Study of structural aspects of thermochemical conversions of compounds modeling oligophenylenes containing acenaphthylenyl and acenaphthenyl groups

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With the aim of elucidating the mechanism of the thermochemical conversion of oligophenylenes containing acenaphthylenyl groups, the thermolysis of model compounds: 1,3,5-tris(5-acenaphthylenyl)benzene (1), 1,3,5-tris(5-acenaphthenyl)benzene (2), acenaphthylene, and acenaphthene, was studied by differential thermal analysis (DTA), dynamic thermogravimetric analysis (TGA), and mass spectrometry. Compounds 1 and 2 were studied by X-ray structural analysis. A scheme for the formation of secondary structures was suggested. Optimum temperature conditions were found for preparing thermostable, heat-resistant, and stable to thermooxidation polymers based on compounds containing the acenaphthylenyl groups.

Key words: 1,3,5-tris(5-acenaphthylenyl)benzene, 1,3,5-tris(5-acenaphthenyl)benzene, acenaphthylene, acenaphthene, thermochemical conversions; decacyclene; polymers, thermal properties; X-ray structural analysis.

Previously,^{1,2} it has been demonstrated that the introduction of reactive acenaphthylenyl groups to oligophenylenes prepared by trimerization polycyclocondensation of acetylaromatic compounds or of their diethyl acetals substantially simplifies the process of converting oligomers to three-dimensional polymers. This work is devoted to the study of thermochemical conversions of acenaphthylenyl groups over a wide range of temperatures with the aim of revealing the possibilities of forming thermostable secondary structures based on the above mentioned groups, which should result in enhancement of the thermal characteristics of the final polymers. 1,3,5-Tris(5-acenaphthylenyl)benzene (1), which serves as a model for oligophenylene containing acenaphthylenyl groups, was chosen as the main subject of investigation.

Figure 1 shows the results of DTA performed in air for the original samples of compound 1 and those preheated in an inert atmosphere at different temperatures. In the spectrum of the nonheated sample (curve I) at 250 °C, an exothermal peak is observed, which is attributable to the polymerization of the acenaphthylenyl groups. The temperature at which polymerization of these groups occurs depends essentially on the experimental conditions. For example, the study of compound 1 by differential scanning calorimetry under nitrogen demonstrated that exothermal polymerization occurs at 269 °C. It follows from the results of an analogous study carried out in air that the exothermal peak at 195 °C is attributable to the polymerization process initiated by atmospheric oxygen.

DTA shows that the exothermal peak in the region of 250 °C is partially retained for the sample of compound 1 preheated at 250 °C (see Fig. 1, curve 2), which is attributable to the presence of non-polymerized acenaphthylenyl groups, though, based on the sol-gel analysis, the sample under study is a completely crosslinked polymer (100 % gel fraction). In the region of 370-380 °C, one more exothermal peak is observed; based on the dynamic TGA performed in air, according to which a substantial increase in weight (up to 10 %) is observed for samples of compound 1 in the region of 370-380 °C, this peak is attributable to the oxidation of the acenaphthylene type groups that result from thermal depolymerization of the polyacenaphthylene fragments of the chain formed. It should be noted that the increase in weight of 1,3,5-tris(5-acenaphthenyl)benzene (2) in the same temperature range is not so pronounced (< 2 %).

The shape of the DTA curves of compound 1 preheated at 300 °C and above indicates that the products of the thermal treatment initially contain almost no acenaphthylenyl groups. For the sample obtained by thermal treatment of compound 1 at 350 °C (see Fig. 1, curve 4) and, especially, at 400 °C (curve 5), a decrease in the intensity of the thermal effect is observed, which

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Fig. 1. Differential thermal analysis of compound 1 preheated at 20 °C (1), 250 °C (2), 300 °C (3), 350 °C (4), and 400 °C (5).

