racemic diastereomeric complex containing *syn*-2-amino-3-methyl-5-oxopentanoic acid. Decomposition of the complex and the synthesis of racemic *trans*-3-methylproline were carried out as described previously for the optically pure compound.[16] Yield 0.24 g (63 %). M.p. 215 °C. The ^{1}H NMR spectrum corresponded to that reported.

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Investigation of the chemical heterogeneity of polyphenylenes using the condensation of methyl aryl ketones as a model reaction

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The chemical heterogeneity of polyphenylenes obtained by trimerization polycyclocondensation of acetylaromatic compounds has been investigated by GLC-MS analysis of the products of trimerization cyclocondensation of acetophenone. The mechanism for the formation of side products of the reaction is discussed. The presence of dypnone fragments in the polyphenylene structure results in a decrease in the thermal stability of these polymers.

Key words: condensation of acetophenone, mechanism; GLC-MS analysis, heterogeneity of polyphenylenes, thermal stability.

It is known[1] that in addition to the main units, any polymer contains a certain number of defective units that can, to some extent, affect the properties of the polymer. We performed a chromato-mass-spectrometric study of the products of a model reaction, *viz.*, trimerization cyclocondensation of acetophenone in the presence of triethyl orthoformate under the standard conditions for polyphenylene synthesis,[2] in order to

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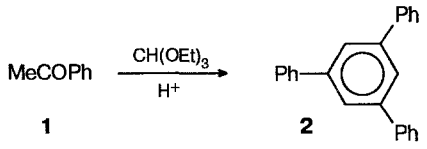
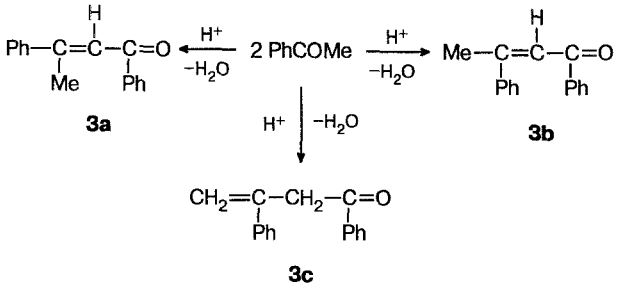
investigate the chemical heterogeneity of polyphenylenes obtained by polycyclocondensation of acetylaromatic compounds and to reveal the effect of the defective fragments on the properties of the polymers.



1 **2**

Along with 1,3,5-triphenylbenzene (**2**),[3] the reaction products contain an array of side products (Table 1), among which dypnone (**3**) (*m/z* 222, 221, 207, 145, 117, 115, 105, 77) and ethyl benzoate (**4**)[3] predominate (Fig. 1).

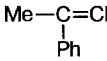
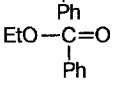
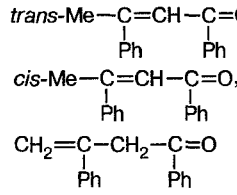
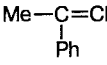
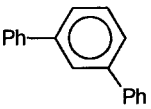
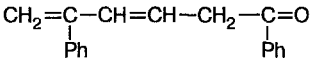
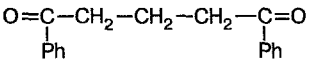
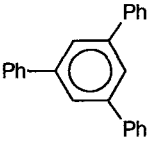
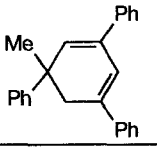
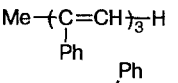
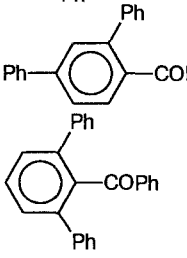
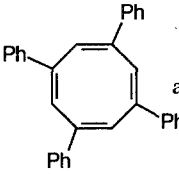
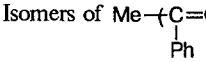
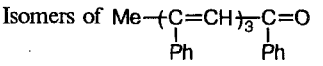
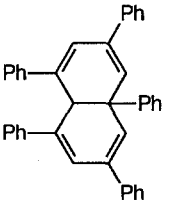
There are three reaction products whose mass spectra contain a molecular ion with *m/z* 222; here the ion peak with *m/z* 221 $(M-H)^+$ has higher intensity than the peak of the molecular ion (1 : 0.7—0.9). The structures of these isomers are given below:



