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## Evaluation of Pyrocondensates as a Polymerization Raw Material

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Two pyrocondensate samples were examined in order to evaluate them as polymerization raw materials. The components were identified or undoubtedly characterized by means of mass spectral data taken by GC-MS and by gas chromatography retention data. Quantitative analysis of pyrocondensates and the residues which remained after cationic, thermal or free radical polymerizations was made by high resolution gas chromatography.

Pyrocondensates contained mainly alkyl and alkenyl substituted benzenes and fused ring compounds. In one sample bicyclic components, with cyclopentadiene and cyclohexadiene as constitutive bases, were found. As the samples contained a fairly high portion of components able to polymerize, they were found to be of interest for polymerization into resins.

Polymerization yields of the whole sample and of a single reactive component depended on the type of polymerization. Cationic polymerization gave the highest and polymerization by peroxides the lowest polymerization yield in the whole sample. Alkenylbenzenes and indenes reacted in the cationic polymerization better than in the other two kinds of polymerization, while bicycles gave the best yield in the polymerization of thermal type.

### INTRODUCTION

In order to determine the composition of the residues of pyrolytic processes of straight run gasolines, pyrocondensates, and to evaluate them as possible polymerization raw materials, their composition was studied. The investigation comprised the identification or characterization and quantitative determination of the components of pyrocondensate fractions and of the residues that remained after polymerization.

Identification of pyrocondensate constituents was performed by means of high resolution gas chromatography/mass spectrometry coupled system (GC-MS), by distinguishing the isomers with similar mass spectra on the grounds of gas chromatographic retention data. Quantitative determination was accomplished by means of flame ionization detection of the components resolved by high resolution gas chromatography.

Polymerization yields with respect to the pyrocondensate mixture as well as with respect to individual components were determined by comparing the pyrocondensate to the composition of the polymerization residue.

## EXPERIMENTAL

Two samples were investigated in this study. One of them, pyrocondensate P1, was a technologically determined sample, the other one, P2, being a mixture of pyrocondensates of different origins, was not technologically precisely defined but it was of analytical and polymerization interest.

P1 was derived from straight run gasoline with the following characteristics:

— distillation range (ASTM D 86—78):

|                     |       |
|---------------------|-------|
| start at            | 313 K |
| 10% distilled up to | 326 K |
| 50% distilled up to | 341 K |
| 95% distilled up to | 378 K |
| end at              | 411 K |

— composition after hydrocarbon type (ASTM 1319—77):

|            |       |
|------------|-------|
| paraffins  | 84.3% |
| aromatics  | 0.5%  |
| olefins    | 0.0%  |
| naphthenes | 15.2% |

Gasoline was pyrolyzed at 1103 K in a Foster-Wheeler oven for pyrolytic production of ethylene. From the heavy end, the fraction in the boiling point range between 403 and 473 K was taken by fractional distillation (sample P1).

Sample P2 was taken in the same boiling point range (403 to 473 K) from mixtures of pyrocondensates which were generated as the heavy end (boiling point range between 383 and 577 K) in a process including pyrolytic production of ethylene from gasoline in a Foster-Wheeler oven and hydrogenation of heavy end which remained after separation of light components by distillation.

In order to resolve and identify the components the samples were analysed by means of a high resolution gas chromatography/mass spectrometry coupled system, under the following conditions:

|                                      |   |
|--------------------------------------|---|
| Gas chromatograph                    | Varian 3700   |
| Column                               |   |
| Stationary phase                     | SE-54, 1.0%, low polar                              |
| Type                                 | wall coated open tubular                            |
| Inner diameter                       | 0.5 mm  |
| Length                               | 25 m  |
| Resolution after Kaiser <sup>1</sup> | 26  |
| Temperature                          | 320 K (4 min) $\xrightarrow{4 \text{ K/min}}$ 400 K |
| Carrier gas                          | He  |
| Pressure                             | 0.18 MPa  |
| Flow                                 | 2 mL/min  |
| Sample size                          | 0.2 $\mu$ L   |
| GC-MS coupling                       | open split  |
| Mass spectrometer                    | Varian MAT 112 S                                    |
| Scanning rate                        | 1 s/decade  |
| Interscan time                       | 0.2 s   |
| Resolution                           | 1 : 500   |
| Ionization                           | electron impact                                     |
| Electron energy                      | 70 eV   |
| Emission current                     | 0.7 mA  |
| Ion source temperature               | 500 K   |
| Ion source pressure                  | $10^{-5}$ Pa  |

Distinction among the isomers having very similar mass spectra was made possible by complementing mass spectrometry data with gas chromatography retention data. For the identified components the differences in Kováts retention indices<sup>2,3</sup> and boiling point differences were used. For the characterized components (*i. e.* those whose structure was not fully elucidated) the difference was obtained with the help of relative retention times which were determined in the described column, at 335 K, isothermally.

