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## Pyrolysis of Polystyrene in Heavy Petroleum Residues: Main Regularities and Effect on Characteristics of Bituminous Materials

E. I. ANDREIKOV, YU. A. DIKOVINKINA, O. V. KRASNIKOVA, M. G. PERVOVA

*Postovsky Institute of Organic Synthesis, Ural Branch of Russian Academy of Sciences, Ekaterinburg, Russia**E-mail: cc@ios.uran.ru*

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### Abstract

Pyrolysis of polystyrene in the medium of heavy petroleum residue (bitumen) was explored in the 360–380 °C temperature range at ambient pressure. The composition of liquid products of pyrolysis was determined by GS-MS. When investigating the co-pyrolysis residues, modified bitumens, <sup>1</sup>H NMR and FTIR were used. The softening temperature, penetration, and asphaltene content were determined. It was found that the main products of polystyrene pyrolysis in bitumen were saturated compounds, such as ethylbenzene, cumene, toluene, and 1,3-diphenylpropane that were formed resulting from hydrogen transfer from bituminous components to polystyrene thermal decomposition products. The maximum rate of polystyrene decomposition shifts to a high temperature range. Modification of bitumen proceeds mainly due to hydrogen transfer-initiated condensation reactions of its components. The effect of residual polystyrene on the properties of bitumen is much weaker.

**Keywords:** bitumen, polystyrene, pyrolysis, hydrogen transfer, modification

### INTRODUCTION

Pyrolysis is an efficient method of polymer wastes processing yielding fuel or chemical raw materials [1, 2]. Carrying out a process in solvent media allows improving mass and heat transfer conditions in the reaction medium that are unfavourable due to high viscosity of polymer melts and thereby reducing process temperature [3, 4]. Solvents may also have an effect on the thermal decomposition process, entering into chemical reactions with the initial polymer or products of its decomposition [5–8]. When heavy petroleum residues are used as solvents, pyrolysis can be carried out at ambient pressure, producing two production types: reactor residue, *i.e.* modified petroleum pitch or bitumen, and also as low-molecular-mass organic compounds released from the reactor as distillate products [9, 10].

A number of papers discuss the mechanism and process aspects of polystyrene pyrolysis [11–17]. Papers [18–25] are devoted to polystyrene pyrolysis in highly-boiling solvents, coal tar, and coal tar and petroleum pitches. As demonstrated by the authors of [25], polystyrene pyrolysis in coal-tar pitch and petroleum pitch produced from ethylene pyrolysis tar is accompanied by hydrogen transfer from the solvent to intermediate radical products of the polymer thermal decomposition and pyrolysis products with double bonds. Consequently, the composition of distillate products and characteristics of coal-tar pitch and petroleum pitch change.

Pyrolysis of polystyrene in heavy petroleum residues has been unexplored until now and is of interest not only in terms of utilization of the spent polymer and aromatic raw materials production but also modified bitumens manufacture.

Additives of copolymers of polystyrene [26] and expanded polystyrene [27] were used to modify bituminous materials used in road construction and as insulation coatings.

The work objective was to explore regularities of polystyrene pyrolysis in heavy petroleum residues medium, its effect on their characteristics and opportunities of their further use as bituminous materials.

## EXPERIMENTAL

The research used polystyrene PSM-115 and an industrial sample of bitumen BND 90/130. The characteristics of the latter are: softening temperature ( $T_s$ ) of 47 °C (by ring-and-ball method); contents of asphaltenes of 27.6 % and hexane-soluble substances of 72.4 %. The elemental composition is (in %): C 85.7, H 10.8, S 2.8, N 0.7.

Pyrolysis of mixtures of polystyrene and bitumen was carried out under isothermal conditions at 360–380 °C in a metal reactor at ambient pressure, in a similar fashion to that described in [25]. Polystyrene content in the mixtures varied from 5 to 31 %. Mixtures of bitumen (B) and polystyrene (PS), and also heat treatment conditions are encrypted as BPSX-Y-Z, where X is the percentage of polystyrene in a mixture of bitumen and polystyrene; Y is the temperature, °C; Z is heat treatment duration, h.