3a **3b** **3c**

Dypnone is hydrolyzed to benzoic acid in the presence of acid catalysts.[4] By analogy, the formation of ethyl benzoate **4** can be explained by the alcoholysis of dypnone and a number of other compounds under the

Table 1. Products of the condensation of acetophenone (according to GLC-MS)

M^+	Compound	Retention time	Compound corresponding to the molecular ion
118	**5**	11'48"	
150	**4**	13'37"	
222	**3a—c**	23'14", 23'45", 24'55"	
224	**26**	23'24"	
230	**25**	26'26"	
248	**6**	27'42"	
252	**27**	27'32"	
306	**2**	38'43"	
322	**20**	34'20"	
322	**7**	34'40"	
334	**24a,b**	38'57", 39'36"	
408	**12, 18a—e**	56'31", 62'34", 64'28"	 and its isomers
424	**8**	58'30"	Isomers of 
426	**16a—e, 17**	60'09", 60'18" 61'22"	Isomers of 
510	**19**	81'58"	

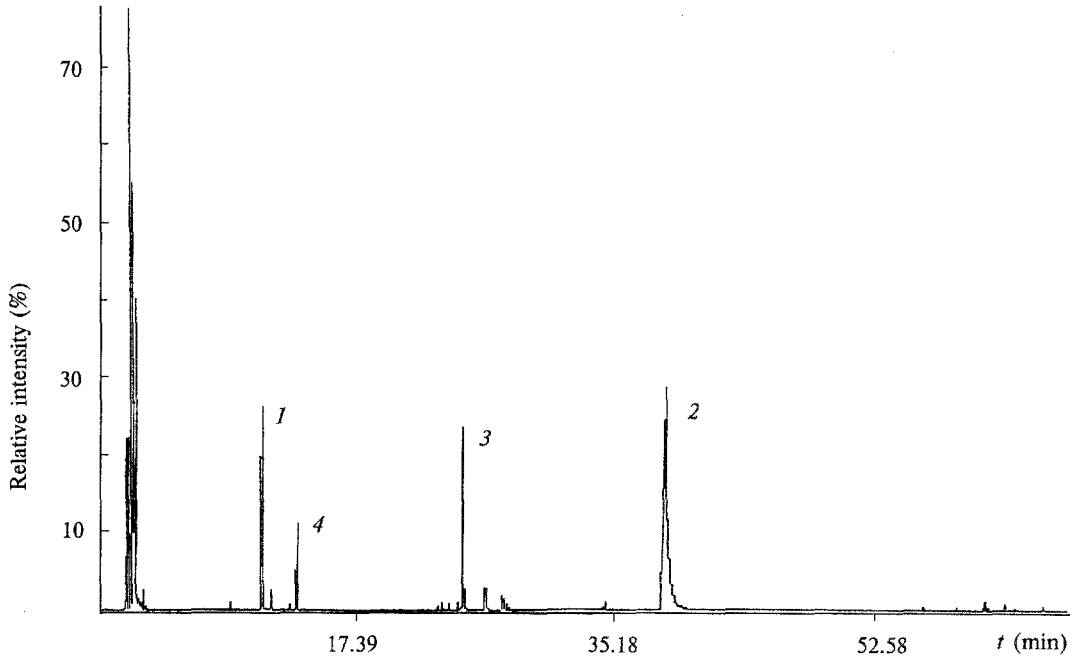
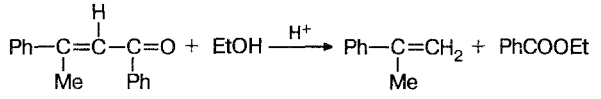


