Studies of Formation Mechanism, Structure, and Properties of Network Copolymers Obtained by Cocuring of Rolivsan Thermosetting Resins with Aromatic Diamines

B. A. Zaitsev, L. G. Kleptsova, and I. D. Shvabskaya

Institute of Macromolecular Compounds, Bolshoy Prospect 31, Russian Academy of Sciences, St. Petersburg 199004, Russia

Correspondence should be addressed to B. A. Zaitsev; zaitsev@hq.macro.ru

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Rolivsan thermosetting resins (ROLs) demonstrate high glass-transition temperatures and excellent processability. In our work, high-temperature properties of ROLs were significantly improved using a novel technique for structural and chemical modification of microheterogeneous network polymers. This technique involves, among other procedures, cocuring of rolivsan resins with aromatic diamines (ADA). The most noticeable increase in storage moduli and glass transition temperatures \( T_g \) of these copolymers was achieved when ROLs were modified with 10-15 wt.% of ADA and the resulting blends were subjected to thermal treatment in air in the temperature range 180 to 320°C for several hours. FTIR, \( ^{13}C \)NMR spectroscopy, and dynamic mechanical and thermal analyses were used for studying the structure and properties of the obtained products. It was demonstrated that the mechanism of formation of ROL-ADA copolymers includes the following high-temperature reactions: (i) three-dimensional radical copolymerization of unsaturated ROL components and (ii) cleavage of heat-sensitive methacrylate crosslinking units inside the polymer network. The second process is accompanied by formation of pending units of methacrylic acid and methacrylic anhydride, which participate in condensation reactions with ADA.

1. Introduction

Rolivsan thermosetting resins (ROLs) are a new class of unsaturated thermosetting resins featuring high glass-transition temperatures \( T_g \), excellent processability, low relative permittivity and mechanical losses, low moisture absorption, good mechanical properties, and satisfactory compatibility with various substrates [1–3]. They are obtained via acid-catalyzed reactions between dissecondary aliphatic-aromatic diol (bis-(4-(\( \alpha \)-hydroxyethyl)phenyl) ether) (BHEPE) and methacrylic acid (MAA) [1]. It was established that during thermal curing of ROLs, thermostable network copolymers are formed; these copolymers are capable of changing their chemical structure, microstructure, crosslink density and, correspondingly, thermal, mechanical, and other properties [1].

In the first low-temperature stage of curing (140-170°C), bulk three-dimensional free radical polymerization (TFRP) of unsaturated components of ROLs occurs and the initial highly crosslinked copolymers are formed. When the temperature exceeds 170-180°C, thermosensitive methacrylate bridges start to cleave gradually and form MAA and styrene-like \((\text{CH}_2 = \text{CH}-\text{Ar}-)\) pending units. Upon further increase in curing temperature (up to 200-300°C), the adjacent MAA units and the fragments containing styrene-like aromatic rings become involved in solid-phase intramolecular reactions. These reactions include dehydration, intramolecular cyclization (high-temperature acylation of neighboring aromatic units by MAA carboxyl groups and anhydridization of carboxyl groups of neighboring MAA units within the chain). Thus, the processes result in specific self-functionalization of polymer grains and interlayers between these grains [1, 2].

Formation of microheterogeneous-crosslinked polymers is accompanied by microphase segregation (microsyneresis) of the initially homogeneous unsaturated system (e.g., the one consisting of oligoetheracrylates or other unsaturated monomers and/or oligomers). It is preceded by a sharp increase in viscosity of the system caused by formation and
association of polymer chains and by nucleation and growth of crosslinked microgel particles (grains). As microgel particles (grains, microdomains) continue to grow, the surrounding liquid reaction medium is transformed into interlayers between the grains. In these interlayers, nonreactive impurities (such as solvents and/or various functional additives) are accumulated. The size of grains (dispersed phase) increases during formation of polymer chains in their surface (boundary) layers by “extraction” of unsaturated monomers and oligomers from the reaction medium into the continuous dispersion medium. While three-dimensional free radical polymerization (TFRP) proceeds in bulk, the grains fuse together, form a monolith, and are transformed into a continuous phase. At the same time, the reaction medium enriched in reactive (polyfunctional) compounds (that do not participate in the main TFRP process) into IBGs. However, these latent compounds, which are present in IBGs as a peculiar kind of “microreactors,” can be activated under the appropriate conditions (e.g., at elevated temperatures and/or after changing acidity of a medium). After activation, they take part in additional reactions of structurization (crosslinking) of microheterogeneous network polymer [2, 5–7]. Thus, we propose to use certain implications of mechanism of the obtained network copolymers.

2. Experimental

2.1. Materials. m-Phenylenediamine (m-PDA, 99%), p-phenylenediamine (p-PDA, 99%), 3,4′-oxydianiline (3,4′-ODA, 97%), 4,4′-oxydianiline (4,4′-ODA, 97%), 4,4′-methylene diamine (4,4′-MDA, 97%), 1,3-bis(4-aminophenoxy)benzene (1,3-BAPB, 98%), toluene (99.8%), methacrylic acid (MAA, 99%), p-toluenesulfonic acid monohydrate (p-TSA, 98.5%), and hydroquinone (HQ, 99%) were purchased from Sigma-Aldrich. 1,4-Bis-(4-aminophenoxy)benzene (1,4-BAPB, 98%) was purchased from TCI America and used as received.

