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Thermo-oxidative Oligomerization of Aromatic Diamine

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ARTICLE INFO	ABSTRACT
	Molecular spectroscopy (electronic, FT-IR, NMR), methods of thermal and elemental analysis were used for the first time to describe the process of thermo-oxidative oligomerization of 1,3-bis-(4-aminophenoxy)benzene. Introduction of this monomer into linear and network copolymers makes it possible to improve processability, mechanical strength and heat resistance of materials. The structures of copolymers obtained by thermo-oxidation of the diamine in various thermal regimes were studied. It was demonstrated that during prolonged heating of this diamine in air in the temperature range from 220 to 320°C, oligomeric aromatic diamines were formed; these products contained fragments of benzenoid and quinoid types.

1. Introduction

Aromatic diamines (ADA) find wide application in organic and polymer chemistry, for example, in polyimide synthesis [1-4], as crosslinking additives (curing agents for epoxy resins) [5-7], for polymer stabilization [8]. 1,3-Bis-(4-aminophenoxy)benzene (BAPB) is of special interest. Introduction of units of this diamine into linear and network copolymers considerably improves their useful properties (processability, strength and heat resistance) [9-13]. Our recent publications [14-16] reported preparation of novel network copolymers by high temperature (160-320°C) co-curing of rolivsans (thermosetting polyester-based composites) and aromatic diamines (ADA) in air. These products demonstrated good adhesive properties,

high temperature strength and prolonged thermo-oxidative stability at 260-350°C as compared to those of the initial (non-modified) rolivsans (ROL). It was suggested to use BAPB as a comonomer or modifying agent in order to impart lower rigidity, higher temperature strength, and higher thermo-oxidative stability to cured ROL. It was established that co-curing of rolivsans with ADA in air in the temperature interval from 160 to 300 (320)°C involved a set of consecutive-parallel reactions. In the course of these reactions, additional poly(amide) networks were formed as a result of chemical interactions between carboxyl (anhydride) groups (which appeared during thermal transformations of ROL) and amino groups of ADA [17]. However, it was still unclear whether the presence of ADA in the cured ROL-ADA system led only

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to the above-mentioned interactions, or other thermo-oxidative transformations of aromatic diamines were possible in this temperature range. In the present work, ROL was not included in the studied system, since it undergoes various chemical transformations in air and thus renders it difficult to investigate reactions of aromatic diamines. It is well known that aromatic diamines form oligomeric polyaniline-like products in the presence of various oxidants [18-20].
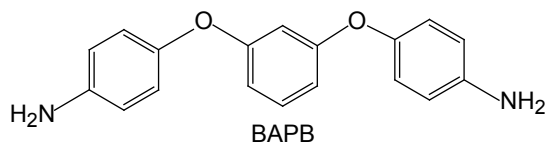
BAPB

The aim of this work was to study chemical structures, compositions and some properties of the products of high-temperature oxidation of aromatic diamines using BAPB as an example.

2. Materials and Method

1,3-Bis-(4-aminophenoxy)benzene (BAPB, 98%, m.p. = 115-118°C) was purchased from TCI America (Portland, USA) and used as received; before obtaining electronic spectra, BAPB was additionally purified by recrystallization from ethanol (m.p. = 117-118°C).

Thermal treatment of BAPB monomer was carried out in siliconized brass mold 30×25 mm in size in air thermostat. The samples were melted down at 120–122°C (the thickness of melt layer was ~2 mm) and heated stepwise for 1 h until the predefined final temperature (T_{fin}) was reached. The following initial (monomeric) and thermally treated diamine samples were obtained under different heating conditions: 1(*20°*), 2(*20°-125°*), 3(*20°-150°*), 4(*20°-160°*), 5(*20-170*), 6(*125°-180°*), 7(*150°-180°*), 8(*125°-200°*), 9(*125°-220°*), 10(*150°-220°*), 11(*125°-240°*), 12(*125°-260°*), 13(*150°-260°*), 14(*125°-280°*), 15(*125°-300°*), 16(*125°-320°*), 17(*150°-350°*), 18(*170°-320°*), 19(*150°-260°/2h,260/20h*), 20(*150°-260°/2h, 260/40h*). The time of temperature rise between steps was approximately 15 min.