Relative retention times were calculated as related to ethylbenzene according to the relation:

$$t'_R = \frac{t'_x}{t'_{EB}},$$

where  $t'_R$  was the relative retention time of the compound,  $t'_x$  the difference between the compound's and methane retention times in the conditions chosen, and  $t'_{EB}$  the difference between ethylbenzene and methane retention times in the conditions chosen.

Quantitative analysis was performed by using high resolution gas chromatography and flame ionization detection, applying the normalization method under the column temperature conditions as mentioned above for GC-MS analysis. Flame ionization detector was supplied with 300 mL/min needle valve regulated air and 30 mL/min needle valve regulated hydrogen. Peak area was determined by an electronic integrator (Pye Unicam DP 88). No correction factors for detector response were used.

The samples examined were polymerized by applying cationic ( $AlCl_3$ ) and thermal (504 K) polymerizations and by polymerization in the presence of organic peroxide (2,4,4-trimethylpentyl-2-hydroperoxide). Details of the polymerization procedures can be found elsewhere<sup>4</sup>.

Total pyrocondensate yield and the single-component yields were determined by comparing the compositions of the sample and of its polymerization residue, using gas chromatography in the conditions as mentioned above, with ethylbenzene, an inert constituent, as the internal standard. The amount of benzene, added during the isolation of the resin (which remained in the residue) was subtracted, neglecting the amount ( $\leq 0.2\%$ ) initially present in the sample.

#### RESULTS AND DISCUSSION

The investigation of pyrocondensates showed that the fractions examined were rather complex mixtures whose high resolution gas chromatograms contained a large number of peaks (Figures 1 and 2) of varying intensity. The compositions of pyrocondensates are presented in Tables I and II, where the components are classified according to their gas chromatographic retention times. The ordinal numbers of the components were used to label the appropriate peaks in the chromatograms in Figures 1 or 2. The component content is given as mass fraction. In each of the samples more than forty components were identified.

In sample P1, of which the identified 45 components make up about 97%, the aromatic compounds predominate while aliphatics are present in quantities not higher than 0.1%. The origin of aromatics can hardly be attributed to straight run gasoline composition (containing only 0.05% of aromatics), but rather to the pyrolysis. Comparing the pyrolysis and thermo-oxidation products of polymers<sup>5-7</sup>, it can be seen that the aromatics can be formed from organic compounds of different structures released during their thermal decomposition. Their occurrence could be explained by fragment stabilization through six- and five-membered ring cyclization of radicals, which are missing a number of hydrogens because of disproportionation and dehydrogenation reactions. Their structures can vary depending on the radical size and the number and place of missing hydrogen atoms.

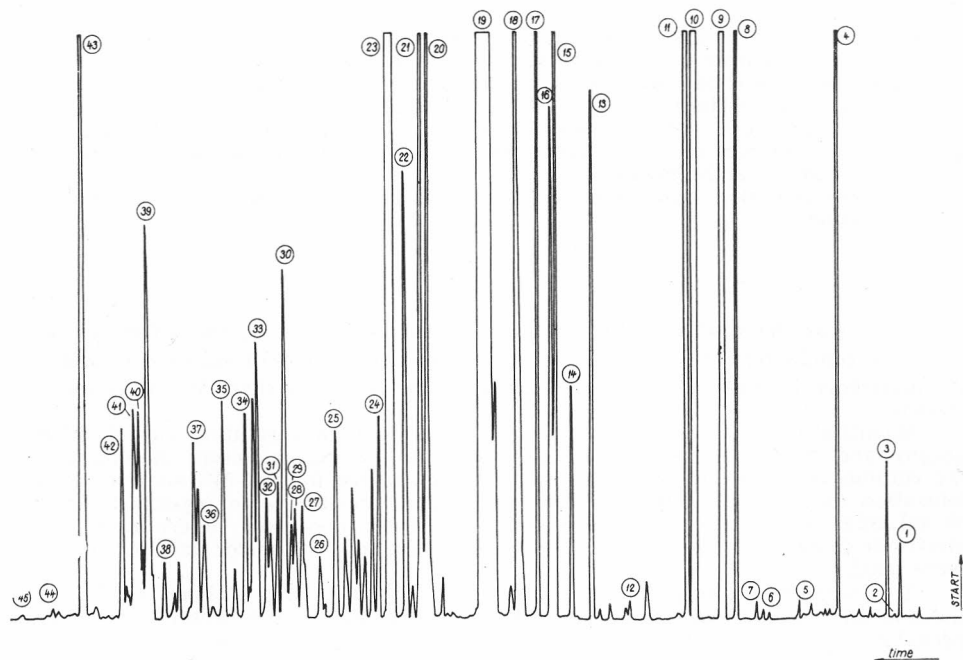


Figure 1. Gas chromatogram of the pyrocondensate sample P1 column SE-54, 1.0%  
 $T = 320 \text{ K (4 min)} \xrightarrow{4 \text{ K/min}} 400 \text{ K}$   
 Peak numbers correspond to the ordinal numbers of the appropriate components in Table I.