2.2. Preparation of ROLs and the Cured ROL-ADA Blends. ROL samples were synthesized by condensation of bis(4-(α-hydroxyethyl)phenyl) ester (BHEPE) [1] with methacrylic acid (MAA) that was catalyzed by p-TSA, in accordance with the following procedure. The mixture of 140.0 g (0.542 mol) of BHEPE, 3.5 g of CuCl, 1.4 g of HQ, 1300 mL of toluene, and 70.0 g (0.813 mol) of freshly distilled MAA was heated at stirring at the temperature of 70°C for ~15 min. After that, 0.420 g of p-TSA was added to the solution; the mixture was stirred, and boiling temperature (102-111°C) was maintained until the dehydration process ceased (i.e., for ~1.5 h).

The water released during the process was distilled off as a toluene-water azeotrope. When water release stopped, the resin solution was cooled down to room temperature, precipitate was filtered off, and the solution was washed successively with distilled water (several times, ~50 mL at a time), with 5% solution of NaHCO₃ (three times, 50 mL at a time), and with water (several times, 100 mL at a time), until pH = 7 was reached. The solution was dried over CaCl₂ and filtered again, and toluene was removed by distillation under reduced pressure. The yield of the resin was 145 g. Several characteristics of uncured neat ROLs are given in Table 1.

For the present study, we have selected ADA which are widely used in industry, e.g., for curing epoxy resins, in the synthesis of bismaleimides and aromatic polyimides. The bulk polymer samples were prepared by casting neat ROLs and ROL-ADA blends into preheated open brass molds followed by heating the resins (blends) according to the following stepwise temperature-time regime until the final curing temperature Tfin.cure was achieved (°C/h): 150/2, 160/2, 160–180/0.5, 180/1, 180-220/0.5, 220/1, 220–260/0.5, 260/1, 260-300/0.5, 300-320/0.5, 320/1, and 350/3 (Table 2).

2.3. Characterization. Fourier transform infrared spectroscopy (FTIR) was performed using a Bruker Vertex 70 spectrometer (Bruker, Germany; 4000–600 cm⁻¹) equipped with an ATR (attenuated total reflection) attachment (PIKE Technologies, USA). The samples were studied in a thin layer and in the form of finely ground powder. Solid-state ¹³C cross-polarization (CP)/magic angle spinning (MAS) NMR spectra of powdered samples of 1,3-BAPB and the cured ROL-1,3-BAPB blends were taken with a Bruker AVANCE 400 spectrometer at an operating frequency of 125.77 MHz in the CP MAS mode (10 kHz). The ¹³C chemical shifts were externally referenced to tetramethylsilane (TMS). Temperature dependences of the storage (dynamic) Young’s (E’) or shear (G’) moduli and mechanical loss tangent (tan δ) were obtained by dynamic mechanical analysis (DMA) using a DMA 242C/1/F dynamic mechanical analyzer (NETZSCH, Germany) at a frequency (ν) of ~1 Hz, torsion pendulum at ν = 0.30, and a setup operating at ν = 660 Hz in a tension mode [2]. DMA studies were performed using rectangular bars of cured samples at a heating rate of 5°C/min. Accelerated thermo-oxidative aging of the cured neat ROLs and ROL-ADA blends (with masses of 0.50 ± 0.10 g and average
dimensions of 32 × 5 × 4 mm) was conducted in air thermostat at constant temperature (350°C); weight loss (WL) was determined every 1–3 h. Dynamic thermogravimetric analysis (TGA) of grinded samples was performed using a Paulik-Paulik-Erdei “Derivatograph C” (MOM, Hungary); the heating rate was 10°C/min. For determining gelation time ($t_G$), a liquid resin sample was placed in the Pyrex test tube immersed into oil bath with a constant temperature and timing was started. In these experiments, we chose the following temperatures: 140°C, 155°C, and 170°C. In the beginning (at 140°C), the resin system demonstrated very low viscosity (similar to that of water). As the copolymerization proceeded, gelation occurred; beginning of the gelation process was taken as a start of crosslinking.

### Table 1: Characteristics of uncured rolivsan thermosetting resins.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$n_D^{20}$</th>
<th>$M_n$</th>
<th>$t_G$ (min)</th>
<th>Unsaturated groups (mol per 100 g of resin) [2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROL-I</td>
<td>1.581</td>
<td>430</td>
<td>65$^{140}$</td>
<td>CH$_2$ = CH$^-$: 0.274, CH$_2$ = C(CH$_3$)$_2$: 0.239, -CH = CH$^-$: 0.120</td>
</tr>
<tr>
<td>ROL-II</td>
<td>1.592</td>
<td>470</td>
<td>82$^{155}$, 17.3$^{170}$</td>
<td>0.283, 0.192, 0.109</td>
</tr>
</tbody>
</table>

$^a$Number average molar mass. $^b$Gelation time at a given temperature ($t_G$, °C).