In order to explore the reaction of styrene and heavy petroleum residue, 10 mL of styrene was fed into a metal reactor containing 60 g of bitumen using a piston feeder for 30 min at 360 °C.

Liquid pyrolysis products were identified by the Trace GC Ultra DSQ II GC-MS-mass spectrometer (USA).

Quantitative analysis was performed according to the internal normalization method using the Shimadzu GC 2010 gas chromatograph (Japan) with a flame ionization detector (GC-PID), a ZB-5 quartz capillary column (polydimethylsiloxane, 5 mass % of phenyl groups), 30 m length, 0.25 mm, diameter, and 0.25 m film thickness. The initial temperature of the column is 40 °C (exposure time 3 min), programming at a rate of 10 °C/min to 280 °C (exposure time of 30 min), evaporator temperature of 250 °C, detector – 300 °C, nitrogen carrier gas, a split ratio of 1 : 30, the flow rate through the column of 1.0 mL/min.

Infrared spectra of solid residues of pyrolysis were collected using the Perkin-Elmer Spectrum One FTIR Spectrometer by diffuse reflection FTIR

spectroscopy. The  $^1\text{H}$  NMR spectra of toluene-soluble fractions of pyrolysis residues after distilling off the solvent were collected using a Bruker DRX-400 spectrometer with TMS as internal standard in  $\text{CDCl}_3$  solution at room temperature. TG-DSC analysis of polystyrene and bitumen-polystyrene mixtures was performed using a SETARAM SETSYS Evolution instrument. The samples were heated from 20 to 1000 °C with a rate of 10 °C/min, argon flow of 110 mL/min.

Along with physicochemical methods during exploring polystyrene pyrolysis residues in bitumen, softening temperature, penetration, and asphaltene content were determined. The latter was determined according to the following technique: 5 g of bitumen was placed into the flask and 200 mL of hexane was added, the mixture was stirred for 4 h and left overnight in a dark place. Afterwards, the mixture was filtered through double white filter paper, pre-washed with hexane, and kept to a constant mass at a temperature of 95–100 °C. Asphaltenes content was computed as residue mass ratio on the filter to the weight of the bitumen sample. The softening temperature and penetration of bitumen and pyrolysis residues were determined according to GOST 22245-90.

Micrographs of thin layers of pyrolysis residues were received using the Olympus BX-51 optical microscope in the transmitted light mode (the Ural Centre for Collective Use “Modern nanotechnologies”, the Institute of Natural Sciences, UFU, Ekaterinburg).

## RESULTS AND DISCUSSION

Figure 1 gives TG and DSC curves for polystyrene and a mixture of bitumen and polystyrene. Polystyrene decomposition in the bitumen medium takes place at higher temperatures and endothermic peak maximum that falls together with the maximum rate of polymer mass loss shifts from 424 to 450 °C.

Table 1 gives polystyrene pyrolysis in the medium of bitumen results. Liquid products of polystyrene thermal decomposition are released at 360 °C with a low rate, and a significant amount of the polymer undecomposed to low molecular mass products also remains in the reactor at 380 °C for 1 h. A high degree of transformation of polystyrene into liquid products is reached at 380 °C for 2 h.

Table 2 gives the qualitative and quantitative composition data of liquid distillate products