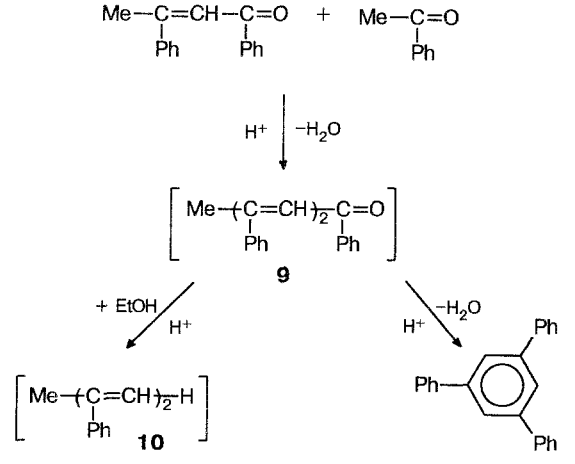
Fig. 1. Chromatogram of products of the model reaction of trimerization cyclocondensation of acetophenone: *1*, *2*, *3*, and *4* denote compounds **1**, **2**, **3**, and **4**, respectively.

action of ethanol formed in the reaction:

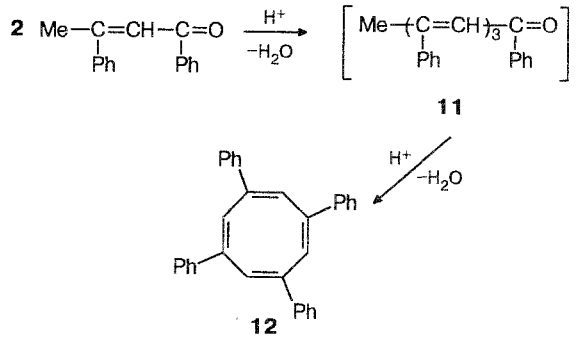


This interpretation is supported by the presence of methylstyrene (**5**) (M^+ 118) and other vinylidene-containing compounds (M^+ 248 (**6**), 322 (**7**), 424 (**8**)) and the absence of benzoic acid (M^+ 122) among the reaction products (see Table 1).

The absence of tripnone, *i.e.*, the linear trimer (**9**) (M 324), and its alcoholysis product (**10**) (M 220) in the mixture attests to the high reactivity of compound **9** leading to its almost immediate cyclization after formation:

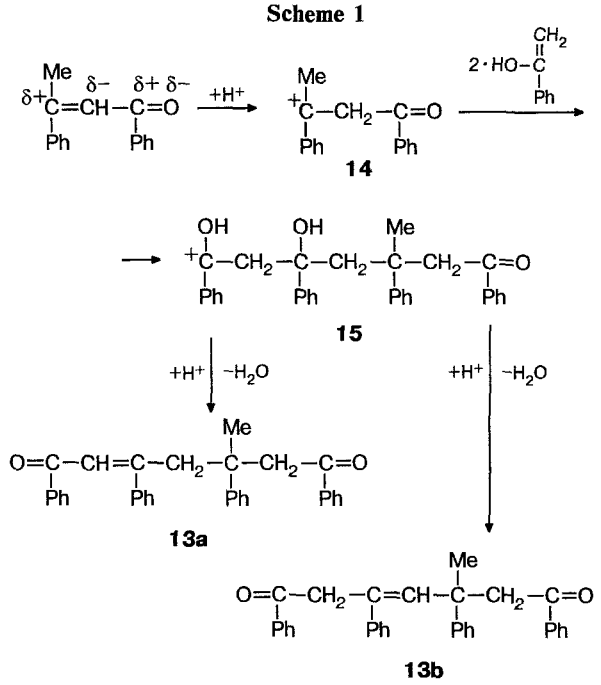


The formation of tetrapnone (the linear tetramer) (**11**) (M 426) should occur through the dimerization of dypnone:



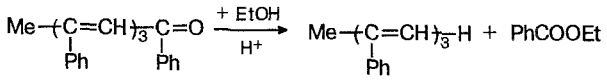
However, the presence of a rather large amount of a compound with M^+ 426 in the reaction products is probably not due to compound **11**, as was stated earlier[5] in a study of the self-condensation of acetophenone diethyl ketal, since compound **11** should have almost the same cyclization ability as compound **9** (1,3,5,7-tetraphenylcyclooctatetraene **12** is formed from **11**). Rather, this ion is due to compounds whose inter- and intramolecular condensation is hindered. These compounds can be obtained from linear tetramers (**13a,b**). One of the possible mechanisms for the formation of the latter is presented in Scheme 1. According to this mechanism, the protonation of compound **3** can proceed not only at the oxygen atom but also at the carbon atom bearing a partial negative charge due to conjugation.

Scheme 1



The carbocation (**14**) successively reacts with two molecules of compound **1** in the enol form to give a new carbocation (**15**), which can intramolecularly split off a molecule of water and a proton to give compound **13a** or **13b**. Apparently, the latter compounds undergo intramolecular condensation to give at least three cyclic compounds isomeric to compound **11**. Unfortunately, mass spectra alone do not permit the unambiguous identification of these compounds from a mixture of others which, in principle, can be formed in this reaction (**16a—e, 17**).[6—8] Further condensation of compound **16** with a molecule of **1** is probably hindered for steric reasons, since the C=O group in compounds **16** is located between two cycles. This results in the accumulation of compounds with M^+ 426 in the reaction products. Some of compounds **16** undergo further intramolecular condensation to give three cyclic compounds with M^+ 408. The mass spectra of the latter two isomers exhibit fragmentary ions with *m/z* 393 suggesting the presence of a methyl group in these compounds, whereas the spectrum for the third isomer does not contain this ion. This fact is additional indirect evidence that cyclic compounds with M^+ 426 are formed in the model reaction. The assignment of compounds with M^+ 408 to a particular one of the series of the theoretically possible compounds (**18a—e**)[5—7] is also problematic for the above reason. Compound **17**, suffering no steric hindrance, can undergo condensation with a molecule of **1** to give 9,10-dihydro-2,4,5,7,9-pentaphenylnaphthalene (M^+ 510) (**19**).[5]

The presence of two compounds with M^+ 322 (**7** and **20**) among the reaction products may be rationalized by the alcoholysis of compound **11** to give a vinylidene-containing compound (**7**) (*m/z* 322, 307, 291, 245, 231, 103, and 77), on the one hand:



7

and the alcoholysis of compound **13a** (Scheme 2) followed by intramolecular condensation which results in 5-methyl-1,3,5-triphenyl-1,3-cyclohexadiene (**20**) (*m/z* 322, 307, 306, 289, 247, 77), on the other hand.

Subsequent analysis of the products of the model reaction indicates that, along with the self-condensation of acetyl fragments and the alcoholysis of the condensed molecules, there occurs condensation of triethyl orthoformate (**21**) (Scheme 3) with acetyl groups. For instance, compound **21** reacts with two molecules of **1** to produce 1,5-diphenyl-1-pentene-1,5-dione (**22**),[9] which undergoes either cyclization to give a pyrilium salt (**23**) (isolated directly from the mixture of reaction products), or various reactions which result, *e.g.*, in 2,4- and 2,6-diphenylbenzophenones (**24a** and **24b**, respectively) and *m*-terphenyl (**25**).[10]

It is almost impossible to unambiguously identify compounds with M^+ 224 (**26**) M^+ 252 (**27**) (Table 1). However, it may not be ruled out that they are products of hydrogenation of compounds **3** and **22**, respectively, formed by the ionic hydrogenation mechanism.[11] In this case, ethanol or triethyl orthoformate probably serve as donors of the hydride ion.