### Table 2: Contents of ADA in blend samples and their final curing temperatures $T_{fin\text{-}cur}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ADA (wt.%)</th>
<th>$T_{fin\text{-}cur}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROL-I</td>
<td>0.0</td>
<td>300</td>
</tr>
<tr>
<td>ROL-I-1,3-PDA (I)</td>
<td>12.0</td>
<td>300</td>
</tr>
<tr>
<td>ROL-I-1,3-PDA (II)</td>
<td>7.0</td>
<td>260</td>
</tr>
<tr>
<td>ROL-I-1,4-BAPB (II)</td>
<td>10.0</td>
<td>260</td>
</tr>
<tr>
<td>ROL-II (I)</td>
<td>0.0</td>
<td>180</td>
</tr>
<tr>
<td>ROL-II (II)</td>
<td>0.0</td>
<td>220</td>
</tr>
<tr>
<td>ROL-II (III)</td>
<td>0.0</td>
<td>260</td>
</tr>
<tr>
<td>ROL-II (IV)</td>
<td>0.0</td>
<td>320</td>
</tr>
<tr>
<td>ROL-II-1,3-PDA (II)</td>
<td>25.0</td>
<td>260</td>
</tr>
<tr>
<td>ROL-II-1,3-PDA (III)</td>
<td>25.0</td>
<td>320</td>
</tr>
<tr>
<td>ROL-II-1,3-PDA (IV)</td>
<td>25.0</td>
<td>350</td>
</tr>
<tr>
<td>ROL-II-1,3-BAPB (I)</td>
<td>3.0</td>
<td>320</td>
</tr>
<tr>
<td>ROL-II-1,3-BAPB (II)</td>
<td>5.0</td>
<td>320</td>
</tr>
<tr>
<td>ROL-II-1,3-BAPB (III)</td>
<td>7.0</td>
<td>320</td>
</tr>
<tr>
<td>ROL-II-1,3-BAPB (IV)</td>
<td>10.0</td>
<td>320</td>
</tr>
<tr>
<td>ROL-II-1,3-BAPB (V)</td>
<td>15.0</td>
<td>180</td>
</tr>
<tr>
<td>ROL-II-1,3-BAPB (VI)</td>
<td>15.0</td>
<td>220</td>
</tr>
<tr>
<td>ROL-II-1,3-BAPB (VII)</td>
<td>15.0</td>
<td>260</td>
</tr>
<tr>
<td>ROL-II-1,3-BAPB (VIII)</td>
<td>15.0</td>
<td>320</td>
</tr>
<tr>
<td>ROL-II-1,3-BAPB (IX)</td>
<td>25.0</td>
<td>320</td>
</tr>
<tr>
<td>ROL-II-1,3-BAPB (XI)</td>
<td>30.0</td>
<td>320</td>
</tr>
<tr>
<td>ROL-II-1,3-BAPB (XII)</td>
<td>35.0</td>
<td>320</td>
</tr>
<tr>
<td>ROL-II-1,3-BAPB (XIII)</td>
<td>50.0</td>
<td>320</td>
</tr>
<tr>
<td>ROL-II-1,3-BAPB (XIV)</td>
<td>50.0</td>
<td>350</td>
</tr>
<tr>
<td>1,3-BAPB (XV)</td>
<td>100.0</td>
<td>320</td>
</tr>
</tbody>
</table>

### 3. Results and Discussion

#### 3.1. FTIR Studies of Neat ROL-II Samples in the Process of Curing.

Three-dimensional free radical polymerization (TFRP) of ROLs in bulk at 140–170°C yielded glassy highly crosslinked copolymers with heat-sensitive methacrylate crosslinks. In the course of subsequent chemical transformations occurring at higher temperatures (180–320°C), these initial copolymers change their chemical, topological, and supramolecular structures and properties [1]. Figure 1 presents FTIR spectra of crosslinked ROL copolymers formed after curing neat ROL-II resin. The process involved stepwise heating from 140 to 160°C up to different final temperatures $T_{fin\text{-}cur}$ (180, 220, 260, and 320°C) for several hours (Table 2).

All spectra include two broad high-frequency absorption regions. The first one is a region of weak absorption (3600–3300 cm$^{-1}$, with the maximum at ~3400 cm$^{-1}$, associated with carboxyl and phenol groups). The second one is the 3100–2850 cm$^{-1}$ area attributed to the following C–H stretching vibrations: 3030 (C–H in the methyl group), 2928 (C–H in the methylene group), and 2872 cm$^{-1}$ (C–H in the methyl group).

Restructurization of the initial network copolymer that is formed during heating of the ROL-II sample in the thermal regime up to $T_{fin\text{-}cur}$ = 180°C (spectrum 4) is very clearly manifested in the FTIR spectra. The process can be indicated using position, shape, and intensity of the stretching vibration band of the carbonyl ($\nu_{C=O}$) group (Figure 1, spectra 1–3). There is a strong absorption band at 1717 cm$^{-1}$ attributed to monomeric and oligomeric methacrylate components that are present in all neat (uncured) ROLs. In these components, the CH$_2$ = C(CH$_3$)$_2$ – and >C = O groups are conjugated with each other. As TFRP proceeds (when ROL-II is heated at 150°–180°C), the carbonyl group appears to be in the nonconjugated position. As the intensity of this band gradually decreases, it becomes broader and shifts toward higher frequencies (spectrum 4, 1732 cm$^{-1}$). During further heating of ROLs in the temperature range from 180° to 260 (320°C), heat-sensitive methacrylate crosslinks of the initial network ROL copolymer begin to cleave with the formation of MAA units. The absorption band attributed to the carboxyl groups of these MAA units lies in the 1697-1699 cm$^{-1}$ area (Figure 1, spectra 2 and 3). Therefore, transformation of ester groups into carboxyl groups leads first to broadening of the carbonyl band and then to shifting of this peak toward lower frequencies. In the course of heating of the neat ROL-II resin up to $T_{fin\text{-}cur}$ = 260°–320°C (spectra 1 and 2), new bands appear. They are associated with carbonyl fragments formed after intramolecular cyclization of neighboring methacrylic units in the ROL copolymer chains. The
3.2. FTIR Studies of the ROL-ADA Blends in the Process of Curing