For obtaining electronic spectra, samples of the initial (1) and thermally treated BAPB (2-6, 8, 9, 11, 12) in the form of thin powder were treated with chloroform ($CHCl_3$) at room temperature for approximately 24 h. The resulting solutions (extracts) were filtered to remove the precipitate; chloroform was evaporated, and the residue was dried until constant weight was reached (80-85 wt.% of the initial sample mass). These extracts were used to prepare diluted solutions of required concentrations in ethanol and chloroform. Electronic spectra of samples were registered in quartz cuvettes 1 cm wide at room temperature using

an SF-256 spectrophotometer (LOMO PHOTONICA, Russia) in the wavelength range of 250–900 nm.

FT-IR spectra of monomeric and thermally treated BAPB in the form of thin powder were taken using a Vertex 70 FT-IR spectrometer (Bruker, Germany) (4000 – 600 cm^{-1}) equipped with an attenuated total reflectance (ATR) attachment (Pike). The FT-IR ATR spectrum of monomeric BAPB (sample 1) included the following absorption bands (cm^{-1}): 3425 and 3406 (symmetric and antisymmetric vibrations of hydrogen atoms in NH_2 groups [18]), 3339 and 3213 (hydrogen bonds involving nitrogen and oxygen atoms), 3082, 3040, and 3013 (valence vibrations of C-H aromatic rings [21]) and 1607 (C_{Ar}), 1582 (C_{Ar} and deformation vibrations of NH_2 [21]), 1503 (C_{Ar}), 1479 (C_{Ar}), 1462, 1312 (C_{Ar}-N), 1269 (valence vibrations of C_{Ar}-N [21]), 1204 (-O- in C_{Ar}-O-C_{Ar}), 1159 (C-O-C), 833 (=C-H). The spectrum of thermally treated BAPB (sample 18) included the bands similar to those of monomer (sample 1). However, the following absorption bands were wide (diffuse) in comparison to those in the monomer spectrum, and had different intensities (cm^{-1}): 3490-3406 (the maximum at 3410), 3400-3300 (the maximum at 3340), 3221-3211 [the maximum at 3213 (valence vibrations of –NH-)], 1589 (C_{Ar}), 1503 (C_{Ar}), 1474 (the benzenoid-type unit [22]), 1447, 1312, 1269 (C_{Ar}-N [21]), 1254 (the benzenoid-type unit C-N [22]), 1204, 1167 (C_{Ar}-O), 1119 (C_{Ar}-O), 1080, 1011, 1003, 964, 831, 770, 683.

The ^{1}H NMR spectra of monomeric and thermally treated diamines were obtained with the use of a Bruker Avance instrument (400 MHz) in deuterated chloroform ($CDCl_3$). Solid state ^{13}C NMR spectra of powdered samples were registered with the use of a Bruker Avance spectrometer (400 MHz) [operating frequency 125.77 MHz, CP MAS (10 kHz)]. The spectra of the initial BAPB (sample 1) contained peaks with the following chemical shifts (δ, ppm). ^{1}H NMR: 7.28-6.57 (12H_{Ar}), 3.54 (4H_N for two NH_2 groups); ^{13}C NMR: 209.8, 202.9, 161.7, 159.9, 147.0 (148.4 for aniline [23]), 144.2, 130.4 (129.5 for aniline [23]), 123.3, 122.4, 117.6, 114.8 (115.0 for aniline [23]), 106.6, 103.7, 43.9.

The spectra of thermally treated sample (18) contained peaks with the following chemical shifts (δ, ppm). ^{1}H NMR: 7.28-6.57 (Ar-H), 3.60 (NH_2). ^{13}C NMR: 210.8, 202.6, 161.6, 156.4 (C_{Ar}) 145.7 ($C_{p-Ar–N}$) (142.4-146.4 for polyaniline units [24, 25]), 131.1, 130.4, 122.9 (C_{Ar} at 121.7-124.4 for polyaniline [24,25]), 116.4 (116.7-124.4 for polyaniline units [24,25]), 111.9, 82.0, 65.7, 51.3, 42.7, 37.2.

Elemental analysis of sample 1. Found (%): C 73.95, H 5.97, N 9.64; for $C_{18}H_{16}N_2O_2$: calculated (%) C 73.90, H 5.47, N 9.58. Elemental analysis of sample 18: found (%) C 74.29, H 5.47, N 9.60.