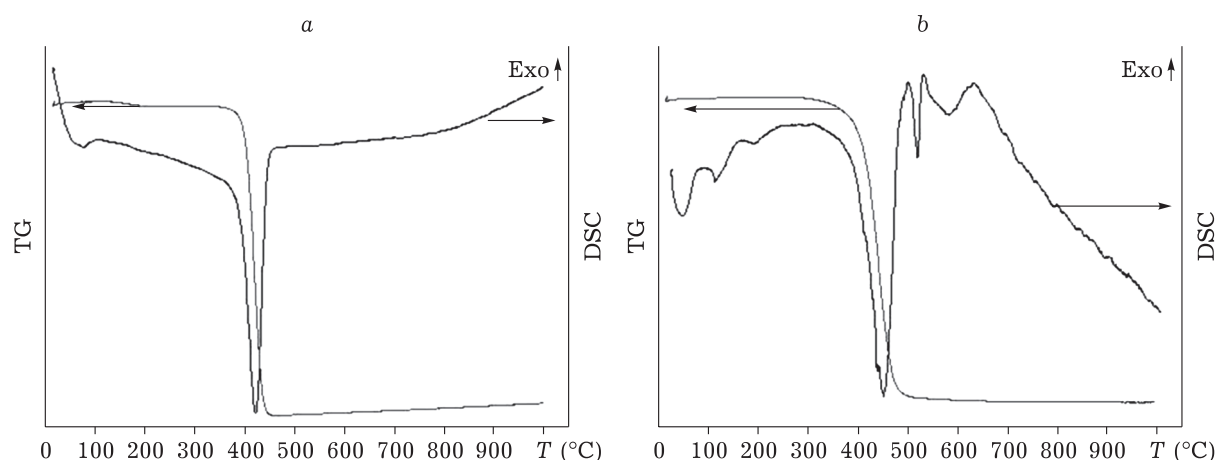


Fig. 1. TG/DSC curves of polystyrene (a) and BPS23 (b).

formed during the pyrolysis of polystyrene and its mixtures with bitumen. According to the data [11, 28], during pyrolysis of one polystyrene styrene (69–73 %), and also its dimer (15–16 %) and trimer are mainly formed. The composition of distillate products during polystyrene pyrolysis in bitumen changes dramatically: the content of styrene is significantly reduced and there are no styrene dimer and trimer; alkyl-substituted benzene hydrocarbons (ethylbenzene, cumene, and toluene) and 1,3-diphenylpropane are prevailing. There are similar changes in the composition of polystyrene pyrolysis products in the medium of coal-tar pitch and petroleum pitch due to hydrogen transfer from the solvent both to intermediate radical products of polymer decomposition, and products with double bonds [25]. The composition of styrene products, as a result of styrene transmission through bitumen at 360 °C, is as follows, mass %: toluene 2.2, ethylbenzene 36.6, styrene 59.8, 1-methyl-1,2-diphenylethan 1.3. The

findings prove an opportunity to transfer hydrogen from the heavy petroleum residue to styrene with generating ethylbenzene, and also toluene and 1-methyl-1,2-diphenylethane (*via* an intermediate benzyl radical) in minor amounts. Hydrogen transfer from solvents to intermediate macromolecular radicals formed during the decomposition of the main chain of polystyrene facilitates reducing the rate of polymer decomposition reactions [3, 25] initiated by them and shifting the maximum decomposition rate to a high temperature range (see Fig. 1).

Table 3 gives characteristics of the initial bitumen, and also the residue of pyrolysis of bitumen and mixtures of bitumen and polystyrene heat-treated at 380 °C. Heat treatment of bitumen results in reduced softening temperature, increased penetration and has an insignificant effect on asphaltene content in a similar fashion to the visbreaking process of heavy petroleum residues [29]. In the case of pyrolysis of polystyrene in bitu-

TABLE 1

Mass balance of polystyrene pyrolysis in bitumen

Sample	Reactor loading, g		Products					
	Bitumen	PS	Reactor residue,		Distillates		Gases	
			g	%	g	%	g	%
B-380-1	58.0	–	56.0	96.5	0.85	1.5	1.1	2.0
B-380-2	61.5	–	57.7	93.8	2.2	3.6	1.6	2.6
BPS23-360-2	63.9	19.2	76.5	92.1	5.6	6.7	1.0	1.2
BPS23-380-1	63.2	18.6	67.3	82.2	11.7	14.3	2.8	3.4
BPS5-380-2	64.6	3.3	61.9	91.1	4.3	6.4	1.7	2.5
BPS9-380-2	64.9	6.5	61.4	86.0	8.3	11.6	1.7	2.4
BPS13-380-2	65.3	9.8	63.1	84.0	10.3	13.7	1.7	2.3
BPS25-380-2	60.6	19.9	60.1	74.7	19.0	23.6	1.4	1.7
BPS31-380-2	60.2	27	56.4	64.7	28.0	32.1	2.8	3.2