3.2.1. ROL-II- (75 wt.%) m-PDA (25 wt.%) Blends. In contrast to the copolymers prepared by thermal cure of neat ROL-II resin (Figure 2, spectrum 1), no absorption bands of MA units (1801 and 1756 cm\(^{-1}\)) were observed in the IR spectra of cured ROL-II-1,3-PDA (II-IV) blends (Figure 2, spectra 2-4). The observed bands attributed to carbonyl groups at 1724-1726 and 1680 cm\(^{-1}\), as well as weak bands at 1375, 1103, and 691 cm\(^{-1}\), represent the characteristic absorptions of amide and, possibly, imide fragments [8–14]. However, it should be noted that the bands at 1780 and 727 cm\(^{-1}\) (typical of imide absorbance) were not observed in the spectra of the studied blend samples.

3.2.2. ROL-II- (85 wt.%) 1,3-BAPB (15 wt.%) Blends. Let us consider FTIR spectra of ROL-II-1,3-BAPB (V-VIII) blends cured in the thermal regime up to final temperatures of 180 (V), 220 (VI), 260 (VII), and 320°C (VIII). In the high-frequency regions of their spectra (Figure 3), a wide absorption band is observed (3440-3250 cm\(^{-1}\)) with a peak at 3368 cm\(^{-1}\). This absorption is typical of O-H and amide N–H stretching vibrations in polyamic and polymethacrylic acids [8–14]. In contrast to thermally cured neat ROL-II heated at temperatures not exceeding 180°C (Figure 1, spectrum 4), no peaks attributed to anhydride (1801 and 1757 cm\(^{-1}\)) and carboxylic groups (1701 cm\(^{-1}\)) were observed in this case. The band of the carbonyl group (>C=O) at ~1715 cm\(^{-1}\) (Figure 3, spectra 1 and 2) that is attributed to monomeric methacrylate components of ROL becomes broader. This is caused by formation of methacrylate units in the initial ROL copolymer. Upon further heating, this band splits (see Figure 3, spectra 3 and 4 of the ROL-II-1,3-BAPB-VII and VIII samples, cured up to final temperatures \(T_{\text{fin,cur}}\) of 260° and 320°C, respectively).

At the same time, the peaks at 1728-1732 cm\(^{-1}\) and 1690-1695 cm\(^{-1}\) appear. They indicate formation of the nonconjugated C=O group of the methacrylate unit in ROL copolymer and, apparently, formation of MAA and methacrylamide units (Figure 5, spectra 3 and 4). Weak absorption at 1801 cm\(^{-1}\) is related to the presence of traces of MA units in the studied samples (Figure 3, spectra 3 and 4). Note that the spectrum of the diamine sample subjected to similar heat treatment (1.3-ВАРВ) does not include absorption bands in the 1850–1650 cm\(^{-1}\) region [6]. To summarize, IR spectra of the cured ROL-II-1,3-BAPB (V-VIII) blends with relatively low concentration of amino groups (Figure 3) contain the peaks typical of amide rather than of imide units. It is seen that in the spectrum of the ROL-II-1,3-BAPB (VIII) sample cured in the regime with the final temperature \(T_{\text{fin,cur}} = 320°C\), virtually no absorption at 1780 cm\(^{-1}\) is present.

3.2.3. ROL-II- (50 wt.%) 1,3-BAPB (50 wt.%) Blends. Analysis of FTIR spectra of the ROL copolymers prepared from ROL-II-1,3-BAPB blends with relatively low amounts of amino groups has not clarified the point of efficiency of the thermochemical interaction between the carboxylic (anhydride) and amino groups. Therefore, we carried out the experiments...
involving the blends with higher concentration of this diamine and those cured at the highest temperatures ($T_{\text{fin,cur}} = 320° - 350°C$).

As seen from Figure 4, in the high-frequency area of FTIR spectra of cured blends, two broad bands at (i) 3500-3400 cm$^{-1}$ (with a maximum at 3445 cm$^{-1}$) and (ii) 3400-3300 cm$^{-1}$ (with a maximum at 3370 cm$^{-1}$) are observed. As $T_{\text{fin,cur}}$ is increased from 320° to 350°C (ROL-II-1,3-BAPB (XIII and XIV), spectra 2 and 4), these bands become more intense. Intensity of the bands related to the neat 1,3-BAPB (XV) heat-treated (oligomerized) in air (spectrum 1) depends on the content of this diamine in the initial ROL-II-1,3-BAPB blend. Intensity of the bands attributed to stretching vibrations of hydrogen atoms in methyl and methylene groups (3100-2800 cm$^{-1}$) is apparently determined by the ROL-II content in the blends. The bands associated with possible formation of (poly)amic acid units in the cured ROL-II-1,3-BAPB blends are overlapped with the abovementioned broad bands of carboxyl and phenol groups of the restructured ROL-II copolymers and amino groups of 1,3-BAPB (XV). Therefore, this range is hardly suitable for evaluating the efficiency of the reactions under consideration.

