The synthesis of phenol–formaldehyde copolymers based on phthalide-containing monophenol

L.N. Machulenko, A.I. Nechaev, S.N. Salazkin, L.I. Komarova, and P.V. Petrovskii
A.N. Nesmeyanov Institute of Heteroorganic Compounds, Russian Academy of Sciences

Translated by P. Curtis

SUMMARY
Phthalide-containing monophenol 3-phenyl-3-(41-hydroxyphenyl)phthalide (I) was synthesised by the interaction of o-benzoylbenzoic acid chloride with phenol in a dioxane solution in the presence of catalyst ZnCl₂. Resol-type phenol-formaldehyde cooligomers and heat-resistant polymers based on them were obtained by the interaction of a mixture of the synthesised monophenol and phenol in different weight ratios (from 5:95 to 40:60).

Earlier, phthalide-containing, resol-type, thermosetting homo- and copolymers based on phenolphthalein (3,3-bis(41-hydroxyphenyl)phthalide) [1–6] and phthalide-containing 3-phenyl-3-(21,51-dihydroxyphenyl)phthalide diphenol [7], which are of interest as heat-resistant and electroactive materials, were described.

With the aim of finding ways to improve the properties of phthalide-containing polymers, it is of interest to obtain more complete information on the influence on the synthesis and properties of phthalide-containing phenol–formaldehyde oligomers and polymers based on them of the presence of different quantities of phenol groups in only one of the aromatic nuclei of the diphenylphthalide fragment. In this context, it is important to synthesise cooligomers and crosslinked copolymers using as the phthalide-containing phenol 3-phenyl-3-(41-hydroxyphenyl)phthalide (I), which, in contrast to those mentioned above, is a monophenol and contains one hydroxyl group in only one phenyl nucleus.
The structure of the synthesised phthalide-containing monophenol was confirmed by the results of elemental analysis and by its IR spectrum presented in Figure 1 (spectrum 1). The presence of a phthalide ring in the p-position of the phenol nucleus is confirmed by the presence in its IR spectrum of an intense band with a peak at 1732 cm\(^{-1}\) corresponding to stretching vibrations (C=O) of the phthalide ring and a band at 840 cm\(^{-1}\) corresponding to CH deformation vibrations of the 1,4-substituted aromatic ring.

The structure of the 3-phenyl-3-(41-hydroxyphenyl) phthalide obtained was also confirmed by \(^1\)H and \(^13\)C NMR spectra (see the Experimental section).

The phthalide-containing monophenol (I) synthesised was used as the monomer for the production of phenol-formaldehyde cooligomers. Resol-type phenol–formaldehyde cooligomers were obtained on the basis of compound I and phenol in different ratios by condensation with formaldehyde.

It is known that phenol–formaldehyde resols are obtained in aqueous solution by the interaction of phenol with a small excess of formaldehyde in the presence of an alkaline catalyst. However, the phthalide-containing monophenol (I) synthesised is not water soluble. In this case, resols are obtained in a solution of an organic solvent [1–3]. In spite of this, the synthesis of resol-type cooligomers based on a mixture of phenol and compound I proved possible in an aqueous solution owing to the capacity of the monophenol to dissolve in water in the presence of phenol.

Cooligomers were obtained by the interaction of a mixture of compound I and phenol (weight ratio from 5:95 to 50:50) with formaldehyde (molar ratio of phenols to formaldehyde 1:1.2) in an aqueous solution at a temperature of 90–100°C in the presence of ammonia as the alkaline catalyst by Scheme 2:

The process proceeds via the formation of a transparent aqueous solution. Synthesis was carried out until the clear separation of the reaction mass into two layers. The aqueous layer was decanted, and the resin was washed repeatedly with hot water and dried. The resins were purified by reprecipitation from acetone solution into water.

It should be pointed out that the term “cooligomer” is nominal in relation to the oligomers, as, at the oligomer stage, it may also be a blend of homooligomers. Strictly, the term “copolymer” may be applied only to crosslinked systems obtained by the curing of the indicated cooligomers.

As a result, under these conditions, resol-type soluble cooligomers based on a mixture of phenol and phthalide-containing monophenol (I) were synthesised in a 70.3–83.9% yield. Some characteristics of the cooligomers obtained are presented in Table 1. For comparison, the table gives the characteristics of phenol-based resol (oligomer IIh), and also data for known cooligomers based on a mixture of phenol and phenolphthalein (oligomer III), and based on mixtures of phenol and phthalide-containing diphenol 3-phenyl-3-(2,51-dihydroxyphenyl)phthalide (oligomers IVa to IVc).

In the case of using mixtures containing over 40% of compound I, it was not possible to carry out the process in a homogeneous aqueous solution. Therefore, synthesis was conducted in a solution in 1.4-dioxane. By this method, a cooligomer based on a mixture of phenol and compound I containing phenol and phthalide-containing monophenol (I) in equal quantities and also a homooligomer based on compound I were obtained (see Table 1, oligomers IIIf and IIlg).

The resols synthesised are powder products with T,soft ranging from 98 to 122°C, are soluble in acetone,
ethanol, and dioxane, and contain 4.5–20.1% hydroxymethyl groups, and here their quantity increases as the proportion of phenol increases (and accordingly as the amount of compound I decreases) in the initial mixtures, approaching the index for phenolic resol (oligomer III, content of hydroxymethyl groups 21.1). The given behaviour pattern may be explained by the fact that hydroxymethyl groups are contained only in the phenol fragment, as shown in scheme 2.