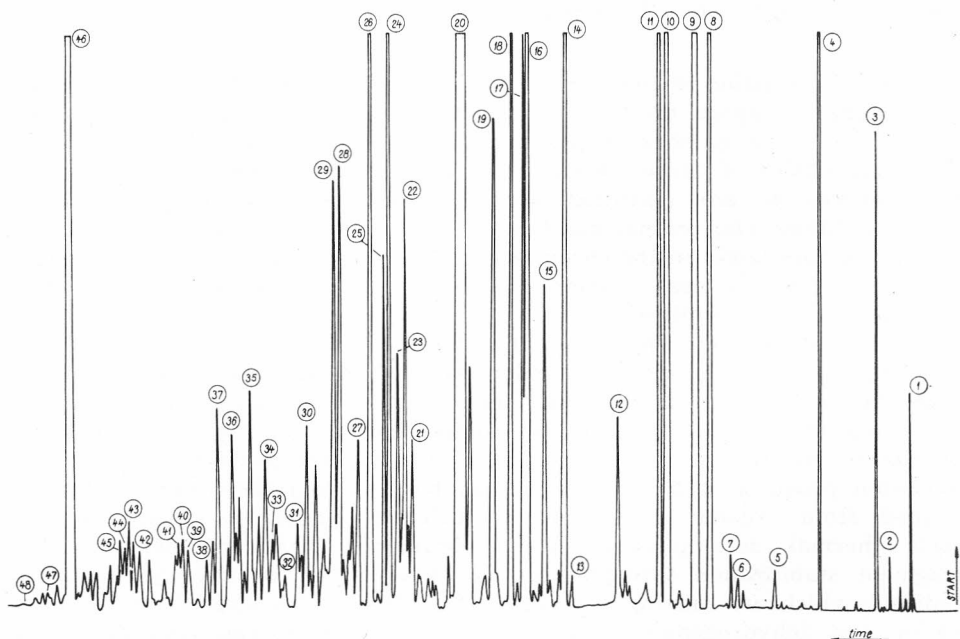




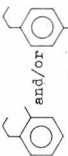







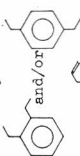



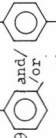




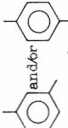











































Figure 2. Gas chromatogram of the pyrocondensate sample P2. Conditions, as in Figure 1. Peak numbers correspond to the ordinal numbers of the appropriate components in Table II.

|    |   |       |    |      |    |   |     |    |   |       |
|----|---|-------|----|------|----|---|-----|----|---|-------|
| 1  |  | 0.1   | 13 | 1.1  | 25 |    | 0.4 | 36 |  | 0.3   |
| 2  |  | < 0.1 | 14 | 0.5  | 26 |    | 0.1 | 37 |  | 0.7   |
| 3  |  | 0.2   | 15 | 2.9  | 27 |    | 0.2 | 38 |  | 0.2   |
| 4  |  | 3.9   | 16 | 0.7  | 28 |    | 0.2 | 39 |  | 2.3   |
| 5  | C <sub>8</sub> *  | < 0.1 | 17 | 1.9  | 29 |    | 0.2 | 40 |  | 0.6   |
| 6  | C <sub>8</sub> **   | < 0.1 | 18 | 1.4  | 30 |    | 1.0 | 41 |  | 1.3   |
| 7  | C <sub>9</sub>  | < 0.1 | 19 | 16.5 | 31 |  | 0.4 | 42 |  | 0.6   |
| 8  |  | 2.2   | 20 | 2.0  | 32 |  | 0.3 | 43 |  | 3.1   |
| 9  |  | 8.6   | 21 | 2.5  | 33 | Divinybenzene   | 1.0 | 44 |  | < 0.1 |
| 10 |  | 15.5  | 22 | 1.9  | 34 | Divinybenzene   | 0.5 | 45 |  | < 0.1 |
| 11 |  | 1.1   | 23 | 15.9 | 35 | Divinybenzene   | 0.6 |    |   |       |
| 12 | 30-   | 0.2   | 24 | 0.3  |    |   |     |    |   |       |