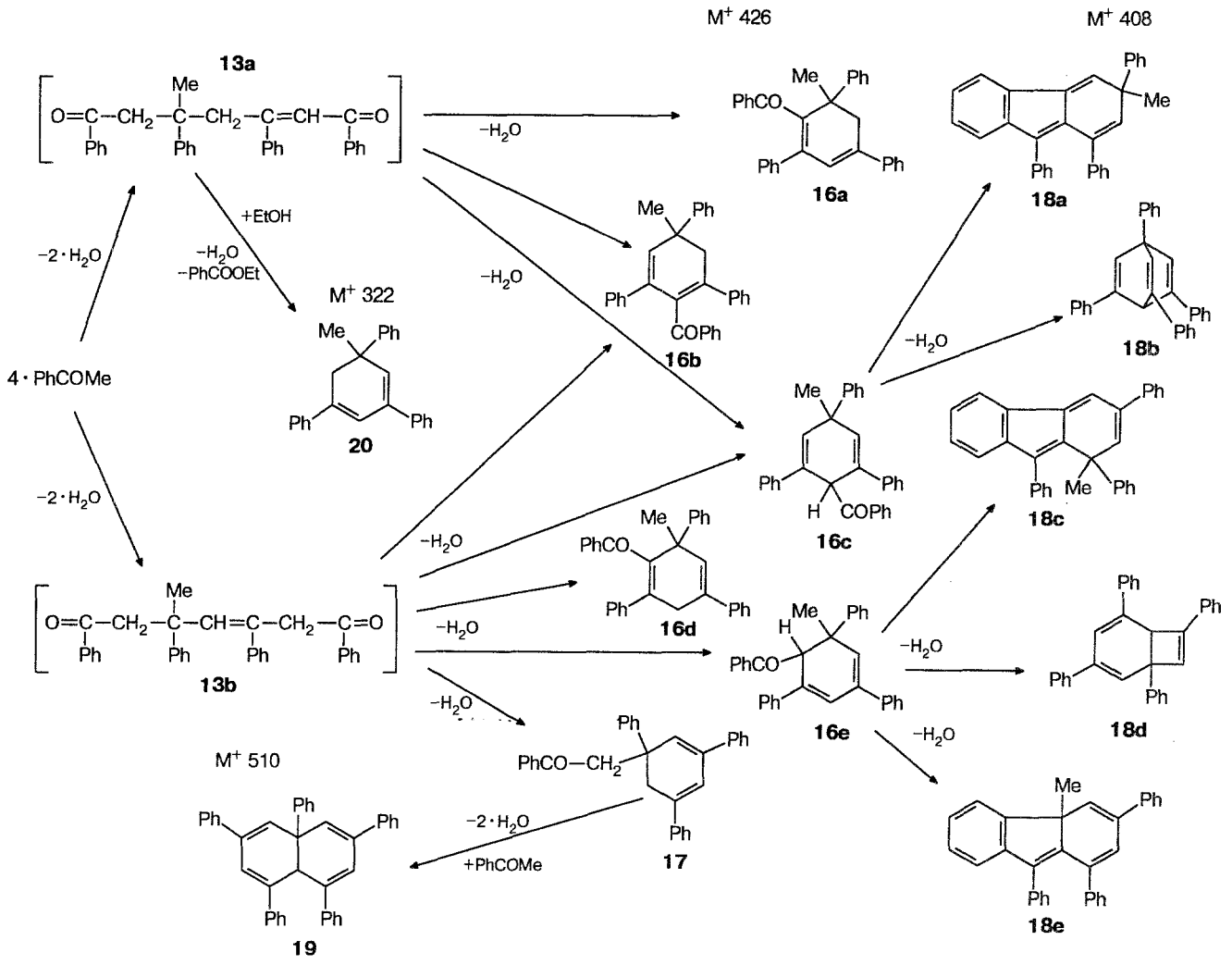
It is of note that the GLC-MS study of the products of the model reaction, the trimerization cyclocondensation of acetophenone, unlike a similar study of the self-condensation of acetophenone diethyl ketal,[5] did not reveal α-ethoxystyrene (M^+ 148) or acetophenone ketal (M 194) (an independent study has shown that the latter does not form a molecular ion in the mass spectrum, but is detected as α-ethoxystyrene (M^+ 148)).