was previously attributed to the oxidation of the acenaphthylene type groups. Based on TGA, the increase in weight in the region of 370-380 °C is 10 % for the sample preheated at 250 °C, whereas it is only 4 % for the sample preheated at 400 °C, which is attributable to secondary conversions of the acenaphthylenyl groups with the formation of more thermostable structures also exhibiting thermooxidation stability. The results of the study of the character of the deformation curves for samples of compound 1 obtained at different temperatures (Fig. 2) also attest to this fact. Thus, at 250 °C and above, highly crosslinked polymers are formed; their deformation is virtually absent even at an imposed load of 20 MPa up to 430 °C. For the sample preheated at 450 °C, no substantial deformation is observed even at > 430 °C; this is attributable to the formation of a more rigid structure owing to secondary conversions of the acenaphthylenyl groups. It is virtually impossible to analyze these structures for the chosen model, because compound 1 preheated at 250 °C and above is an insoluble three-dimensional polymer.

Taking into account the series of publications, which are unfortunately rather contradictory, on the thermochemical conversions of acenaphthylene,³⁻¹⁴ the soluble portion of the acenaphthylene samples preheated at 400 °C and above was studied to analyze the secondary structures formed as a result of thermochemical conversions of the acenaphthylenyl groups (Fig. 3).



Fig. 2. Deformation curves for samples of compound 1 pressed at 20 °C (1), 200 °C (2), 250 °C (3), 300 and 350 °C (4), 400 °C (5), and 450 °C (6).

Among the products of thermochemical conversions, decacyclene (3) and acenaphthene were identified by comparison with the available authentic samples using liquid chromatography (Fig. 4). Decacyclene is the major product, while acenaphthylene is not observed at all. Other products were determined by mass spectrometry, the results of which are given in Table 1. As can be seen



Fig. 3. Sol-gel analysis of samples of 2 (1), 1 (2), acenaphthene (3), and acenaphthylene (4) preheated at 400-550 °C.

Com-	•		n/2					
po-	m/z	Tentative structure of the product	Acenaphthylene		Acenaphthene			
und			400 °C	450 °C	400 °C	500 °C	550 °C	
5	152		+	+	+	+	+	
	154		+	+	+	+	+	
10	252		+	+	-	+	+	
12	266	а Н Н Н Н Н Н	_	_	_	÷	+	
11	276—278		0, 1	0, 1	_	0	0	
13	292	H H H H H	÷	+		+	+	
9.	302		+	+	+	+	+	
4	306		+	+	+	+	+	
7	326—328		0, 1	0, 1	_	0	0	
3	450—456		0—3	0-3	0, 2, 3	0, 1	0	
8	476—484		0—4	0—4	_	0, 1		
6	600—606		0—3	0—3	_	0, 1		

Table 1. Mass spectrometric analysis of the products of thermal treatment of acenaphthylene and acenaphthene



Fig. 4. The chromatogram of the products of thermal treatment of acenaphthylene at 400 °C.

from this table, among the products of the thermochemical conversion, there are acenaphthene type compounds (acenaphthene, bisacenaphthenyl (4), and polyacenaphthylene (5)), decacyclene and fluorocyclene (6) with a different degree of hydrogenation, their fragments (7, 8), zethrene (9), and a series of compounds, whose formation will be discussed below. It should be noted that almost no gas evolution is observed during thermochemical conversions of acenaphthylene at 400-450 °C (Table 2), which is attributable to the occurrence of two concurrent processes *viz.*, dehydrogenation and hydrogenation yielding products with carbonized structures (3, 6, and 9) and acenaphthene type compounds, respectively.

It is difficult to interpret the mechanism for the formation of compounds 10-13 unambiguously. Possibly, these compounds are the products of the reaction of the biradicals formed as a result of the destruction, for example, of compounds 3 and 6 (perylene (10)), compound 9 (dibenzopyrene (11a)), compounds 9 and 3 or 6 (benzohydrochrysene (12a), benzopleiadene (12b), and the quinoid form of benzoperylene (13)), etc. How-

Table 2. The composition of the gaseous products of pyrolysis of the model compounds under a vacuum ($p_{res} \approx 10^{-4}$ Torr)