\* Number of C atoms

\*\* Double bond

TABLE II  
Components of the Pyrocondensate Sample P2

| Peak No. (Fig. 2) | Component  | Content % | Peak No. | Component  | Content % | Peak No. | Component  | Content % | Peak No. | Component  | Content % |
|-------------------|--|-----------|----------|--|-----------|----------|--|-----------|----------|--|-----------|
| 1                 |         | < 0.1     | 13       | A* $m/z: 66, 132$<br>$t_R = 1.18$  | 0.1       | 25       |       | 0.8       | 37       | A $m/z: 80, 146$<br>$t_R = 3.24$   | 1.0       |
| 2                 |         | < 0.1     | 14       |         | 2.6       | 26       |       | 8.8       | 38       |   | 0.2       |
| 3                 |         | 0.1       | 15       |         | 0.8       | 27       |       | 0.4       | 39       |   | 0.2       |
| 4                 |         | 3.1       | 16       |         | 3.2       | 28       | 4 C-  | 1.6       | 40       |   | 0.2       |
| 5                 | C <sub>8</sub>   | < 0.1     | 17       |         | 1.0       | 29       | 4 C-  | 1.7       | 41       |   | 0.2       |
| 6                 | C <sub>8</sub>   | < 0.1     | 18       |         | 2.9       | 30       |       | 0.5       | 42       |   | 0.3       |
| 7                 | C <sub>9</sub>   | < 0.1     | 19       |         | 1.1       | 31       |       | 0.2       | 43       |   | 0.3       |
| 8                 |         | 3.4       | 20       | and/or  | 13.8      | 32       | 20-   | 0.1       | 44       |   | 0.2       |
| 9                 | and/or  | 13.0      | 21       |         | 0.3       | 33       |       | 0.1       | 45       |   | 0.3       |
| 10                |         | 13.6      | 22       | A $m/z: 66, 132$<br>$t_R = 1.65$   | 0.7       | 34       | A $m/z: 80, 146$<br>$t_R = 2.65$   | 0.6       | 46       |   | 4.8       |
| 11                |         | 4.7       | 23       | A $m/z: 66, 132$<br>$t_R = 1.88$   | 0.4       | 35       | A $m/z: 80, 146$<br>$t_R = 2.76$   | 1.1       | 47       |   | 0.1       |
| 12                | 3 C-    | 0.3       | 24       | A $m/z: 66, 132$<br>$t_R = 1.96$   | 6.9       | 36       | A $m/z: 80, 146$<br>$t_R = 2.94$   | 0.5       | 48       |  | 0.1       |

\* Bicyclic compounds characterized by mass spectrum ( $m/z$ ) and gas chromatographic retention data ( $t_R$ )

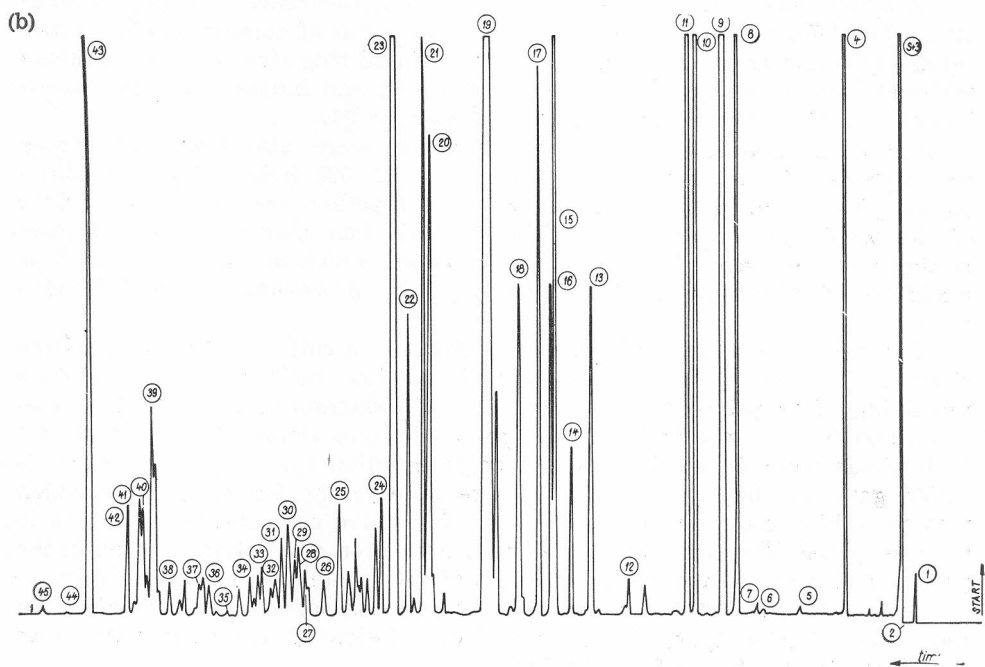
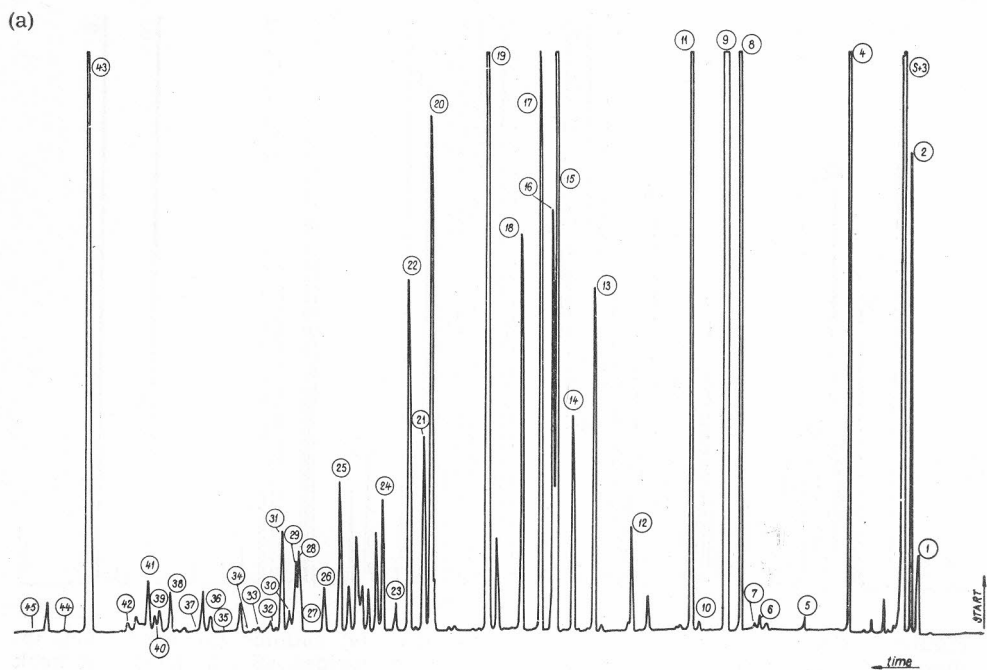