We proceed now to discussing the 1900-550 cm$^{-1}$ range of the FTIR spectra (Figure 4). First of all, it should be noted that carbonyl absorption bands in the 1850-1600 cm$^{-1}$ interval are naturally not observed for 1,3-BAPB (XV) (spectrum 1). In contrast to the restructured neat ROL-II copolymer (ROL-II (IV), spectrum 5), spectra of ROL-II-1,3-BAPB (VIII) and ROL-II-1,3-BAPB (XIII) blends (spectra 2 and 4) exhibit no band characteristic of MA (1801, 1757 cm$^{-1}$), methacrylate (1736 cm$^{-1}$), and MAA (1701 cm$^{-1}$) units. The broad band of medium intensity appears around 1674 cm$^{-1}$. This band is characteristic of amide units [11]. It should be noted that the absorption band at 1674 cm$^{-1}$ is absent in the spectrum of cured neat ROL-II (IV) (spectrum 5). Spectra 2-5 contain a weak absorption band at 1377 cm$^{-1}$, which could confirm the formation of an imide ring [12–14] if it were absent in the spectrum of cured neat ROL-II (IV).

Comparison of spectra 2 and 4 of the cured blends with that of neat ROL-II (IV) (Figure 4, spectrum 5) reveals appearance of the broad band at 3445 cm$^{-1}$ that can be assigned to N-H bonds [15]. The presence of $C_{\text{Ar, N}}$ bands at 1476 and 1308 cm$^{-1}$ [16] and of the band at 1250 cm$^{-1}$ in spectra 1-3 (while they are absent in spectrum 5 (the cured neat ROL-II)) confirms that the cured blends contain significant amounts of heat-treated 1,3-BAPB fragments.

3.3. $13C$ NMR Spectra of the Cured Neat ROL Samples. The nonrestructured (neat) ROL-II (I) copolymer (obtained by radical copolymerization of styrene-like and (di)methacrylate ROL-components according to the thermal regime with $T_{\text{fin,cur}} = 180°C$ (Figure 5) is similar to amorphous
alternating styrene/methyl methacrylate copolymers (P(S-MMA)) in the chemical structure and ratio between comonomer units. Solid-state CP/MAS $^{13}$C NMR spectra of the neat ROL-II-copolymers (Figure 6) and the cured ROL-II-1,3-BAPB blends (Figure 7) were obtained. The majority of the observed resonance lines were very broad, since they are attributed to $^{13}$C carbon atoms surrounded by kindred units of amorphous polymers (which differ in composition). Many of the peaks produced by different types of carbon atoms are superimposed on each other. The spectra of neat ROLs (Figure 6) consist of numerous resonance lines, which originate from carbon sites in aromatic rings (160-110 ppm). The resonances at 158, 154, 140, and 136 ppm are assigned to substituted (nonprotonated) aromatic carbons ($^{13}$CAr$^-$), and the resonances at 128 and 122 ppm are assigned to protonated atoms ($^{13}$CAr-H). The signals in the ranges of 185-165 ppm and 60-15 ppm are related to carbonyl, methyl, methylene, and methine groups.

Assignment of chemical shifts in the spectra of neat ROLs and ROL-ADA blends was consistent with the previously reported data [17–24]. These data are related to $^{13}$C atoms included in kindred structures (groups, units, or segments).

For the purpose of comparison, we correlated the signals of $^{13}$C atoms in NMR spectra of the cured neat ROLs and the known kindred (co)polymers (i.e., polystyrene (PS), poly(methyl methacrylate) (PMMA), poly(methacrylic acid) (PMAA), and poly(methacrylic anhydride) (PMAN)). The corresponding resonances were assigned to specified carbons; the data are summarized in Table 3. The sample of neat ROL-II (I) copolymer with $T_{\text{fin,cur}} = 180^\circ$C (Figure 6, spectrum 4) shows wide $^{13}$C signals at 176.6 and 175.4 ppm (>C=O ester group (h)). These signals almost completely coincide with the signals in NMR spectra of an alternating S-MMA copolymer [19] and PMMA [18]. With increasing $T_{\text{fin,cur}}$ of the cured ROL-II samples (II, III, and IV) up to 220, 260, and 320°C, the intensity of $^{13}$C signals (>C=O, heat-sensitive methacrylate units) of the neat ROL copolymer (Figure 6, spectra 1-3) decreases. This change is related to thermocatalytic cleavage of these units (Figure 5) [1]. At the same time, the spectra of samples cured in the regime with $T_{\text{fin,cur}}$ 260° and 320°C (spectra 1 and 2) contain more intensive $^{13}$C signals (>C=O) at 173-172 and 185-183 ppm. These peaks are attributed to MA units (m) [18] and MAA units (j) [18], respectively. Note that there is a significant difference between positions of $^{13}$C (>C=O) signals of cyclic aliphatic (e.g., 1,2,3,4-cyclo-pentanetetrahydroxylic dianhydride, 169.29 and 173.34 ppm [25]) and aromatic anhydrides (164.5 and 165.5 ppm [24]).