Dynamic thermogravimetric analysis (DTGA) of sample 1 was carried out using a Paulik-Paulik-Erdei "Derivatograph C" (MOM, Hungary); the heating rate was 10°C/min [26].

3. Results and Discussion

Thermally treated BAPB samples appeared as dark brown or black homogeneous solid melts; their high temperature viscosity increased with increasing T_{fin}. The solid melts were compositions (mixtures) of monomeric BAPB and products of its thermo-oxidative polycondensation (oligo-BAPB) of various compositions; the products demonstrated good adhesive properties. Upon completion of stepwise thermal treatment (up to T_{fin} = 150-240°C) and subsequent cooling down to room temperature, the melts gradually became solid. They retained stickiness for some time (1-2 days) at room temperature, and it was possible to spun threads of these melts. However, they became solid (rigid, brittle) on long storage due to crystallization processes. When BAPB was treated stepwise up to T_{fin} = 300–320°C, the obtained samples (15–20) became infusible and only partially dissolved in chloroform.

It is known that BAPB and other aromatic (di)amines oxidize easily in air to form colored products of various structures. For example, aniline enters into reaction with relatively weak oxidants, such as H_2O_2, to give polyaniline containing both dehydrogenated and oxidized units $[(-C_6H_4-NH-C_6H_4-NH)/(C_6H_4-N=C_6H_4=N)]_n\sim$ [27]. Strong oxidizing agents not only transform NH_2 fragment to NO_2, but also attack activated aromatic rings, which results in formation of numerous products [28].

In the process of high temperature treatment of BAPB up to T_{fin} = 320°C (sample 18), solid black infusible product was formed; elemental analysis revealed that nitrogen and carbon contents in this substance virtually coincided with those of the initial monomer (sample 1). This temperature regime did not cause noticeable thermo-oxidative destruction of the diamine, which was also confirmed by the data of thermal analysis.
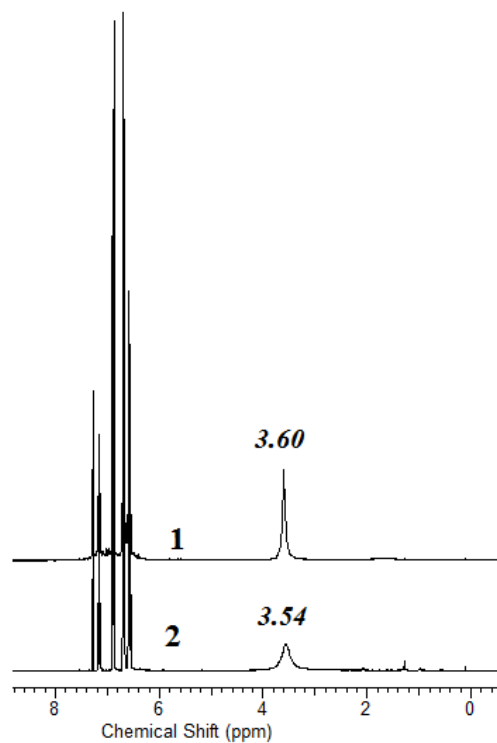
According to the data of thermal analysis (DTGA and DTA) [26], fast heating of sample 1 in air (on thermobalance) in the temperature range from 20 to 400°C leads not only to its thermo-oxidative polycondensation with formation of oligomers (oligo-BAPB), but also to sublimation (~20%). Sublimation rate reaches its maximum at ~ 400°C. At temperatures exceeding 450°C, intensive thermo-oxidative destruction of the sample was observed. Upon heating of infusible samples 19 and 20 (obtained by thermal treatment of BAPB with exposure at T_{fin} = 260°C for 20 and 40 h, respectively), the values of mass loss attributed to sublimation were equal to 15.75%

and 16.33%, respectively. Similar sublimation process occurred during prolonged exposure of sample 18 at 350°C (Figure 1).
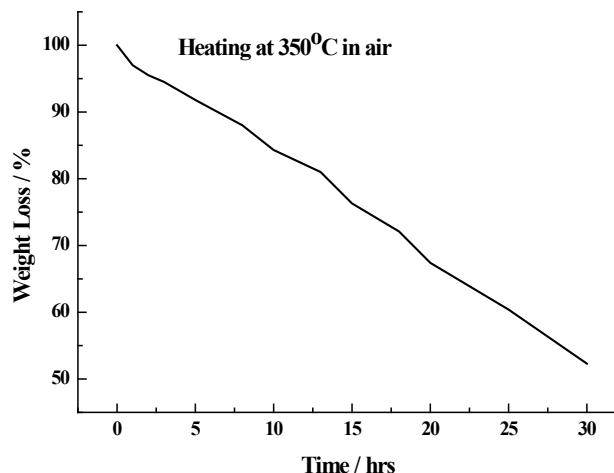
Figure 1. Dependence of mass loss of sample 18 obtained by stepwise heating of BAPB monomer (sample 1) to T_{fin} = 320°C on the time of air exposure at 350°C.

