (15)	M$^{+\bullet}$ (25), 173 (100)
7	5-methyl-2-*o*-tolylthiophene	m 1H, 7.44 (11) m 3H, 7.29 (8–10) d 1H, 6.91 (3) d 1H, 6.79 (4) s 3H, 2.57 (13) s 3H, 2.49 (12)	M$^{+\bullet}$ (100), 187 (163) 129 (35), 115 (31), 155 (26), 173 (25)
8	5-butyl-2-*o*-tolylthiophene	m 1H, 7.42 (11) m 3H, 7.25 (8–10) d 1H, 6.90 (3) d 1H, 6.78 (4) t 2H, 2.87 (13) s 3H, 2.47 (12) m 2H, 1.75 (14) m 2H, 1.49 (15) t 3H, 1.00 (16)	M$^{+\bullet}$ (25), 187 (100)
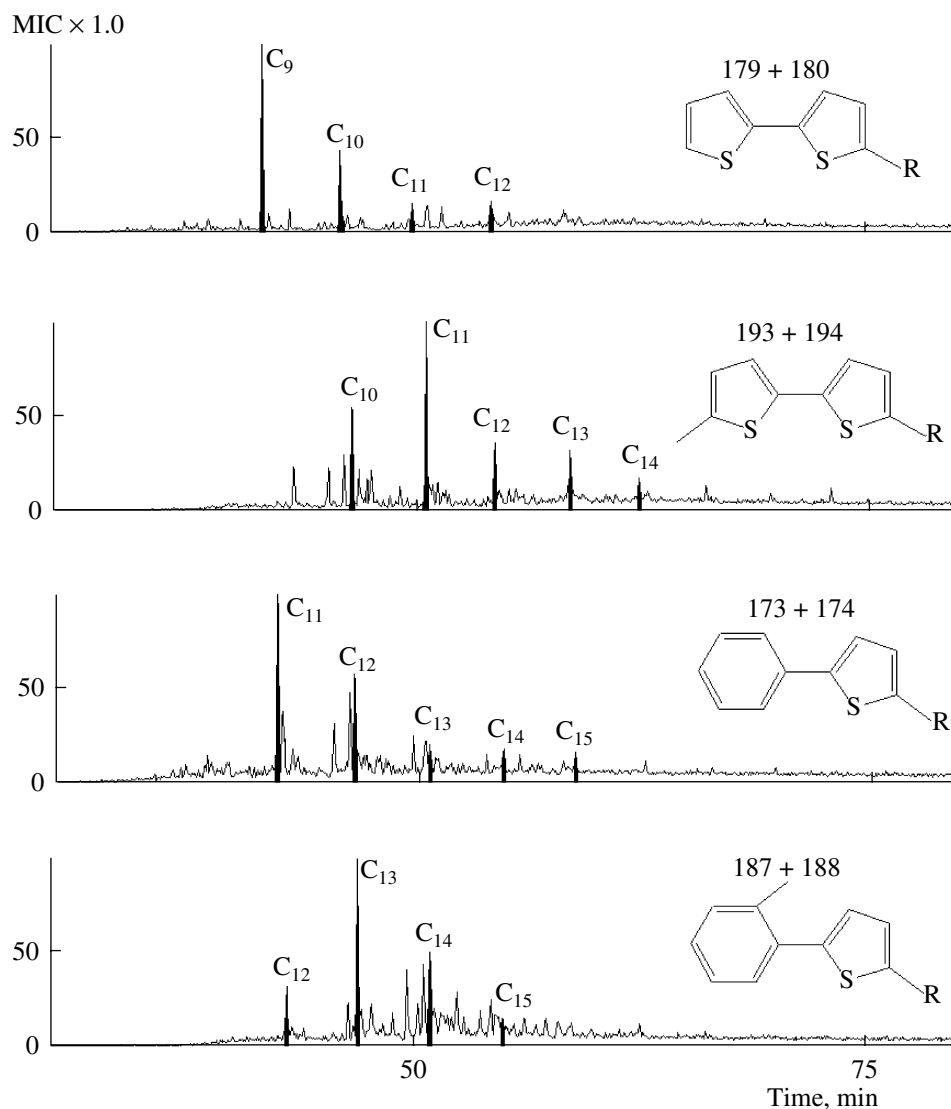
Fig. 1. Mass fragmentograms of the aromatic fraction of the pyrolysis products of the KSh-1/5-03 kerogen constructed by the sums of fragment ions characteristic of biphenyls and phenylthiophenes.