Figure 3.

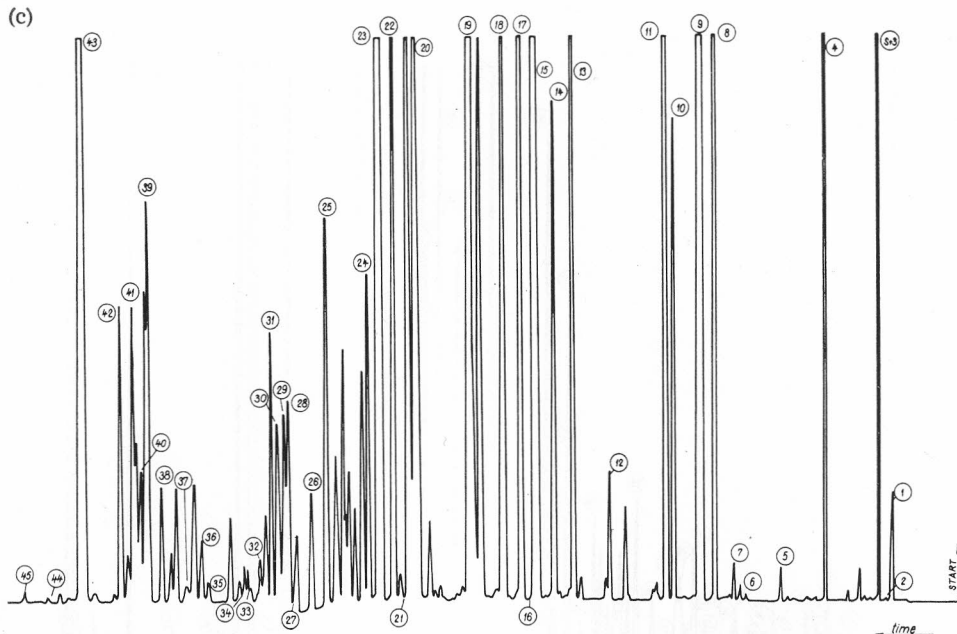


Figure 3. Comparison of residues remaining after (a) cationic polymerization, (b) thermal polymerization and (c) polymerization by peroxides. »S + 3« labels the peak appropriate to benzene present in the sample (3-Table I) and benzene added as a solvent.

Alkylbenzenes (from toluene (4) up to diethylbenzenes of different structures (28, 29)), make an appreciable fraction (27%) of sample P1. The other relatively stable aromatic components have a fused ring structure: naphthalene (43) and homologues (44, 45), methyltetralin (38) and indane (22) with homologues (31, 37). They make up to 6% of sample P1.

The components capable of polymerizing were also identified. These are: styrene (10) and homologues (18—21, 27, 32, 36), indene (23) and homologues (39—42) and divinylbenzenes (33—35). Together, they make about 63% of the whole pyrocondensate sample P1. This fact makes sample P1 interesting as a raw material for petroleum resins which are generally used as modifiers of adhesives, coatings, printing inks, processing agents for polymers etc.<sup>8</sup>

For this reason sample P1 was submitted to a different type of polymerization. Comparison of sample P1 and the low molecular mass residues remaining after polymerization, by gas chromatographic and GC—MS analyses, enabled the monitoring of the polymerization yields. It was found that both yields were determined by the polymerization type. Cationic polymerization gave the best total yield (56% relative to the whole sample), which was quite high compared to the content of reactive components in the whole mixture (63%). The yields of thermal polymerization and polymerization in the presence of peroxide were 49% and 31% of the whole sample, respectively.