The reaction of the trimerization cyclocondensation of 5-acetylacenaphthene mainly results in products analogous to the above compounds (as was revealed by a mass spectrometric study).

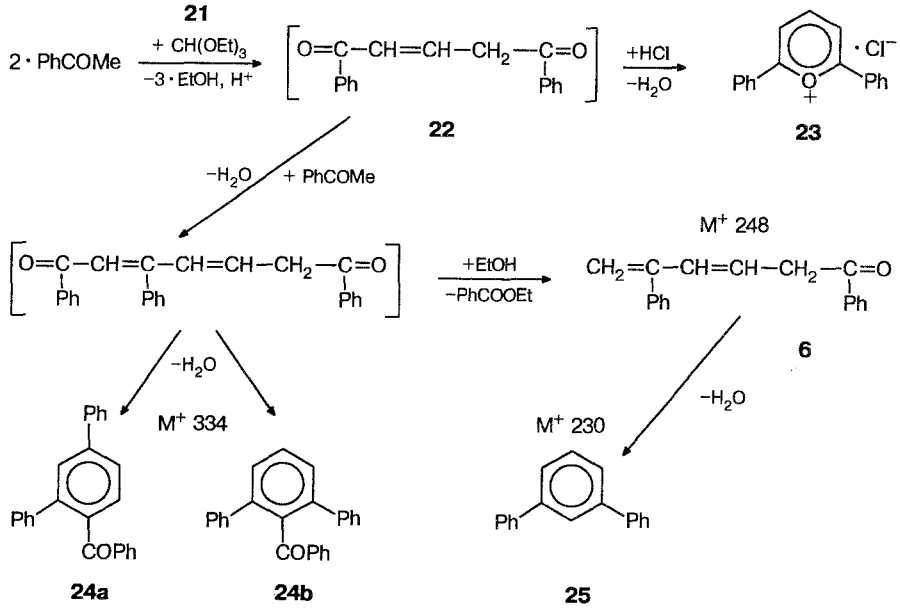
Thus, it follows from the study performed that polyphenylene can contain a wide range of various defective fragments. From the viewpoint of chemical stability, the linear aliphatic segments of the chain are the weak sites (due to alcoholysis and hydrolysis[4]).

Since, judging by the model reaction, dypnone units (Fig. 1) are the main defective fragments in polyphenylene, it was of interest to study the effect of these units on the thermal stability of the polymer. For this purpose, we synthesized some hitherto unknown compounds of the dypnone type, *viz.*, 1,3-bis(5-acenaphthenyl)-2-buten-1-one (**28**) and 1,3-bis(5-acenaphthylenyl)-2-buten-1-one (**29**) (Scheme 4) as well as 1,3,5-tris(5-acenaphthenyl)benzene (**30**), which is a model of polyphenylene.