conditions, sulfur actively interacts with the carbohydrate fraction of the original organic matter [12]. Of course, a polymer with such a complex constitution cannot be modeled on the basis of a certain individual compound or polymer; however, this situation does not rule out the modeling of a *part* of structural fragments of kerogen. The test compounds of the 2,2'-bithiophene and 2-phenylthiophene series are based on the *n*-alkyl carbon moiety (with allowance for ring opening, see the table). Earlier, we assumed the formation of these compounds during the pyrolysis of *n*-alkyl chains linked by numerous sulfide bridges [3]. A possible source of such moieties in the kerogen composition can be natural *n*-alkylpolyenes or polyketones, which interact with the hydrosulfide ion and polysulfides during diagenesis [13].

Polybutadiene molecules contain the *n*-alkyl moiety and are rich in multiple bonds, thus making it possible to obtain, after sulfur vulcanization, a structure that, first, is saturated with S–C bonds and, second, has a linear carbon skeleton. The calculated S/C atomic ratio in the rubber samples that we prepared varies from 0.025 to 0.125, i.e., the sulfur content corresponds to both sulfur-free (less than 0.04) and sulfur-rich (more than 0.04) kerogens. The qualitative analysis of the rubber pyrolysis products showed the presence of a set of sulfur compounds similar to those of the kerogen pyrolysis products (Fig. 3). A quantitative analysis with the use of internal standards revealed that the yield of 2-*n*-alkyl-5-methylthiophenes and 5-*n*-alkyl-2,2'-bithiophenes correlates with the calculated S/C atomic ratio of the rubber sample (Fig. 4). It seems important to emphasize two points that follow from the results of the analysis of
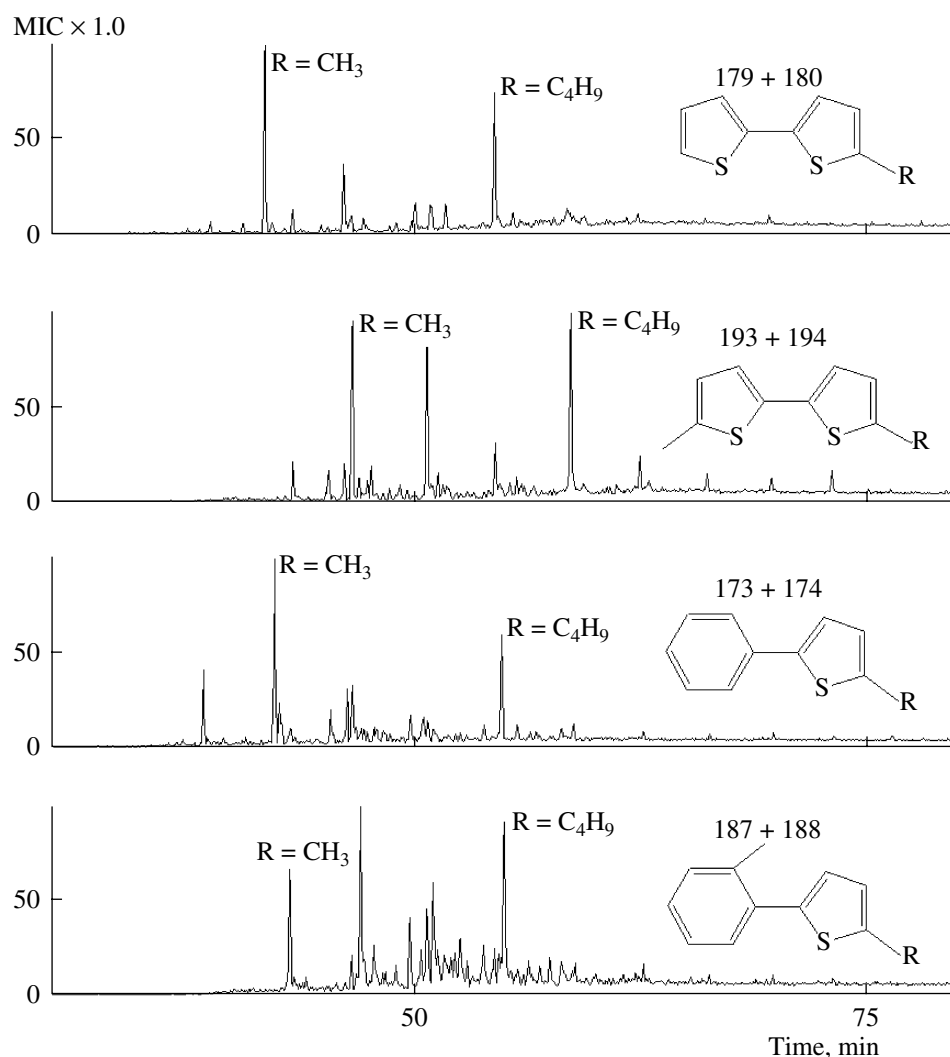
Fig. 2. Mass fragmentograms of the aromatic fraction of the pyrolysis products of the KSh-1/5-03 kerogen constructed by the sums of the fragment ions characteristic of biphenyls and phenylthiophenes with added standards.