Analysis of FTIR and $^{13}$C NMR spectra of the cured neat ROL-II (I-IV) samples (Figures 1 and 6) demonstrates a good agreement between the data obtained by these two methods. The presence of carbonyl groups in the samples is confirmed by (i) the absorption bands related to >C=O valence...
vibrations and (ii) the $^{13}$C NMR signals attributed to carbonyl C atom: (cm$^{-1}$/ppm): (1801 and 1756)/ (171.0-172.5; 172.8 ppm [17]) (MA units), 1732/(176-178); 178 ppm [18] (methacrylate units) and 1700/(181.5-184.5); and 181 ppm [18] (MAA units).

3.4. $^{13}$C NMR Spectra of the Cured ROL-II-1,3-BAPB Blends.

Figure 7 presents $^{13}$C NMR spectra of the samples prepared by curing ROL-II-1,3-BAPB blends according to the same thermal regime as was used in curing the neat ROL-II. Composition of the blend containing comparatively low amount

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**Figure 4**: FTIR spectra of heat-treated 1,3-BAPB (XV) (1) and the following cured blends: ROL-II-1,3-BAPB (XIV) (2), ROL-II-1,3-BAPB (VIII) (3), ROL-II-1,3-BAPB (XIII) (4), and neat ROL-II (IV) (5).

**Figure 5**: Chemical structures of the neat and restructurized ROL copolymers.

where Ph and C$_{Ar}$ are p-phenylene and the aromatic C.
Figure 6: $^{13}$C NMR spectra of samples of neat ROL-II (I-IV) resins cured according to the thermal regime with $T_{\text{fin,cur}}$ increasing from 180° to 320°C.

Figure 7: Schematic representation of interaction between ADA and restructured ROL copolymers; $^{13}$C NMR spectra of the samples of ROL-II- (85 wt.%) 1,3-BAPB (15 wt.%) cured in the thermal regime up to the following $T_{\text{fin,cur}}$ (°C): 1: 320; 2: 260; 3: 220; 4: 180.
Table 3: Assignment of CP/MAS $^{13}$C NMR chemical shifts of neat ROL copolymers and model polymers.

<table>
<thead>
<tr>
<th>ROL copolymer</th>
<th>$T_{\text{fin,cur.}}$ (°C)</th>
<th>$\delta$ (ppm from TMS)</th>
<th>$\delta$ (ppm from TMS)</th>
<th>$\delta$ (ppm from TMS)</th>
<th>$\delta$ (ppm from TMS)</th>
<th>$\delta$ (ppm from TMS)</th>
<th>$\delta$ (ppm from TMS)</th>
<th>$\delta$ (ppm from TMS)</th>
<th>$\delta$ (ppm from TMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ROL-II (I)</td>
<td>180</td>
<td>176.6; 175.4</td>
<td>128; 122</td>
<td>140</td>
<td>154; 158</td>
<td>40</td>
<td>52-56</td>
<td>18.9</td>
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</tr>
<tr>
<td>ROL-II (II)</td>
<td>220</td>
<td>184.5; 182.9; 179.2; 177.0; 175.8; 173.6</td>
<td>128; 122</td>
<td>140</td>
<td>154; 158</td>
<td>40</td>
<td>53.8</td>
<td>19.4</td>
<td></td>
</tr>
<tr>
<td>ROL-II (III)</td>
<td>260</td>
<td>185.1; 184-183; 179.4 177.9; 175.4; 172.4; 169.9</td>
<td>128; 122</td>
<td>140</td>
<td>154; 158</td>
<td>40</td>
<td>56.0</td>
<td>19.8</td>
<td></td>
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<tr>
<td>ROL-II (IV)</td>
<td>320</td>
<td>185.2; 183.0; 179.7; 178.0; 176.0; 172.3; 170.8</td>
<td>128; 122</td>
<td>140</td>
<td>154; 158</td>
<td>40</td>
<td>53-55</td>
<td>19.8; 15.1</td>
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</tr>
<tr>
<td>PMMA</td>
<td>—</td>
<td>178.1</td>
<td>45.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>52.2</td>
<td>16.7</td>
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<tr>
<td>Neat PMAA</td>
<td>—</td>
<td>180.7</td>
<td>44.2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>53.2</td>
<td>16.0</td>
<td></td>
</tr>
<tr>
<td>Neat PMA</td>
<td>—</td>
<td>172.8</td>
<td>—</td>
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<tr>
<td>CPDA</td>
<td>—</td>
<td>169.29; 173.34</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>39.79</td>
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<tr>
<td>Neat PS</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>127</td>
<td>146</td>
<td>—</td>
<td>40</td>
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<td>SMMA copolymer</td>
<td>—</td>
<td>175; 176; 177</td>
<td>44-47</td>
<td>128-126</td>
<td>143-145</td>
<td>—</td>
<td>38-39</td>
<td>25-15</td>
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<tr>
<td>Pα-ms-PPOf</td>
<td>—</td>
<td>—</td>
<td>45</td>
<td>127</td>
<td>145</td>
<td>155</td>
<td>—</td>
<td>57-63</td>
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(15 wt.%) of 1,3-BAPB attracted special interest. As was shown above, the ROL copolymer samples obtained on the basis of this blend possessed maximum high-temperature strength and thermo-oxidative stability. Naturally, the spectra of this blend (Figure 7) are almost similar to that of the neat ROL resin (Figure 6) prepared by curing in the regime with $T_{\text{fin,cur}}$ increasing from 180 to 320°C. This similarity is caused by high content of ROL component. In both series of spectra, wide signals are observed; they originate both from carbon atoms ($^{13}$C) of aromatic rings (at 158, 154, 140, 136, 128-129, and 122 ppm) and aliphatic groups (at 57, 45, 40, 24, and 18 ppm). The differences in spectra are related to carbonyl signals $>^{13}$C=O in the 180-160 ppm area, since these signals are sensitive to the nature of groups adjacent to carbonyl C atom.