Thermal oxidation of BAPB was studied by molecular spectroscopy. Elemental analysis of thermally treated samples and analysis of their ^{1}H NMR spectra (Table 1, Figure 2) showed that oxidative oligomerization of BAPB samples did not lead to substantial changes in their chemical compositions.

Figure 2. ^{1}H NMR spectra of thermally treated (sample 18) and initial (sample 1) BAPB

Table 1. Dependence of hydrogen content in BAPB samples on heating regime in air according to the data of ^{1}H NMR spectroscopy

Sample	T_{fin},[a] °C	$\Sigma H_N/\Sigma H_{Ar}$[b]	$\Sigma H_N/\Sigma H_J$[c]	Elemental analysis, %		
				C	N	H
1	20	0.32	0.24	73.94	9.64	6.15
2	125	0.32	0.24	-	-	-
3	150	0.32	0.24	-	-	-
4	160	0.32	0.24	-	-	-
5	170	0.32	0.23	-	-	-
6	180	0.31	0.23	74.04	9.60	5.80
7	180	0.31	0.23	-	-	-
8	200	0.31	0.23	-	-	-
9	220	0.31	0.23	74.04	9.54	5.75
10	240	0.30	0.22	-	-	-
11	260	0.30	0.21	74.24	9.62	5.68
20	260[d]	0.25	0.17	71.30	9.27	5.55
14	280	0.27	0.21	-	-	-
15	300	0.27	0.20	74.23	9.50	5.62
16	320	0.27	0.20	74.20	9.57	5.53
18	320	0.28	0.21	74.24	9.60	5.37

[a] T_{fin} is the final temperature of thermal treatment.

[b] ΣH_N and ΣH_{Ar} are the integral intensities of proton signals of amino groups (d = 3.57 ±0.03 ppm) and aromatic rings (d = 6.5-7.3 ppm), respectively.

[c] ΣH_N and ΣH_j are the integral intensities of all proton signals.

[d] The sample was exposed at 260°C for 40 h in air.

The values of hydrogen content in heated samples decreased insignificantly with increase in BAPB heat treatment temperature from 260 to 320°C, since its thermo-oxidative (poly)condensation in air was accompanied by liberation of water (Figure 3):
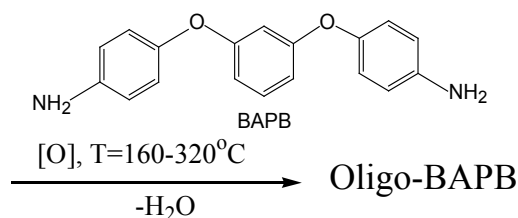
Figure 3. Thermo-oxidative (poly)condensation of BAPB

These first data on the products of thermo-oxidation (oligo-BAPB) obtained in the above-mentioned specific temperature-time regimes raised some questions about composition and chemical structure of oligo-BAPB. It is possible that these oligomers are similar to the well-studied initial products of oxidation of aromatic mono- and diamines (e.g., low molecular weight polyanilines $[(-C_6H_4-NH-C_6H_4-NH)/(C_6H_4-N=C_6H_4=N)]_n\sim$[27]), although polyanilines are obtained under entirely different conditions. BAPB contains two symmetrically arranged sites that possess equal oxidation abilities. The oxidation reaction yields dimers, soluble branched structures, and infusible (insoluble, crosslinked) products (samples 15–20). Thus, it can be concluded that depending on temperature-time regime (which can be harsh or mild), oxidation may involve both one and two sites.