It was found that the reactivity of single components also depended on the polymerization type, though not always following the same pattern as the total yield<sup>9</sup>, (Figure 3a-c, Table III).



TABLE III

Comparison of the Content of Reactive Components in Pyrocondensate Sample P1 and in Their Residues After Polymerization

| Compounds               | Content*<br>in P1 [g] | Residue Content* [g] |         |             |
|-------------------------|-----------------------|----------------------|---------|-------------|
|                         |                       | Cationic             | Thermal | By peroxide |
| Styrene                 | 15.5                  | 0.1                  | 0.4     | 3.9         |
| $\alpha$ -Methylstyrene | 1.4                   | 0.7                  | 1.3     | 1.3         |
| m/p-Methylstyrene       | 16.5                  | 4.3                  | 4.6     | 9.5         |
| o-Methylstyrene         | 2.0                   | 0.1                  | 1.6     | 2.0         |
| Dimethylstyrenes        | 0.5                   | 0.1                  | 0.2     | 0.3         |
| Propenylbenzene         | 2.5                   | 0.6                  | 0.8     | 2.3         |
| Methylallylbenzene      | 1.4                   | 0.3                  | 0.5     | 0.8         |
| Ethylvinylbenzene       | 0.3                   | 0.1                  | 0.1     | 0.1         |
| Divinylbenzenes         | 2.1                   | 0.1                  | 0.1     | 0.1         |
| Indene                  | 15.7                  | 0.1                  | 4.6     | 10.8        |
| Methylindenes           | 4.8                   | 0.4                  | 1.8     | 2.7         |

\* after 100 g of pyrocondensate sample P1

The polymerization yields of styrene, ethylvinylbenzene and, especially, divinylbenzene were higher than the total yields, irrespective of the polymerization type. Some components active in the cationic polymerization process (for example,  $\alpha$ -methylstyrene, o-methylstyrene and propenylbenzene), exhibited either a very low or almost no reactivity in the polymerization by peroxide. Indene almost completely reacted in cationic polymerization, but approximately one and two thirds of its initial amount remained unreacted after thermal polymerization and polymerization by peroxide, respectively. Its homologues showed a similar pattern. Styrene almost completely reacted in the cationic polymerization and very little remained after the thermal polymerization, while an appreciable amount was left after the polymerization by peroxide.

In sample P2, the fourty identified components make up 85%. The results presented in Table II show that relatively stable compounds; alkylbenzenes, indane (25) and homologues (40, 41), naphthalene (46) and homologues (47, 48) make up 46% of the sample. Aromatic reactive components, such as styrene (10), methylstyrenes (20, 21, 32, 38, 39), indene (26) and methylindenes (42—45) make up 38%.

Sample P2 contains 11% of the components which were characterized as alicyclic compounds (labelled as A). Each component had either of the two typical mass spectra shown in Figure 4: (a) having a large even-numbered radical ion fragment of  $m/z$  80 and a molecular ion of 146, and (b) a large even-numbered radical ion fragment with  $m/z$  66 and an easily recognizable molecular ion of a mass of 132. Mass spectra can be interpreted by assuming the presence of a bicyclic basic structure with five- and six-mem-

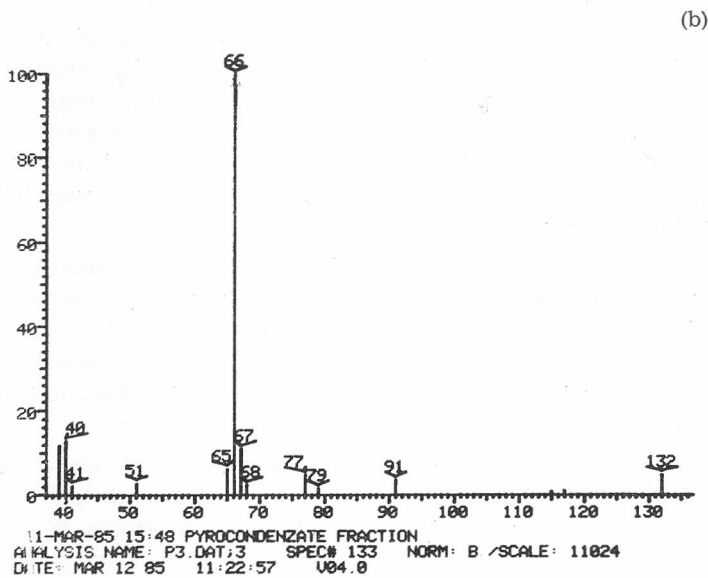
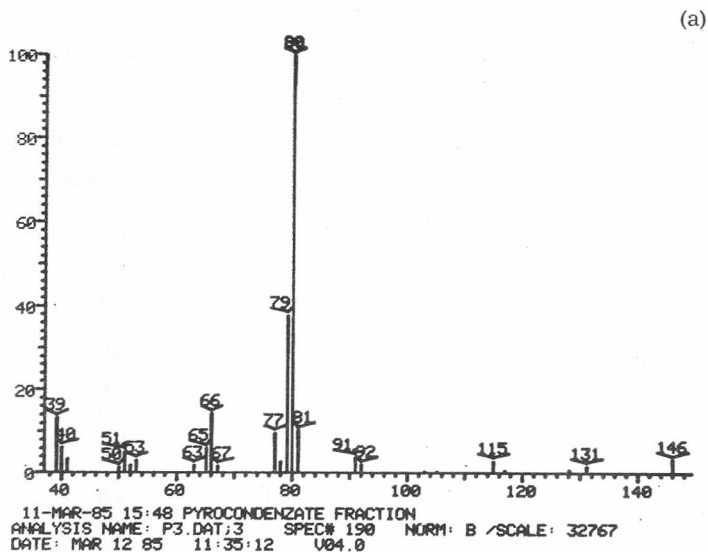
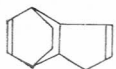