TABLE 2

Selectivity according to pyrolysis products of polystyrene and polystyrene in bitumen

Sample	Toluene	Ethylbenzene	Styrene	Cumene	$\alpha$ -methyl-Methylstyrene	1,3-Diphenylpropane	Styrene dimer	1-Methyl-1,2-diphenyl ethane	Styrene trimer
PS-380-1	2.4	1.2	73.4	–	4.2	0.3	15.4	1.6	1.5
BPS23-360-2	12.2	50.7	8.3	22.4	3.1	3.3	–	–	–
BPS23-380-1	13.3	44.7	14.9	15.5	5.2	6.0	–	0.4	–

Note. Dash means absent.

TABLE 3

Characteristics of pyrolysis residues

Sample	Softening temperature, °C	Penetration, 0 °C/25 °C	Asphaltene content, %
Initial bitumen	47	37/73	27.6
B-380-1	22	93/114	28.8
B-380-2	23	128/142	28.5
BPS23-380-1	43	34/66	33.8
BPS9-380-2	42	45/92	33.8
BPS13-380-2	46	34/66	32.6
BPS23-380-2	62	27/55	39.1
BPS31-380-2	91	7/16	41.3

men, the softening temperature and asphaltene content in the residue of pyrolysis is increased, while penetration is dramatically reduced.

A change in these characteristics is directly related to the added polymer amount and is due to condensation reactions of heavy petroleum residue components that are initiated by hydrogen transfer from the solvent to polymer thermal decomposition products. The effect of incomplete decomposition of polystyrene on these parameters

is significantly smaller. For example, no more than 55 % of polystyrene has transformed into distillate products in case of samples BPS23-380-1, while this parameter for BPS23-380-2 is no less than 85 % (calculated via the content of products of polystyrene pyrolysis in distillate products).

Figures 2 and 3 give  $^1\text{H}$  NMR spectra of the toluene-soluble portion and FT-IR spectra of bitumen heat treatment residues and mixtures of bitumen and polystyrene. For polystyrene and its oligomers with the number of links greater than six, there are by two peaks of absorption of aromatic (in the region of 6.30–7.20 ppm) and aliphatic hydrogen (1.2–2.0 ppm.) in  $^1\text{H}$  NMR spectra [17, 30]. There is absorption in these areas for the residues of pyrolysis of a mixture of BPS23-380-1 and asphaltene isolated therefrom disappears with an increase in the duration of pyrolysis to 2 h (Fig. 2).

The IR-Fourier spectra of the residues of polystyrene pyrolysis in bitumen (see Fig. 3) contain additional adsorption bands of aromatic C–H bonds at 3025 and 3058  $\text{cm}^{-1}$ , and also a monosubstituted benzene ring at 1493 and 698  $\text{cm}^{-1}$  referring to polystyrene compared to the spectrum of bitumen.

Upon the presence of absorption in areas of 6.30–7.20 ppm and 1.2–2.0 ppm, these bands in  $^1\text{H}$  NMR spectra of the residue of pyrolysis of the sample BPS23-380-1 may correspond to oligomers with the number of links  $>6$ , while without it, for the residue of pyrolysis of the sample