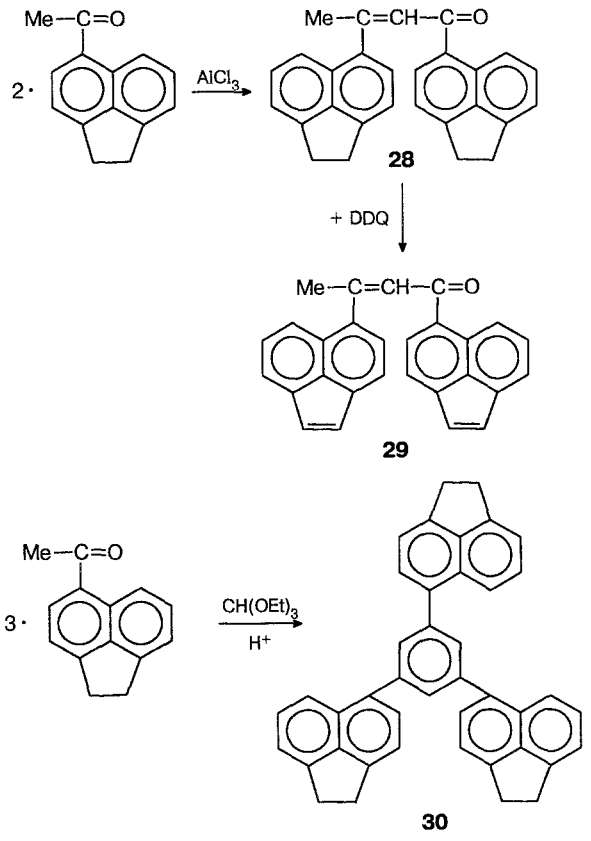
Scheme 2



Scheme 3



Scheme 4



The study of the thermal stability of model compounds by dynamic TGA (thermogravimetric analysis) revealed (Fig. 2) that the temperature for the start of weight loss is almost 200 °C lower for compound **28** than for compound **30** (the weight loss for compound **30** at 120 °C is due to the decomposition of its solvate with benzene, whose existence has been confirmed by X-ray diffraction analysis[12]). The replacement of acenaphthenyl groups in compounds of the dypnone type by acenaphthylenyl groups brings about an 80 °C increase in thermal stability due to the occurrence of polymerization processes.

Thus, the presence of dypnone fragments (the main defective units) in the polyphenylene structure impairs the thermal stability of the polymers. However, it is possible to improve this property for the final polymer by introducing acenaphthylenyl groups into the oligomer.

Experimental

GLC-MS analysis was carried out on a Kratos MS 890 mass spectrometer (Great Britain) with a quartz capillary column (l = 15 m) using a methylsiloxane elastomer as the stationary phase.

Chloroform was used as the solvent. The temperature was programmed from 50 °C to 272 °C at 10° min^{-1} heating rate,

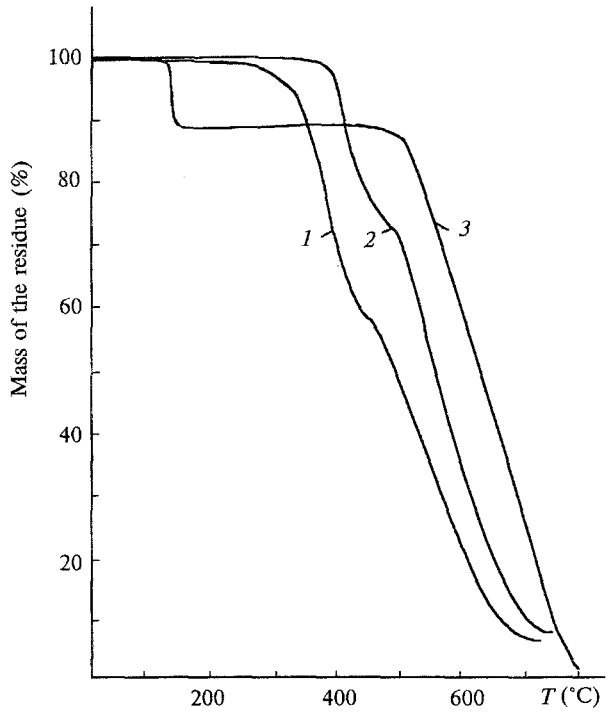


Fig. 2. Dynamic TGA in air for compounds **28** (*1*), **29** (*2*), and **30** (*3*).

and then kept for 1 h 10 min at 272 °C. Helium was used as the carrier gas. The evaporator temperature was 250 °C. Ionization was induced by electron impact with 70 eV impact energy; the ionizing chamber temperature was 250 °C. Mass spectra for individual compounds were recorded on AEI MS 30 (Great Britain) and Kratos MS 890 mass spectrometers at 70 eV at an ionizing chamber temperature of 250 °C.

Dynamic TGA was performed on a MOM derivatograph (Hungary) in air at a heating rate of 5° min^{-1}.

DSC tests were carried out on a DuPont thermoanalyzer (DSC 912 unit) at a heating rate of 5° min^{-1}.

^1H NMR spectra were recorded on a Bruker WP-200-SY spectrometer (200.13 MHz) using $CDCl_3$ as the solvent and hexamethyldisiloxane as the standard. IR spectra were obtained on a UR-20 spectrophotometer.