However, upon prolonged (40 h) exposure of sample 20 at 260°C (Table 1), contents of hydrogen, nitrogen and carbon decreased significantly, which indicated deeper thermo-oxidation processes.
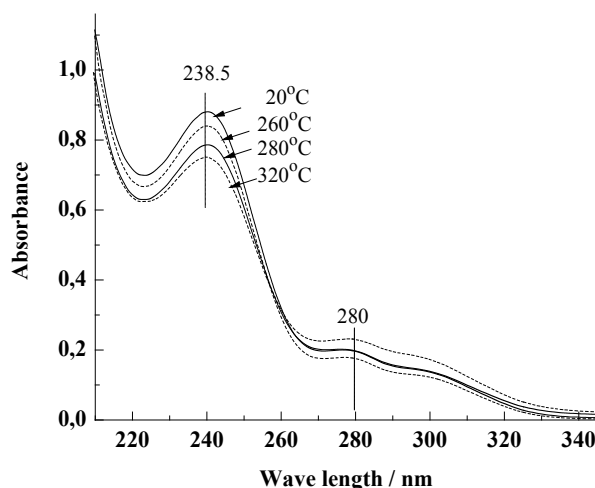

Figure 4. UV spectra of ethanol solutions (c = ~10^{-5} g/mL) of BAPB samples (1, 20, 14, 16) treated according to stepwise regime with various final temperatures T_{fin} (°C): 20, 260, 280 and 320, respectively.

As is seen in Figure 4, UV spectra of ethanol-soluble BAPB samples include intense absorption bands at ~240 and 280 nm, which are typical of (poly)aniline and polymers of other (amino)substituted benzene derivatives [29,30]. Since it is the initial diamine that mainly dissolves in ethanol, under harsh conditions of thermo-oxidative condensation its contents in samples naturally decreases. Therefore, the intensity of absorption band at 238.5 nm also decreases.

Electronic spectra of chloroform extracts (solutions) obtained from thermally treated BAPB samples (Figure 5) contain wide absorption bands in the 340-800 nm region; intensities of these bands increase significantly upon increase in the final temperature (T_{fin}) from 220 to 320°C. The bands at 475, 510 and 580 nm become more pronounced. Since elemental composition of oligomerized samples differs only slightly from that of the initial (monomeric) BAPB (Table 1, samples 5-6), it is believed that the above-mentioned samples virtually do not contain products of deep oxidation. This observation simplifies the problem of composition and chemical structure of oligo-BAPB. Processes of oxidation of its structural analogs (aniline and some aromatic diamines) are well studied, which facilitates comparative analysis. For example, electronic absorption spectra of aniline dimer (N,N′-diphenyl-1,4-phenylenediamine) [31] and N,N′-bis (4'-amino-phenyl)-1,4-quinone diimine [32] (which are used in our work as model compounds) contain wide maximums in the long-wavelength region. These peaks (475 and 575 nm [31] and 550-629 nm [32]) are attributed to benzenoid and quinoid fragments; at the same time,

the spectrum of N,N′-bis(4'-aminophenyl)-1,4-quinone diimine includes the peak at λ_{max}=572 nm [33]. Comparison of electronic spectra of our samples (Figure 4) and the spectra of model compounds and low molecular weight aniline also suggests that these compounds are structurally similar. Moreover, it is expected that, unlike benzenoid structures, conjugated quinoid fragments should give more intensive long-wavelength peaks with higher bathochromic shifts. It is also seen in Figure 5 that the intensity of the band located in the 580-800 nm area is significantly lower than those of the bands observed in the short-wavelength region (350-475 nm), the concentrations of oligo-BAPB being almost equal. These results (together with the data of elemental analysis and ^{1}H NMR spectroscopy) indicate that oligo-BAPB samples contain both quinoid and benzenoid fragments, the latter predominating.