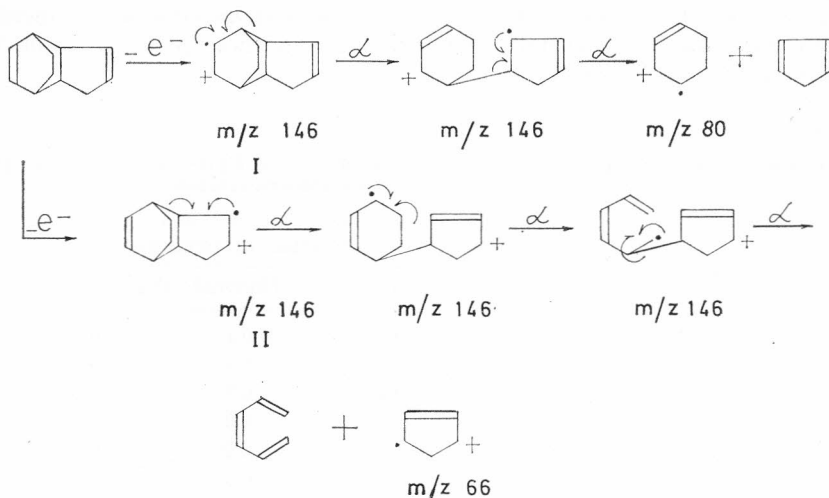
Figure 4. Typical mass spectra of the bicyclic components of the pyrocondensate sample P2.

(Aromatic fragments should be attributed to the contamination).

bered rings. For instance, spectrum (a) could be generated from the structure



which could plausibly be fragmented in the following processes:

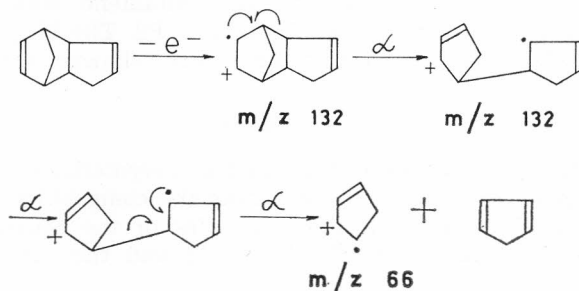


The charge and the unpaired electron can be attributed to a six-membered ring (I) causing double  $\alpha$ -cleavage in a retro-Diels-Alder reaction<sup>10</sup> resulting in a radical ion of mass 80 and a neutral radical of mass 66. If the charge and the unpaired electron are attributed to a five-membered ring (II), the occurrence of the radical ion of  $m/z$  66 can be explained by an analogous mechanism. The difference in the intensities of the radical ions of masses 80 and 66 should be ascribed to the higher ability of the six- than the five-membered ring to stabilize the charge and the unpaired electron.

In an analogous way the spectrum (b) could be ascribed to a group of isomers with a typical structure of



which can be expected to cleave as follows:



The presence of the aromatics fragment series in the mass spectra should be attributed to the contamination of the component by aromatics.

Spectra of type (b) belong to the components 13, 22—24, and the spectra of type (a) belong to the components 34—37. As the spectra of individual components within a group were not distinguishable due to their high similarity, the components could still differ in their relative retention times. Owing to this, the isomers, though they could not be completely identified, were unambiguously characterized which allowed their polymerization to be followed, as shown in Table IV.