the sulfur components of rubber pyrolysis products. First, 5-*n*-alkyl-2,2'-bithiophenes are formed only in the pyrolysis of samples that have a S/C atomic ratio above 0.04, a value which corresponds to the boundary between the kerogen types II and II-S [9]. Second, the ratio of total 5-*n*-alkyl-2,2'-bithiophenes to total 2-*n*-alkyl-5-methylthiophenes increases with an increase in the S/C atomic ratio (Fig. 4). Thus, the obtained data corroborate the earlier proposed scheme assuming that the direction of the thermal transformation of the *n*-alkyl chain of kerogen linked by numerous sulfide bridges depends on the saturation of the structure with sulfur atoms (Fig. 5).

CONCLUSIONS

(1) Eight compounds belonging to the series of alkylated 2,2'-bithiophene and 2-phenylthiophene were synthesized. The structures of the compounds were proven by synthesis and mass spectral and $_1$H NMR data.

(2) Joint chromatographing of the aromatic fraction of the pyrolysis products of type II-S kerogen from the Kashpirskoe deposit with the authentic standards proved that the pyrolysis products of the homologous series contained 5-*n*-alkyl-2,2'-bithiophenes, 5-*n*-alkyl-5-methyl-2,2'-bithiophenes, 5-*n*-alkyl-2-phenylthiophenes, and 5-*n*-alkyl-2-*o*-tolylthiophenes.