Since thermally treated samples are mixtures of monomeric BAPB and oligo-BAPB, their FT-IR spectra contain the absorption bands typical of each related compounds, although with different intensities. The spectrum of thermally treated BAPB (sample 18) includes the same absorption bands as that of the monomer (1), but they are diffuse and have lower intensities. Thus, intensities of the Ar band (1607 cm^{-1}) and the bands attributed to terminal amino groups (1312, 1269, 1092, 1009, 746 cm^{-1}) in the spectra of thermally treated samples decrease sharply in comparison to those in the spectrum of monomeric BAPB. A new band (1254 cm^{-1}) typical of C–N group near benzenoid ring appears [22,34]. As seen in Figure 7, ^{13}C NMR spectrum of insoluble and infusible
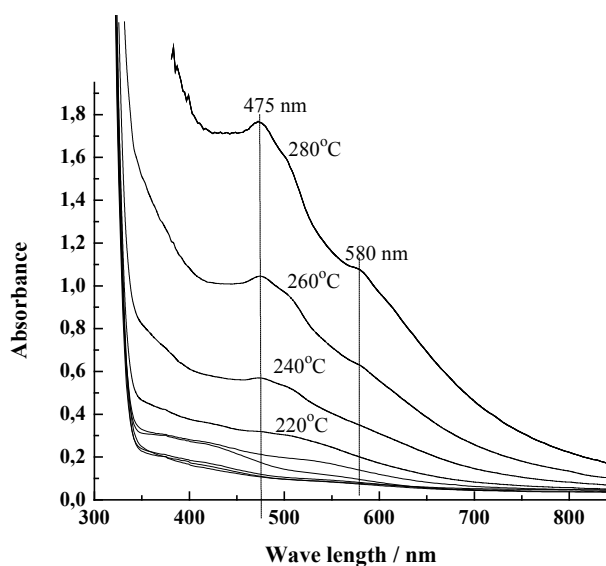
Figure 5. Electronic absorption spectra of chloroform solutions (c = ~10^{-3} g/mL) of thermally treated BAPB samples; the samples were obtained by stepwise heating of BAPB up to final temperatures indicated in the spectra. λ is the wavelength (nm).

(N,N'-diphenyl-1,4-phenylenediamine)

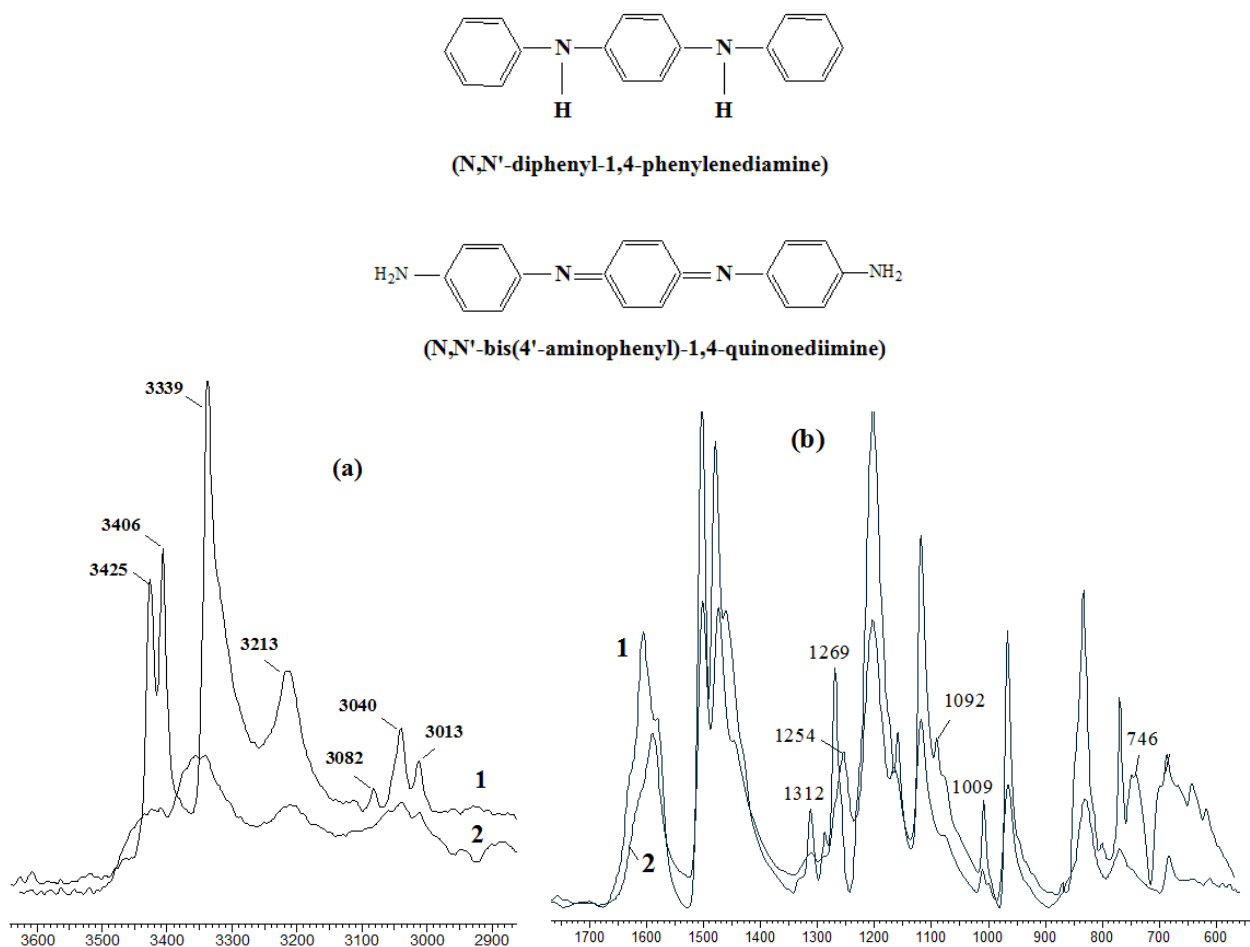**(N,N'-bis(4'-aminophenyl)-1,4-quinonediimine)**