The spectra of cured blends contain a wide signal in the 174-178 ppm area with a peak at 176 ppm. This signal continues to broaden with increasing $T_{\text{fin,cur}}$ from 180° to 220-320°C (Figure 7, spectra 1-3). There is also a relatively narrow signal at 166.5 ppm (spectra 3, 4), which disappears at heating the blend up to $T_{\text{fin,cur}} = 320$°C (spectrum 1).

Unfortunately, the sought-for signals $>^{13}$C=O (C-m and C-n) that arise upon formation of nonaromatic amide and imide derivatives of methacrylic acid (according to the scheme in Figure 7) also lie in this range [11, 23–26]. Thus, for example, the resonance lines at 177.5-177.8 and 173.9 ppm were assigned to the imide carbonyl in cycloaliphatic-aromatic polyimides [25]. The spectrum of aromatic (poly)amic acid contains the signals attributed to carbonyl carbon atoms at 172.80, 171.81, and 166.19 ppm [26], and the signal at 165.8 ppm [27] and 162.9 ppm [28] corresponds to the (O=^{13}$C-N) fragment in polyimides. In the solid-state spectra, the signal related to aromatic imide carbonyl at 166 ppm is observed; three signals at 146.6, 144.2, and 141.1 ppm can be clearly distinguished in the region typical of substituted aromatic rings [29]. The peak at 162.9 ppm in the spectra presented in Figure 7 is possibly overlapped with the wide signal of $^{13}$CAr-O-$^{13}$CAr (C-d, C-e) with the maximum at 158 ppm. Apparently, these wide signals of carbonyl groups in the spectra of the cured blend (Figure 7) do not provide unambiguous confirmation of the expected reactions, when they are considered separately. However, our purpose was to prove the proceeding of thermocatalytical reactions between diamine (1,3-BAPB) and the units of MA and (or) MAA in the restructured ROL copolymer. In order to clarify this point, we analyzed other signals that could serve as indirect confirmation of chemical interactions (appearance of C-m and C-q and/or C-n and C-p signals, see scheme in Figure 7). Indeed, all spectra contain the most intense signal at 128-129 ppm that can be attributed both to $^{13}$CAr-H [19, 21–23] and to C-p (i.e., to $^{13}$CAr-N-C=O) [23, 25]. There is also a signal appearing at

![Figure 8: $^{13}$C NMR spectra of the samples of ROL-II- (50 wt.%) 1,3-BAPB (50 wt.%) (XIII) blends (1), ROL-II (100%) (2), and the 1,3-BAPB sample oligomerized in the regime with $T_{\text{fin,cur}} = 320$°C (3).](image-url)
136 ppm that can be assigned both to nonprotonated \((^{13}\text{C}_{\text{Ar}})\) atom [23] and to imide carbon \((^{13}\text{C}_{\text{Ar-N-C=O}})\) [23].

Thus, the spectra of ROL-II-1,3-BAPB blends (Figure 7) containing relatively low amounts of ADA include wide overlapping signals related to carbon atoms \(^{13}\text{C} = \text{O}\) at 170-180 ppm. These atoms may be incorporated in various units, and it is not possible to ascribe the signals with confidence to the desired amide and/or imide structures.

Figure 8 presents solid-state \(^{13}\text{C}\) NMR spectra of ROL-II-1,3-BAPB blends containing 50% of the diamine (spectrum 1) and spectrum of the cured neat ROL resin (spectrum 2).

Comparison of these two patterns shows that, contrary to expectations, these spectra contain signals of carbonyl carbon atoms (with almost similar positions and intensities) at 178, 176, 172.4, and 170.8 ppm. These signals are absent in the spectrum of oligomerized 1,3-BAPB (spectrum 3). However, the signals at 172.4 and 170.8 ppm are more pronounced in spectrum 1.

3.5. \(^{13}\text{C}\) NMR Spectra of the Cured ROL-II-\textit{m}-PDA Blends. The ROL-II-1,3-PDA (IV) sample heated according to the regime that provides for the highest \(T_{\text{fin, cur}} = 350^\circ\text{C}\) was studied by \(^{13}\text{C}\) NMR spectroscopy. Along with the signal at 177 ppm that is observed in the spectra of blends (Figures 7 and 8), the spectrum (Figure 9, spectrum 1) contains the signal at 173.3 ppm. The latter is absent in the spectra of samples after curing at lower final temperatures. Naturally, all spectra include rather intensive signals of the substituted \(^{13}\text{C}_{\text{Ar-O}}\)-(158 and 154 ppm) and \(^{13}\text{C}_{\text{Ar-N<}}\)-(146, 144, 141, and 138.5) groups and protonated (128, 122, 119, and 108 ppm) aromatic carbons.