(3) Chemical simulation of the *n*-alkyl polysulfur-bound structural fragments of type II-S kerogen by sulfur-vulcanized polybutadiene taken as an example confirmed the feasibility of the formation of the test biaromatic sulfur compounds during the pyrolysis of the *n*-alkyl polysulfur-bound fragments of kerogen.
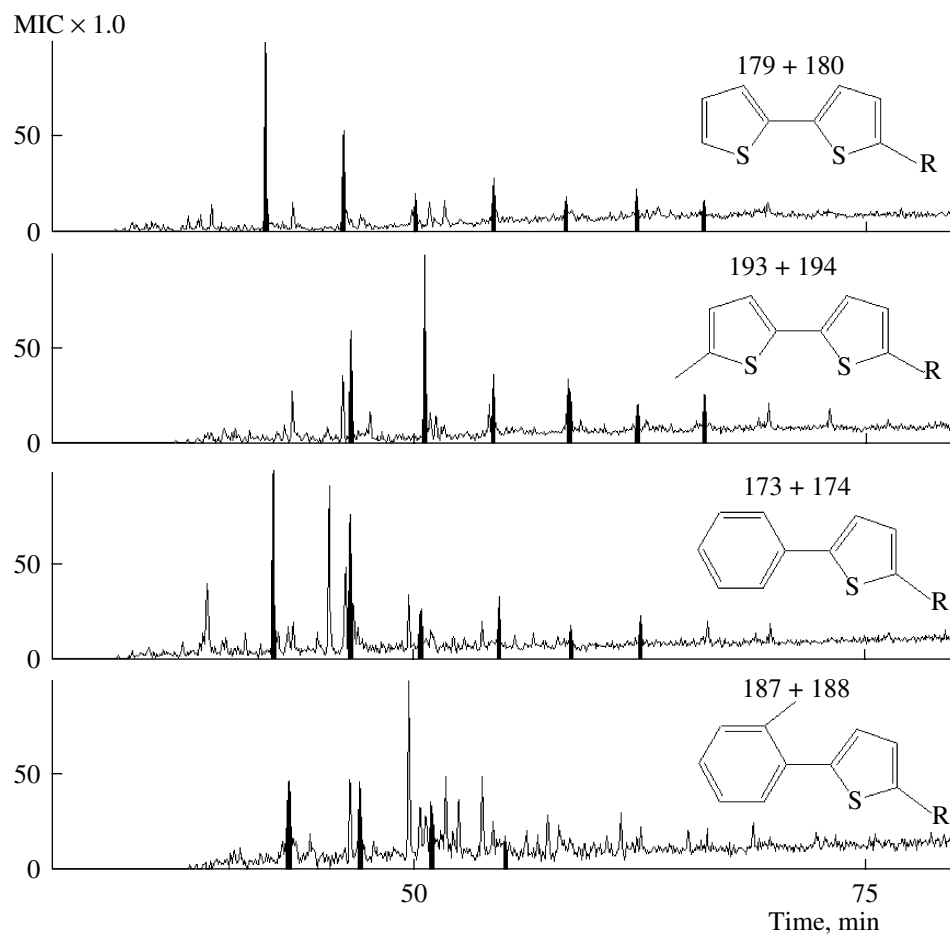
Fig. 3. Mass fragmentograms of the aromatic fraction of the pyrolysis products of the polybutadiene rubber constructed by the sums of the fragment ions characteristic of biphenyls and phenylthiophenes.
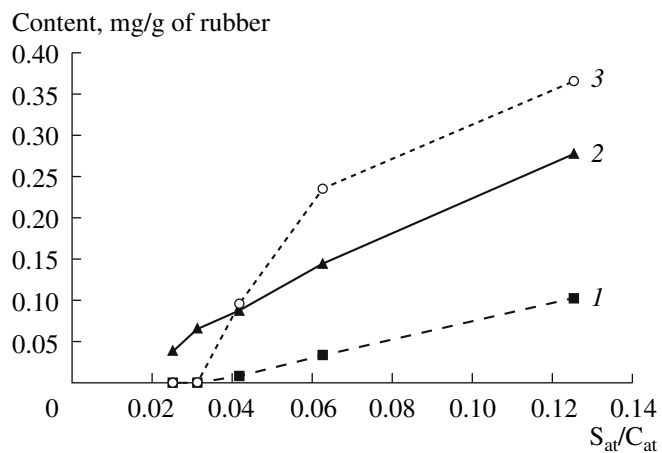