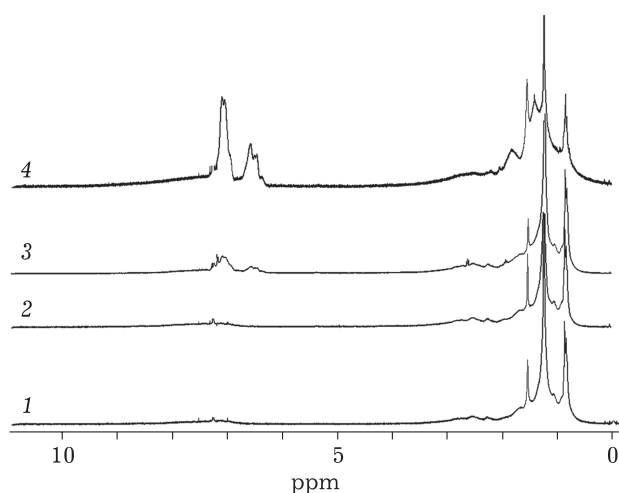


Fig. 2.  $^1\text{H}$  NMR spectra of bitumen (1), pyrolysis residues of BPS31-380-2 (2), BPS31-380-1(3), and asphaltene of pyrolysis residue of BPS31-380-1 (4).

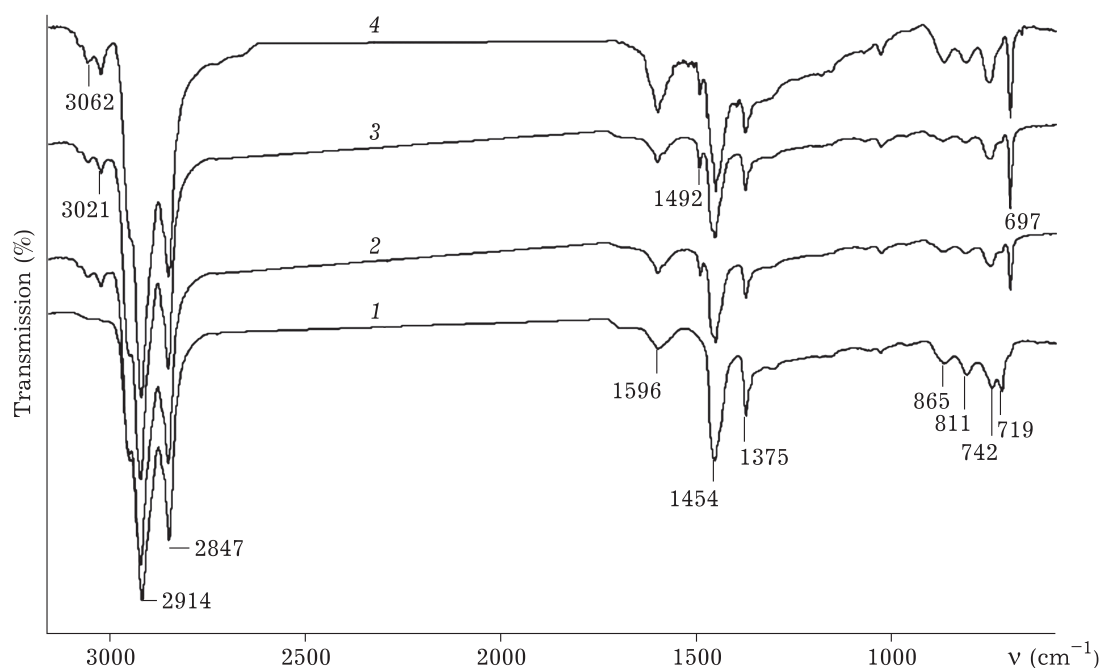


Fig. 3. FT-IR spectra of bitumen (1), pyrolysis residues of BPS31-380-2 (2), BPS31-380-1 (3) and asphaltenes of pyrolysis residue of BPS31-380-1 (4).