Figure 9: \(^{13}\text{C}\) NMR spectra of ROL-II- (75 wt.%) \textit{m}-PDA (25 wt.%) blends, cured in the thermal regime up to the following \(T_{\text{fin, cur}}\) (°C): 1: 350; 2: 320; 3: 260.

Figure 10: Temperature dependencies of storage Young’s modulus \(E’\) of the cured ROL-I-1,3-PDA (I) blend (1) and the cured neat ROL-I (2). The DMA experiments were performed at a frequency \((\nu)\) of ~1.0 Hz.
3.6. Dynamic Mechanical Analysis (DMA). Figures 10–12 show that after thermal cocuring of ROLs with comparatively low amounts of ADA (10 ± 5 wt%), the values of dynamic (storage) Young’s modulus of the modified samples increase significantly over a wide temperature range. Besides, the apparent glass transition temperature \( T_g \) shifts toward higher temperatures by 50-70°C. Moreover, modifying ROLs in this manner causes significant increase in stability of ROL copolymers against thermo-oxidative destruction (as follows from Figure 13).

3.7. Thermal Analysis

3.7.1. Thermal Oxidative Aging of Cured ROL-1,3-BAPB Blends at 350°C. The influence of the composition of cured ROL-1,3-BAPB blends on their resistance to thermal degradation is shown in Figure 13. Samples of ROL-II compounds with small (10 ± 5 wt.%) amounts of 1,3-BAPB showed the smallest weight loss in thermal oxidative aging at 350°C (Figure 13, curve 5). However, for the heat-treated 1,3-BAPB (sample II, curve 1) and samples with high diamine content (curves 2 and 4), the weight loss considerably increases. These experiments show that monomeric 1,3-BAPB sublimes at a high temperature (350-400°C).

3.7.2. The TG and DTA Curves for Cured Neat ROL Resins and ROL-1,3-BAPB Blends. The TG and DTA curves (Figure 14) recorded for the initial monomeric 1,3-BAPB \( (T_m = 115 – 118^\circ C) \) show that, at fast heating in air at a rate of 10 deg-min\(^{-1}\) in the temperature interval 20-280°C, its weight loss is close to zero. In the DTA curve, there is an endothermic peak at \( T \approx 120^\circ C \), apparently corresponding to the sample melting; on further heating, a broad exothermic effect is observed (120-350°C), suggesting the occurrence of oxidative polymerization, with appreciable weight loss observed neither for the diamine nor for its polymerization products. This means that fast oxidative polymerization (OP) of 1,3-BAPB starts virtually immediately after melting (from 130-140°C). Hence, OP can occur simultaneously with acylation of this diamine with anhydride groups of the ROL.
Active decomposition of 1,3-BAPB cured in this temperature interval is observed at temperatures exceeding 400°C. According to the temperature dependence of weight loss, the resistance of this sample to thermal oxidative degradation is appreciably lower than that of the cured ROL-II and its mixtures with 1,3-BAPB.

Standard TGA and DTA experiments are usually performed at a high heating rate (10 deg·min⁻¹), at which the differences in the thermal characteristics of related polymer materials are largely leveled off. Nevertheless, it can be noted that the TG curves of ROL-II-1,3-BAPB are shifted toward higher temperatures compared to neat ROL-II. The temperature peaks in the DTA curves for the regions of initial (425 ± 10°C) and deep (610 ± 4°C) thermal oxidative degradation virtually coincide, suggesting similar mechanisms of the degradation of these materials.

4. Conclusions

One of the goals of this study was to confirm usefulness of the novel method for structural and chemical modification of microheterogeneous network polymers. We investigated thermochemical curing reactions of unsaturated rolivsan thermosetting resins with aromatic diamines that lead to increase in cohesion between morphological formations (grains and interlayers) in the ROL copolymer. Combination
of FTIR and $^{13}$C NMR spectroscopy was used to determine the chemical structure of the cured ROL-ADA blends. IR spectra of the blends demonstrate wide absorption bands typical of amide N–H stretching vibrations in polyamic acid and carbonyl absorption peaks similar to those of amide and imide groups. There is a good agreement between the FTIR and NMR data (the presence of carbonyl groups in the samples was confirmed both by $>\text{C}=\text{O}$ valence vibrations and by signals of $^{13}$C carbonyl atoms). However, some of the signals either are absent in the spectra of the studied blends or overlap with wide bands (carbon signals) attributed to the adjacent groups. Thus, it is concluded that the increase in cohesion between morphological formations in microheterogeneous ROL copolymer occurs at the expense of formation of additional amide fragments (polyamic acid) rather than imide crosslinks.

**Data Availability**

The data used to support the findings of this study are available from the corresponding author upon request.

**Conflicts of Interest**

The authors declare that there is no conflict of interest regarding the publication of this paper.

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**References**