Fig. 4. Dependences of the composition of the pyrolysis products of the sulfur-vulcanized polybutadiene on the S/C atomic ratio: (*1*) total C_9–C_{12} 5-*n*-alkyl-2,2'-bithiophenes, (*2*) total C_{11}–C_{14} 5-*n*-alkyl-2-methylthiophenes, and (*3*) ratio of 1 : 2.
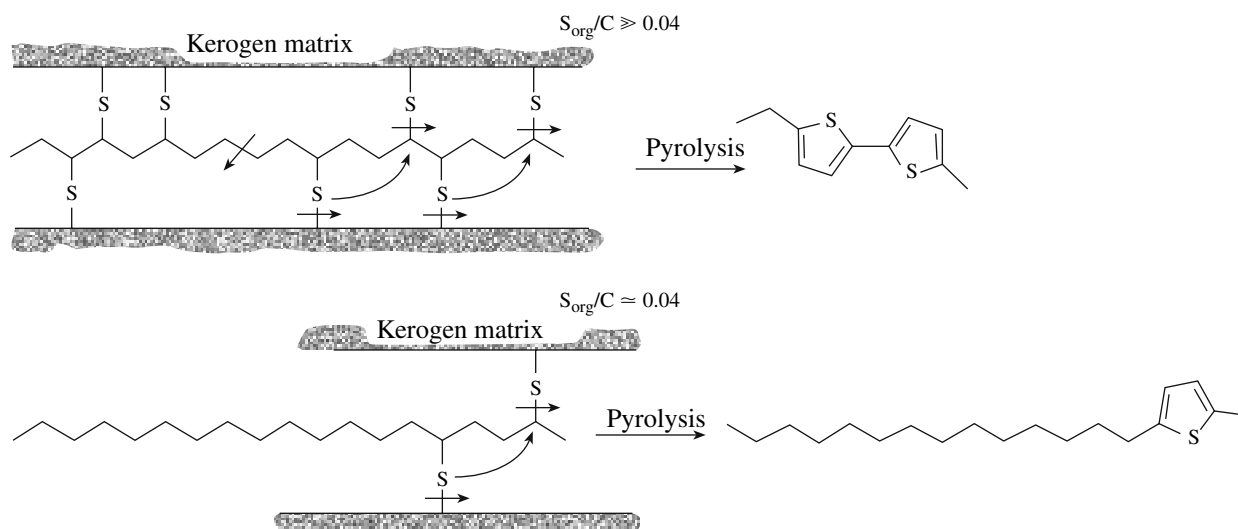
Fig. 5. Hypothetical scheme of the transformation of sulfur-bound lipid fragments of kerogen during pyrolysis at different degrees pf saturation of the kerogen structure with sulfide bridges [3].

(4) The earlier proposed scheme of the dependence of the composition of pyrolysis products from sulfur-rich kerogen on the saturation of its structure with sulfide bridges was experimentally corroborated.

REFERENCES

1. H. M. E. Van Kaam-Peters and J. S. Sinninghe Damste, Org. Geochem. **27**, 371 (1997).

2. A. Riboulleau, S. Derenne, G. Sarret, et al., Org. Geochem. **31**, 1641 (2000).

3. D. A. Bushnev and N. S. Burdel'naya, Neftekhimiya **43**, 256 (2003) [Pet. Chem. **43**, 230 (2003)].

4. J. S. Sinninghe Damste, W. I. C. Rijpstra, A. C. Kock-Van Dalen, et al., Geochim. Cosmochim. Acta **53**, 1343 (1989).

5. K. Tamao, S. Kodama, I. Nakajiama, and M. Kumada, Tetrahedron **38**, 3347 (1982).

6. D. A. Bushnev, Litol. Polezn. Iskop., No. 1, 96 (2001).

7. J. S. Sinninghe Damste, J. W. De Leeuw, A. C. Kock-Van Dalen, et al., Geochim. Cosmochim. Acta **51**, 2369 (1987).

8. T. I. Eglinton, J. S. Sinninghe Damste, M. E. L. Kohnen, and J. W. De Leeuw, Fuel **69**, 1394 (1990).

9. W. L. Orr, Org. Geochem. **10**, 499 (1986).

10. F. Behar and M. Vandenbroucke, Org. Geochem. **11**, 15 (1987).

11. J. Tomic, F. Behar, M. Vandenbroucke, and Y. Tang, Org. Geochem. **23**, 647 (1995).

12. M. D. Kok, S. Schouten, and J. S. Sinninghe Damste, Geochim. Cosmochim. Acta **64**, 2689 (2000).

13. M. P. Koopmans, C. Schaeffer-Reiss, J. W. De Leeuw, et al., Geochim. Cosmochim. Acta **61**, 2397 (1997).