<i>Т</i> /°С	Compound	Amount of gaseous products (mol./mol. of the model compound)					
		H ₂	CH ₄	C ₂ H ₄	C ₂ H ₆		
400	1 2 Acenaphthylene	0.015 0.007 Traces			Traces		
	Acenaphthene	Traces	-				
450	1 2 Acenaphthylene Acenaphthene	0.390 0.330 0.001 Traces	0.210 0.170 0.004 Traces	0.011 0.013 — Traces	Traces 0.027 — Traces		
500	1 2 Acenaphthylene Acenaphthene	0.878 0.676 0.110 0.012	0.340 0.600 0.002 0.005	0.013 0.017 Traces	0.090 0.280 0.006		
550	1 2 Acenaphthylene Acenaphthene	1.930 2.140 0.590 0.960	0.660 0.740 0.285 0.176	Traces Traces Traces Traces Traces	0.095 0.210 0.020 0.011		

ever, it cannot be ruled out that compounds 10-13 are the products of the destruction of graphite-like structures.

The conversion of a portion of the acenaphthylene molecules at high temperatures to acenaphthene molecules required the thermochemical investigations of acenaphthene type compounds. It was demonstrated that acenaphthene begins to form compounds with a carbonized structure even at 400 °C (see Table 1), though, according to the results of chromatographic and mass spectrometric analysis, these compounds appear in substantial amounts only at 500 °C and above; the set of compounds formed is substantially identical with that of the products of the pyrolysis of acenaphthylene, and the major product, like in the pyrolysis of acenaphthylene, is decacyclene. Increasing the temperature of the thermal treatment of both acenaphthene and acenaphthylene to 550 °C is accompanied by substantial gas evolution (see Table 2) to give more dehydrogenated structures (see Table 1). The absence of fluorocyclene type compounds among the products of pyrolysis at 550 °C attests apparently to their rather low thermostability, which is in agreement with the literature data.³

Hence, the thermochemical conversions of acenaphthylene can be represented by Scheme 1. Depolymerization of the polyacenaphthylene that is formed from acenaphthylene at ~250 °C proceeds at 370 °C to form, on the one hand, acenaphthene and, on the other hand, zethrene and decacyclene and fluorocyclene type compounds. Apparently, partial destruction of the latter results in compounds 10-13, which have a graphitelike structure. At T > 500 °C, acenaphthene is converted to zethrene, decacyclene, perylene, and other products owing to dehydrogenation. The formation of



graphite-like compounds is accompanied by deeper graphitization over the whole temperature range.

Thermochemical conversions of compounds 1 and 2, which model acenaphthylenyl-containing oligophenylene, are characterized by a higher contribution of gas evolution processes (see Table 2) than those of acenaphthene and acenaphthylene; a considerable amount of methane is evolved together with hydrogen, which attests to the complicated character of the formation of secondary structures. However, among the products obtained by heating compound 2 at 450 °C and above, we detected mass-spectrometrically the starting compound 2 and 1,3-bisacenaphthenylbenzene together with zethrene (m/z302), acenaphthofluoranthene (m/z 326), and decacyclene (m/z 450), *i.e.*, the major products of secondary conversions of acenaphthylene and acenaphthene.

According to the results of the sol-gel analysis, pyrolysis of compound 2 at 500-550 °C affords a large amount of insoluble products (see Fig. 3), which are mainly graphite-like structures.

The obtained results provide no answer to the question of whether the high thermostability of the polymers based on compound 1 is a specific feature of this particular compound, *i.e.*, whether solid-phase stereoregular reactions of the acenaphthylenyl groups of compound 1 with the formation of crosslinkages of the decacyclene and/or zethrene type to give a highly crosslinked polymer are possible. In an effort to answer this question and to characterize the structure of the fragments of the polymeric networks modelled by compounds 1 and 2, we studied these compounds by X-ray diffraction analysis.