Model reaction of trimerization cyclocondensation of acetophenone. Gaseous HCl was passed (20—30 mL min^{-1}) at ~20 °C for 4 h through a stirred solution of acetophenone (1.15 mL, 0.01 mol) and triethyl orthoformate (2 mL, 0.012 mol) in absolute benzene (6.8 mL). Then the volatile components and the solvent were removed from the reaction solution.

Model reaction of trimerization cyclocondensation of 5-acetylacenaphthene. Gaseous HCl was passed (20—30 mL min^{-1}) at ~20 °C for 4 h through a stirred solution of 5-acetylacenaphthene (1.96 g, 0.01 mol) and triethyl orthoformate (2 mL, 0.012 mol) in benzene (8 mL). Then the volatile components and the solvent were removed from the reaction solution.

1,3-Bis(5-acenaphthenyl)-2-buten-1-one (28). A solution of 5-acetylacenaphthene (39.2 g, 0.2 mol) in carbon disulfide (100 mL) was added dropwise at 20 °C over 1.5 h to a suspension of $AlCl_3$ (14 g, 0.1 mol) in carbon disulfide

(100 mL). After 10 days, $AlCl_3$ (28 g, 0.2 mol) was added. The mixture was kept for a long time, then chloroform (200 mL) was added, and the resulting solution was poured into water acidified with hydrochloric acid. The organic phase was separated from the aqueous layer and washed with water. The solvent was removed, and then compound **28** was isolated from the product by column chromatography (silica gel, benzene, R_f = 0.6). The yield was 4.0 g (10.7 %), m.p. 148.5—151.5 °C.

^{1}H NMR, δ: 2.74 (d, J = 1.5 Hz, 3 H, CH_3); 3.41 and 3.42 (both s, 8 H, CH_2—CH_2); 7.06 (q, J = 1.5 Hz, 1 H, CH=C). IR, ν/cm^{-1}: 1650 (C=O). MS, *m/z* (*I* (%)): 375 (12), 374 (100), 359 (25), 191 (11), 153 (37), 152 (25), 151 (26).

1,3-Bis(5-acenaphthylenyl)-2-buten-1-one (29). 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (1.760 g) was added to a solution of compound **28** (0.965 g) in absolute benzene (77 mL). The reaction mixture was stirred for 6 h and then hexane (75 mL) was added. The precipitate was removed, and compound **29** was isolated from the mother liquior by column chromatography (silica gel, benzene—hexane (1:1), R_f = 0.5) in 50 % yield, m.p. 115—116 °C.

^{1}H NMR, δ: 2.81 (d, J = 1.4 Hz, 3 H, CH_3); 6.98 and 7.13 (AB-q, J = 5.4 Hz, 2 H, CH=CH for acenaphthylenyl at C_1 of butene); 7.04 (q, J = 1.4 Hz, 1 H, CH=C); 7.07 and 7.11 (AB-q, J = 5.0 Hz, 2 H, CH=CH for acenaphthylenyl at C_3 of butene). IR, ν/cm^{-1}: 1420 (CH=CH), 1650 (C=O).

1,3,5-Tris(5-acenaphthenyl)benzene (30). The synthesis was performed according to the known procedure (ref. 13). The product was purified by column chromatography (silica gel, benzene—hexane (1:1), R_f = 0.5) and crystallization from benzene—hexane. The m.p. of its solvate with benzene is 120—122 °C, and m.p. of **30** itself is 296—296 °C (dec.) (*cf.* ref. 13, m.p. 308 °C). For the solvate: m.p. 123 °C, m.p. 320 °C (as determined from DSC under nitrogen).

^{1}H NMR, δ: 3.45 (s, 12 H, CH_2); 7.86 (s, 3 H, 1,3,5-trisubstituted benzene). MS, *m/z* (*I* (%)): 536 (12), 535 (55), 534 (100), 532 (8), 153 (8).

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