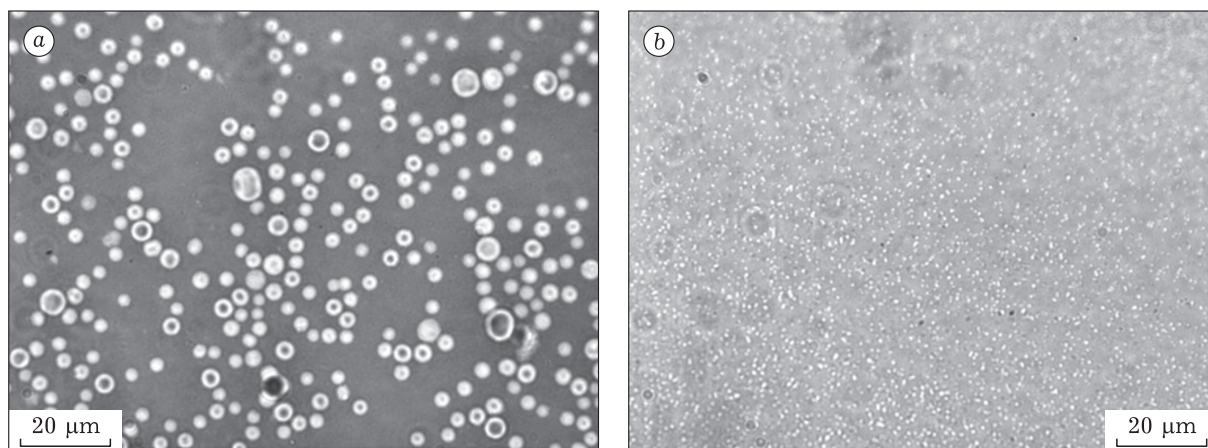


Fig. 4. Optical micrographs of BPS23-380-1(a) and BPS23-380-2 (b).

BPS23-380-2 – to oligomers with a smaller number of links or compounds that are formed resulting from addition of low-molecular-mass products of polystyrene decomposition to bitumen components.

The undecomposed polystyrene is present in optical micrographs as a separate phase (Fig. 4). Larger particles have a dark inner region due to the cavity inside the particle and a lighter shell with a thickness of about 1  $\mu\text{m}$ . There are no cavities in smaller particles. The spherical shape of the particles is due to different rates of polystyrene decomposition inside and at the bitumen-polystyrene interface. Bitumen slows down poly-

styrene decomposition, whereas inside of particles polystyrene decomposition products evolve as vapours with higher rates. Particle sizes depend on polystyrene content in composition with bitumen and mixture heat treatment duration.

For example, with a heat treatment duration of 1 h, they are 2.0–5.5  $\mu\text{m}$  (see Fig. 4, a), while upon longer processing (see Fig. 4, b) are reduced to 0.5–1.0  $\mu\text{m}$ . Apparently, according to  $^1\text{H}$  NMR and FT-IR spectroscopy data, they are aggregates of oligomers of polystyrene or compounds formed resulting from the addition of low-molecular-mass products of polystyrene decomposition to bitumen components.

In order to determine an opportunity to delaminate, a hot residue of the sample BPS23-380-1 was placed into a glass cylinder with a height of 25 cm and aged at 180 °C for 24 h. Afterwards, the residue of pyrolysis was frozen and the upper and lower layers with heights of 1 cm were selected to explore by <sup>1</sup>H NMR spectroscopy. The content of hydrogen being a part of polystyrene fragments and their concentrations in the upper and lower layers (17.5 and 14.6 mass %, respectively) were determined by the integration of <sup>1</sup>H NMR spectra. The findings testify the high temperature resistance to delamination of polystyrene-bitumen materials derived using combined pyrolysis, which is valuable in practical terms.

## CONCLUSION

Reactions involving hydrogen transfer from solvent to radical and unsaturated products of polystyrene thermal degradation determine the regularities of pyrolysis of polystyrene in the medium of heavy petroleum residues. There is a shift in the maximum rate of polystyrene mass loss to a high temperature range and mainly the saturated nature of low-molecular-mass products of polystyrene pyrolysis compared to pyrolysis of only one polymer. The contents of ethylbenzene, cumene, toluene, and 1,3-diphenylpropane are prevailing over those of unsaturated hydrocarbons, styrene, and methylstyrene.

The softening temperature and asphaltene content in the residue of pyrolysis are increased and penetration is reduced during polystyrene pyrolysis in bitumen. These characteristics vary due to both modification of the co-pyrolysis residue by the undecomposed polystyrene and hydrogen transfer from heavy petroleum residue, which initiates condensation reactions with increased asphaltene content therein.

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