The structures of molecules 1 and 2 are shown in Figs. 5 and 6, respectively. Both molecules have asymmetric conformations: one of the substituents in the 1,3,5-trisubstituted benzene ring is rotated toward the other two substituents (the C(51)...C(62) acenaphthylenyl group in molecule 1 and the C(31)...C(42) acenaphthenyl group in molecule 2). The peripheral six-membered rings of the naphthotriyl fragments, which are rotated



Fig. 5. The structure of molecule 1.

toward each other, can be on the same side (in 1) or on the opposite sides (in 2) of the plane of the benzene ring. On the other hand, the groups rotated in the same direction in molecule 1 have their peripheral sixmembered rings of the naphthotriyl moieties located on opposite sides, whereas in molecule 2, they are on the same side of the plane of the central ring. Thus, molecules 1 and 2 can be regarded as "*anti*"-isomers.

This can attest to the small mutual effect of the orientation of the acenaphthylenyl (acenaphthenyl) substituents. Apparently, the conformations of 1 and 2 observed in crystals are determined largely by packing factors, though the freedom of rotation of the substituents is substantially restricted by steric hindrances due to hydrogen atoms of the benzene ring and by the hydrogen atom at the C atom at position 6 in the acenaphthylenyl (acenaphthenyl) group. This results in rather close dihedral angles between the plane of the benzene ring and the mean planes through the C(11)...C(22), C(31)...C(42), and C(51)...C(62) substituents (55.4, 49.9, and 44.8° in molecule 1, 44.7, 51.6, and 53.7° in molecule 2). Because these steric intramolecular hindrances evidently exclude the rotation of the substituents by 180°, both molecules under study are the "anti"-isomers of these compounds (see above). The questions of the possibility of the existence of "syn"-isomers of 1 and 2 (which are statistically three times less probable) and of the correspondingly built units of polymeric networks still remain obscure. However, it can be suggested that the samples of 1 and 2 that have been used for studying the thermochemical conversions of the acenaphthylenyl and acenaphthenyl groups, contain a substantial portion of "syn"-isomers. It can not be excluded that the mechanisms for the thermochemical conversions of the "syn"and "anti"-isomers of compounds 1 and 2 might differ.



Fig. 6. The structure of molecule 2.

However, because the isolation of pure isomers of compound 1 and 2 presents certain experimental difficulties, this question will be studied in detail later.

The presence of bulky substituents has virtually no effect on the geometry of the benzene nucleus of molecules 1 and 2; in both cases, this ring remains planar within 0.001 Å, though the key carbon atoms of the substituents can significantly deviate from the benzenering plane (up to 0.18 Å for C(51) in 1 and up to 0.08 Å for C(11) in 2). The acenaphthylenyl (acenaphthenyl) groups remain nearly planar (within 0.02 Å); except in molecule 2, where the C(39) and C(40) atoms of the C(31)...C(42) acenaphthenyl group deviate by 0.04 Å to the opposite sides of the plane of the naphthotriyl fragment. It is interesting that the acenaphthylenyl and acenaphthenyl substituents significantly differ in their electronic (donor-acceptor) properties. This manifests itself in an increase in the endocyclic bond angles at the substituted carbon atoms of the benzene nucleus to 123.1° in molecule 1 and in a decrease in these angles to 119.0° in molecule 2 (the electron-acceptor effect of the acenaphthylenyl groups and the electron-donor effect of the acenaphthenyl substituents). The geometric parameters for molecules 1 and 2 are given in Fig. 7. The presence of bulky substituents at the central ring of molecule 2 is one of the reasons for its loose crystal packing, which involves benzene molecules of solvation (in a 1:1 ratio). This is analogous to the structures of the 1,3,5-trisubstituted benzene derivatives that we have studied previously.^{15,16} Apparently, the solvent molecules in the crystal structure of 2 have the function of the geometrically filling the formed cavities, because we did not find any manifestations of specific "host-guest" type interactions in these crystals. The observed disorder of the benzene molecules of solvation also indicates that the "host-guest" interactions are weak.