TABLE VI

*Comparison of the Content of Bicyclic Components in Pyrocondensate Sample P2 and in Their Residues After Polymerization*

| Component | Mass fraction<br>in P2/% | Mass fraction of residue/% |         |          |
|-----------|--------------------------|----------------------------|---------|----------|
|           |                          | Cationic                   | Thermal | Peroxide |
| A (13)*   | 0.1                      | <0.1                       | <0.1    | <0.1     |
| A (22)    | 0.7                      | 0.3                        | 0.4     | 0.7      |
| A (23)    | 0.4                      | 0.2                        | 0.3     | 0.3      |
| A (24)    | 6.9                      | 3.3                        | 0.8     | 5.7      |
| A (34)    | 0.6                      | <0.1                       | 0.2     | 0.3      |
| A (35)    | 1.1                      | 0.2                        | 0.1     | 0.8      |
| A (36)    | 0.5                      | <0.1                       | 0.1     | 0.2      |
| A (37)    | 1.0                      | 0.2                        | 0.1     | 0.5      |

\* ordinal number of the component labelled as A in Table 2

In the thermal polymerization, 82% of the total bicyclic constituents polymerized, their reactivities being different in spite of equal conditions. Thus, the bicycles A(24), A(35) and A(37) gave the best relative yields. In cationic polymerization and the polymerization by peroxides, the conversion yields of bicyclic components were 63% and 25%, respectively, differing also in relative yields of individual components. The yield for the thermal polymerization of the whole sample P2 was 40% and it amounted to 50% for the cationic polymerization (3—4% of sample P2 was neither identified nor characterized); to the contrary, the yield of the polymerization by peroxides was a mere 24%.

The presence of bicyclic components could probably be attributed to the dimerization of cyclohexadiene and/or cyclopentadiene which, although in very low concentrations, were present in sample P2. The bicyclic components in sample P2, when left at room temperature, showed some spontaneous oligomerization.

#### CONCLUSION

Pyrocondensate samples were evaluated as polymerization raw materials. The analytical approach enabled to determine the composition of pyrocondensate samples regarding the type and quantities of the constituents, as well as to determine the total polymerization yield and the yields of individual reactive components.

Pyrocondensate samples are rather complex mixtures containing alkyl- and alkenylbenzenes, fused aromatics and cyclic compounds, as well as low concentrations of some aliphatics. Among the components there are potentially reactive ones, accounting for a fairly high fraction of both samples studied. This makes the samples interesting for polymerization into petroleum resins without previous separation of reactive components.

In sample P1, reactive components (alkenylbenzenes and indenenes) make up 63% wt. Sample P2 is made up of 49% wt. of the reactive components such as alkenylbenzenes, indenenes and bicyclic compounds with cyclopentadiene and/or cyclohexadiene as constitute bases.

Comparing the polymerization yields, both samples gave the highest yields in the polymerization of cationic type and the lowest one in the polymerization by peroxide.

The single-component reactivity showed a selectivity to the polymerization type and often did not follow the same yield pattern as the whole sample. Divinylbenzenes, ethylvinylbenzene and styrene gave in all types of polymerization much higher yields than the whole sample. Alpha-methylstyrene, o-methylstyrene and propenylbenzene showed good polymerization activity in the cationic, but a very low one in the polymerization by peroxide. All indenenes readily polymerized at cationic initiation but gave significantly lower polymerization yields in thermal and free radical polymerization. Bicyclic components of high structural similarity regarding their mass spectra differed in the polymerization activity under the same conditions. Their total activity depended on the polymerization type as well; the highest reactivity was shown in thermal polymerization and the lowest one in the polymerization by peroxides.

The applied evaluation approach permits to find out the selective reactivity of the components as controlled by synthesis conditions and in this way to optimize the polymerization conditions for the most interesting component type.

As the produced polymer resin structure was expected to be rather complex, the knowledge about the reacted components served also to predict the resin structure.

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**SAŽETAK****Ispitivanje pirokondenzata kao sirovina za polimerizaciju**

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Ispitana su dva uzorka pirokondenzata kako bi se ocijenile mogućnosti njihove primjene kao sirovina za polimerizaciju. Sastojci pirokondenzata su identificirani ili nedvojbeno karakterizirani na osnovi podataka sa spektara masa dobivenih vezanim sustavom GC-MS i na osnovi podataka o zadržavanju na plinskromatografskoj koloni. Kvantitativna analiza pirokondenzata i ostataka koji su ostali nakon kationske i termičke polimerizacije, te polimerizacije sa slobodnim radikalima, provedena je s pomoću plinske kromatografije visokog razlučivanja.

Pirokondenzati sadrže uglavnom alkil- i alkenilbenzene te kondenzirane aromatske spojeve. U jednom su uzorku pronađeni biciklički spojevi s ciklopentadienom i cikloheksadienom kao sastavnom osnovom. Budući da uzorci sadrže prilično visok udio sastojaka koji mogu polimerizirati, zanimljivi su za polimerizaciju u smole.

Iscrpak polimerizacije cijelog uzorka i pojedinih reaktivnih sastojaka ovisi o tipu polimerizacije. Kationska polimerizacija daje najviši, a polimerizacija s peroksidima najniži iscrpak polimerizacije cijelog uzorka.

Alkenilbenzeni i indeni reaktivniji su u uvjetima kationske polimerizacije, a biciklički spojevi daju najbolji iscrpak u termičkoj polimerizaciji.