Figure 6. FT-IR spectra of monomeric (1) and thermally treated BAPB (2, sample 18)(Wavenumber, cm^{-1})
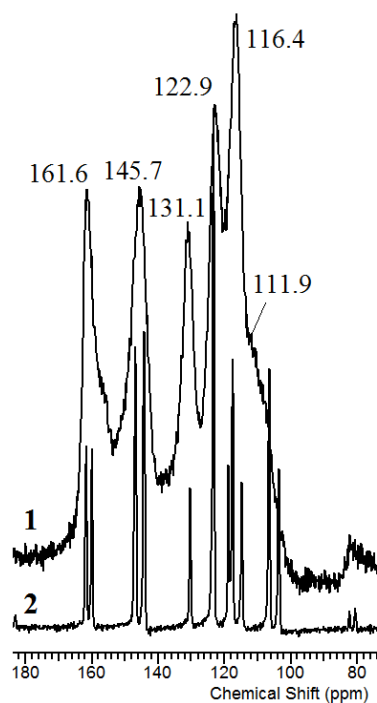
Figure 7. ^{13}C NMR spectra of thermally treated sample 18 (1) and the initial BAPB sample 1 (2).

sample 18 is poorly resolved. However, it can be noted that resonance peaks of protonated carbon atoms at 156.4 (C$_{Ar}$), 145.7 (C$_{para-Ar-N}$), 131.1, 130.4, 122.9, and 116.4 ppm are related both to benzenoid and quinoid fragments [21,22]; the peak at 116.4 ppm (benzenoid rings) has the highest intensity.

4. Conclusions

Using 1,3-bis-(4-aminophenoxy)benzene (aromatic diamine applied in preparation of various heat-resistant polymers, polymer materials and composites) as an example, the process of thermo-oxidation of aromatic diamines by air oxygen was investigated. It was revealed that during heating in air up to ~200-220°C this diamine retained its chemical stability, and at higher temperatures (260-320°C) it underwent oxidative (poly)condensation accompanied by release of water.

It was demonstrated that oligomeric products of thermo-oxidation were mixtures of 1,3-bis-(4-aminophenoxy)benzene and its dimers, soluble linear and branched oligomers, and crosslinked (insoluble) polymers; they retained chemical stability during heating in air at 350°C for several tens of hours. Using molecular spectroscopy methods, elemental and thermal analysis, it was established that the obtained oligomers contained fragments of benzenoid and quinoid types. The obtained results are of practical importance, since they reveal thermo-oxidative transformations of aromatic diamines that are possible in the temperature range from 170 to 350°C. These temperatures are relevant for preparation and operation of thermosetting polyimides, epoxides and other materials (e.g., rolivsans modified with aromatic diamines).

Acknowledgements

Conflict of Interests

The authors have no conflicts of interests to declare.

Author Contributions

Zaitsev Boris A.: formulation of the problem; general direction, analysis and interpretation of the results obtained by molecular spectroscopy and thermal analysis.

Kleptsova Larisa G.: synthesis, studies of thermal properties of the obtained monomer-oligomer compositions.

Shvabskaya Irina D.: preparation of samples for FT-IR and NMR spectroscopy and analysis of the obtained results.

Bursian Anna E.: electronic spectroscopy of solutions of samples of various compositions (at constant concentration) and comparative analysis of the obtained results.

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