On the other hand, the crystal structure of compound 1 is characterized by dense packing without



Fig. 7. Geometric parameters $(d/\dot{A}, \omega/deg)$ for compounds 1 (left) and 2 (right) averaged over three chemically equivalent portions of the molecules.

molecules of solvation. Moreover, its characteristic feature is the existence of short distances between the potentially reactive double bonds of the acenaphthylenyl groups of the adjacent molecules (Fig. 8). Thus, the distance between the centers of the C(39)=C(40) bonds in two molecules of 1, which are related by an inversion center [[001]], is 3.67 Å; these bonds are parallel to each other with a shift angle of 16.5° (the deviation from 90° of the angle between these bonds and the line that connects their centers). This orientation makes chemical interaction (dimerization) of these bonds to form a saturated four-membered cycle possible under rather strong external action (heating, irradiation). However, there are no acenaphthylenyl groups in the crystals of compound 1 that are topochemically "prepared" for cyclotrimerization or for linear polymerization. Note that in the crystal, the C(19)=C(20) double bonds of the other adjacent molecules are also close to the abovementioned bonds (the distance between their centers is 4.30 Å), but they have an unfavorable orthogonal mutual orientation (see Fig. 8).

Thus, the thermochemical interaction of the acenaphthylenyl groups of compound 1, which is predominantly the "*anti*"-isomer, at the temperatures of polymerization apparently affords a statistical polymer, whose properties should be in general the same as those of three-dimensional polymers based on oligophenylenes with acenaphthylenyl groups.



Fig. 8. Projection of the crystal structure of compound 1 on the *bc* plane. The molecules of the lower layer are shown with double lines. The centers of the double bonds located at close distances (3.67 Å) are connected with thin solid lines, the centers of the double bonds which are more remote (4.30 Å) are connected with thin dashed lines.

Atom	Structure 1					Structure 2				
	<i>x</i>	у	z	В	x	у	z	В		
C(1)	243(10)	3023(9)	6844(6)	4.0(8)	1499(1)	1205(6)	2508(4)	3.0(3)		
C(2)	374(11)	2463(10)	7269(6)	4.1(8)	1189(1)	1344(6)	2111(3)	3.2(3)		
C(3)	-450(9)	2360(9)	7619(6)	3.6(7)	993(1)	2081(6)	2499(4)	3.5(3)		
C(4)	-1379(10)	2779(8)	7561(6)	3.8(8)	1104(1)	2703(7)	3288(4)	3.7(3)		
C(5)	-1453(10)	3331(9)	7130(6)	3.9(8)	1414(1)	2565(6)	3691(4)	3.4(3)		
C(6)	-651(10)	3456(9)	6758(6)	4.0(8)	1603(1)	1829(7)	3292(3)	3.5(3)		
C(11)	1137(10)	3175(8)	6480(6)	3.6(7)	1706(1)	476(6)	2056(4)	3.3(3)		
C(12)	2041(11)	3406(9)	6706(7)	4.3(8)	1685(1)	782(7)	1224(4)	4.4(3)		
C(13)	2892(11)	3632(8)	6386(7)	4.7(9)	1878(1)	185(8)	745(4)	5.5(4)		
C(14)	2782(10)	3596(8)	5827(6)	3.8(8)	2105(1)	-689(7)	1142(4)	4.8(4)		
C(15)	1845(9)	3322(9)	5063(6)	3.4(7)	2364(1)	-1996(6)	2289(5)	6.3(4)		
C(16)	1036(11)	3054(9)	4781(7)	4.6(8)	2423(1)	-2409(8)	3102(5)	7.3(5)		
C(17)	179(11)	2804(9)	5085(6)	4.3(8)	2229(1)	-1933(8)	3612(5)	6.5(4)		
C(18)	122(11)	2803(9)	5646(6)	4.5(8)	1993(1)	-993(7)	3319(4)	4.9(4)		
C(19)	3417(11)	3774(9)	5363(7)	4.8(9)	2351(1)	-1485(9)	840(5)	8.9(6)		
C(20)	2874(10)	3622(9)	4908(6)	4.3(8)	2520(1)	-2381(9)	1597(6)	9.9(6)		
C(21)	1831(9)	3324(9)	5630(6)	2.8(6)	2130(1)	-1041(7)	1978(4)	4.6(4)		
C(22)	997(10)	3113(9)	5926(6)	3.2(6)	1936(1)	-492(7)	2471(4)	4.0(3)		
C(31)	-373(10)	1813(9)	8078(6)	4.1(8)	661(1)	2127(7)	2057(4)	3.5(3)		
C(32)	-1114(10)	1207(9)	8160(6)	4.2(8)	509(1)	859(7)	1788(4)	4.6(4)		
C(32)	-1013(10)	599(9)	8562(7)	4.3(8)	200(1)	789(7)	1367(5)	5.5(4)		
C(34)	-159(11)	569(9)	8866(7)	4 7(9)	39(1)	2035(7)	1232(4)	5 2(4)		
C(35)	1407(11)	1100(10)	9134(6)	4 9(9)	-3(1)	4552(7)	1284(5)	5 7(4)		
C(36)	2204(11)	1672(11)	9124(7)	5 7(9)	110(1)	5876(8)	1498(5)	7.7(5)		
C(37)	2112(11)	2356(10)	8747(6)	4 8(9)	418(1)	5995(7)	1922(5)	67(4)		
C(38)	1317(11)	2439(10)	8399(6)	4 2(8)	607(1)	4834(8)	2121(5)	5 5(4)		
C(39)	236(13)	$\frac{2}{82(11)}$	9316(7)	5.8(9)	-290(1)	2375(8)	821(5)	7 5(5)		
C(40)	1146(13)	388(9)	9470(7)	5.6(9)	-317(1)	4017(8)	817(5)	69(5)		
C(41)	584(10)	1187(9)	8772(6)	4 0(8)	187(1)	3336(9)	1490(4)	4 1 (4)		
C(42)	504(10)	1842(10)	8403(6)	4 1(8)	497(1)	3436(7)	1911(4)	4.0(3)		
C(51)	-2384(11)	3874(9)	7087(7)	4 2(8)	1534(1)	3256(7)	4535(4)	3.8(4)		
C(52)	-2773(9)	4236(8)	7563(7)	3 9(8)	1785(1)	4154(7)	4644(4)	4 4(4)		
C(53)	-3632(10)	4774(8)	7555(7)	4 5(9)	1912(1)	4841(8)	5415(4)	5 5(4)		
C(54)	-4075(10)	4922(9)	7062(7)	4 0(8)	1782(1)	4623(7)	6068(4)	4 1(3)		
C(55)	-4218(11)	4804(10)	6145(8)	54(9)	1417(1)	3575(7)	6669(4)	4.8(4)		
C(55)	-3932(12)	4471(11)	5660(7)	6 3(9)	1168(1)	2724(8)	6644(4)	5 7(4)		
C(57)	-3123(11)	3930(10)	5637(7)	5 5(9)	1034(1)	1986(8)	5899(4)	5 3(4)		
C(58)	-2571(11)	3667(8)	6083(6)	4.0(8)	1145(1)	2103(7)	5198(4)	3 9(3)		
C(50)	-4925(11)	5447(9)	6882(7)	5.8(9)	1845(1)	5178(8)	6970(5)	6 2(4)		
C(60)	-5016(12)	5384(9)	6327(8)	5 9(9)	1601(1)	4481(8)	7353(4)	6 3(4)		
C(61)	-3661(9)	4552(9)	6598(6)	3.8(8)	1531(1)	3711(7)	5956(3)	3 9(3)		
C(62)	-2854(9)	3998(9)	6590(6)	3.7(7)	1397(1)	3006(7)	5191(4)	3 9(3)		
C(1s)	203 (())	5776(7)	000000	5.7(7)	753(3)	1071(15)	8911(9)	60		
C(2s)					646(3)	1750(15)	9549(9)	6.0		
C(3s)					816(3)	2875(15)	9956(9)	6.0		
C(4s)					1069(3)	3314(16)	9756(8)	6.0		
C(5s)					1196(3)	2646(15)	9176(9)	6.0		
C(6s)					1031(3)	1491(15)	8734(9)	6.0		
C(1sA)					673(3)	1451(16)	9227(9)	6.0		
C(2sA)					681(3)	2503(15)	9854(9)	6.0		
C(3sA)					939(3)	3364(16)	9987(8)	6.0		
C(4sA)					1160(3)	3202(16)	9584(8)	6.0		
C(5sA)					1146(3)	2068(16)	8988(9)	6.0		
C(6sA)					895(3)	1235(15)	8843(8)	6.0		

Table 3. Fractional atomic coordinates ($\times 10^4$) and isotropic equivalent temperature factors (B^{eq}_{iso} /Å²) for C atoms is structures 1 and 2

Experimental

Compounds of purity no less than 99 % were used as model compounds. Compounds 1 and 2 were synthesized according to the known procedure.¹⁷ The model compounds were heated: (a) in an atmosphere of inert gas (Ar) in condensation test tubes for 4 h (for the study by DTA); (b) in sealed test tubes ($p = 10^{-3}$ Pa) for 1 h (for studying gas evolution and for the sol-gel analysis); (c) by hot pressing at a specific pressure of 100 MPa for 1 h (for thermomechanical experiments).

Differential thermal analysis (DTA) and dynamic thermogravimetric analysis (TGA) were performed on a MOM derivatograph (Hungary) in air with heating at a rate of 5 °C/min. Differential scanning calorimetric analysis was performed on a DuPont thermoanalyzer (a DSC 912 unit) with heating at a rate of 5 °C/min.

Mass spectra (electron impact) were recorded on a Kratos MS 890 instrument (Great Britain); the energy of the ionizing electrons was 70 eV, and the temperature of the ionization chamber was 250 °C.

Liquid chromatography was carried out at ~20 °C on a Bruker LC-31 instrument equipped with an UV detector ($\lambda = 254 \text{ nm}$) and a column packed with Tessek C18 silica gel (particle size 5 µm). A mixture of dichloroethane (0 \rightarrow 15 % in 10 min) and methanol was used as the eluent at a flow rate of 1 mL/min.

The samples used for **the sol-gel analysis** were preheated and then extracted for 24 h with chloroform in a Soxlet apparatus.

Thermomechanical experiments were performed on a PP-1 planar plastometer¹⁸ at a unit load of 20 MPa and with heating at a rate of 10 $^{\circ}$ C/min.

X-ray diffraction study. The unit-cell parameters and intensities of reflections from single crystals of compounds 1 and 2 (1:1 benzene solvate) were measured on a Synthex P2₁ automated four-circle diffractometer at -120 °C and 20 °C, respectively (λ (Mo-K α) radiation, graphite monochromator, $\theta/2\theta$ -scan technique, $2\theta_{max} = 50^{\circ}$). Crystals of 1 are orthorhombic, at -120 °C a = 13.32(1) Å, b = 16.44(1) Å, c = 25.32(2) Å, V = 5543(3) Å³, space group is *Pcab*, Z = 8, $d_{calc} = 1.267$ g cm⁻³. C₄₂H₂₄. Crystals of monobenzene solvate 2 are monoclinic, at 20 °C a = 45.28(1) Å, b = 9.258(2) Å, c = 16.387(3) Å, $\beta = 103.82(2)^{\circ}$, V = 6671.0(5) Å³, space group is C2/c, Z = 8, $d_{calc} = 1.218$ g cm⁻³. C₄₂H₃₀ · C₆H₆.

The structures were solved by the direct method (the MULTAN program) and refined by the block-diagonal least-squares method with anisotropic thermal parameters for carbon atoms (in the crystal structure of 1, only the diagonal elements of the tensors were refined). The benzene molecule of solvation disordered over two sites with equal occupancies (G = 0.5) in

the crystals of 2 was located from the difference Fourier synthesis and refined isotropically with the fixed $B_{\rm iso} = 6.0$ Å². The positions of the H atoms (including those of the disordered benzene molecule) were calculated geometrically after each cycle of the refinement and were not refined taking into account their contribution with $B_{\rm iso} = 3.0$ and 5.0 Å² (for structures 1 and 2, respectively) to the values $F_{\rm calc}$. The final values of the reliability factors are R = 0.109 ($R_{\rm w} = 0.083$) using 1099 reflections with $I > 3\sigma(I)$ for 1 and R = 0.057($R_{\rm w} = 0.031$) using 1212 reflections with $I > 2\sigma(I)$ for 2. Atomic coordinates for structures 1 and 2 are given in Table 3.

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