The structure of the oligomers synthesised was confirmed by their IR spectra (Figure 1, spectra 2 to 5). The IR spectra of cooligomers IIc and Ile (spectra 3 and 4) and also of homooligomer (spectrum 5), like the spectrum of the initial monomer (spectrum 1), contain an intense band with a peak at 1741 cm\(^{-1}\) corresponding to stretching vibrations (C=O) of the phthalide ring, which indicates its presence in the cooligomers. For resin IIa based on a mixture with the minimum amount of phthalide-containing monophenol I (5%), the given band is weak (spectrum 2). Similar behaviour patterns were observed earlier for the IR spectra of cooligomers of phthalide-containing diphenol [7].

The presence of hydroxymethyl groups in the synthesised resols was confirmed by bromometric titration by Kebner’s method [10], and also by the presence in their IR spectra of 1016 and 3340 cm\(^{-1}\) bands relating respectively to stretching vibrations (C–O) and (OH) of the hydroxymethyl and phenol groups.

Thus, as a result of the interaction of mixtures of phenol and 3-phenyl-3-(41-hydroxyphenyl)phthalide (I) with formaldehyde in the presence of an alkaline catalyst, soluble resol-type cooligomers including both phenolic and phthalide-containing fragments were obtained, and here hydroxymethyl groups are contained only in the phenol fragments, as presented in Scheme 2 (structures Ila to II).

Owing to the presence of hydroxymethyl groups, cooligomers Ila to Ile, when heated in air at 180°C for 2–3 min, are cured, with the formation of non-melting and insoluble crosslinked systems. Cooligomer IIf could not be cured under the given conditions in view of the low content of hydroxymethyl groups (6.3%).

It was also not possible to obtain a crosslinked polymer based on homooligomer Ilf. When it was heated in a melt at 180°C, there was an increase in melt viscosity, with the formation of a linear polymer soluble in organic solvents.

Table 2 gives the physicochemical properties of cured cooligomers Ila to Ile. For comparison, the results for a cooligomer based on a mixture of phenol and phenolphthalein (III) and cooligomers based on mixtures containing 3-phenyl-3-(21,51-dihydroxyphenylphthalide) (cooligomers IVa and IVe) are also given in the table.

As can be seen from Table 2, the cured copolymers have the following physicochemical properties: bending stress causing failure 41.7–49.0 MPa, specific impact strength 1.6–1.9 kJ/m\(^2\), which are at the level of the properties for copolymers based on a mixture of phenol and phenolphthalein (III), and also based on mixtures of phenol and phthalide-containing diphenol (IVa, IVb).

The small amounts of acetone-soluble low-molecular-weight substances (no more than 3.2%) indicate the

<table>
<thead>
<tr>
<th>Oligomer</th>
<th>Composition of initial mixture, wt%</th>
<th>Yield, %</th>
<th>(T_{\text{cure}}) °C</th>
<th>Curing time at 180°C</th>
<th>Content of elements</th>
<th>Content of CH(_2)OH groups, § %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PM* Phenol PP† PD‡</td>
<td>t</td>
<td></td>
<td></td>
<td>C</td>
<td>H</td>
</tr>
<tr>
<td>Ila</td>
<td>5 95</td>
<td>73.2</td>
<td>108–110</td>
<td>2 min 10 s</td>
<td>72.9</td>
<td>5.7</td>
</tr>
<tr>
<td>Ilib</td>
<td>10 90</td>
<td>76.2</td>
<td>106–108</td>
<td>1 min 20 s</td>
<td>72.2</td>
<td>6.0</td>
</tr>
<tr>
<td>IIc</td>
<td>20 80</td>
<td>75.8</td>
<td>100–101</td>
<td>1 min 50 s</td>
<td>74.1</td>
<td>5.4</td>
</tr>
<tr>
<td>IIId</td>
<td>30 70</td>
<td>73.3</td>
<td>98–100</td>
<td>1 min 55 s</td>
<td>72.5</td>
<td>5.8</td>
</tr>
<tr>
<td>IIe</td>
<td>40 60</td>
<td>80.0</td>
<td>120–122</td>
<td>3 min 20 s</td>
<td>75.7</td>
<td>5.1</td>
</tr>
<tr>
<td>IIIf</td>
<td>50 50</td>
<td>70.3</td>
<td>90–92</td>
<td>Does not cure</td>
<td>74.9</td>
<td>5.1</td>
</tr>
<tr>
<td>IIg</td>
<td>100</td>
<td>83.9</td>
<td>97–99</td>
<td>Does not cure</td>
<td>74.3</td>
<td>5.2</td>
</tr>
<tr>
<td>IIh</td>
<td>100</td>
<td>80.0</td>
<td>108–110</td>
<td>2 min 50 s</td>
<td>72.5</td>
<td>6.1</td>
</tr>
<tr>
<td>III</td>
<td>— 60 40</td>
<td>78.0</td>
<td>99–101</td>
<td>3 min 10 s</td>
<td>72.4</td>
<td>5.3</td>
</tr>
<tr>
<td>IVa</td>
<td>— 95</td>
<td>77.3</td>
<td>88–90</td>
<td>2 min 5 s</td>
<td>69.1</td>
<td>6.1</td>
</tr>
<tr>
<td>IVb</td>
<td>— 60</td>
<td>74.0</td>
<td>95–98</td>
<td>2 min 55 s</td>
<td>73.9</td>
<td>5.7</td>
</tr>
<tr>
<td>IVc</td>
<td>— 50</td>
<td>60.8</td>
<td>93–95</td>
<td>Does not cure</td>
<td>70.2</td>
<td>5.7</td>
</tr>
</tbody>
</table>

* Phthalide-containing monophenol
† Phenolphthalein
‡ Phthalide-containing diphenol – 3-phenyl-3-(21,51-dihydroxyphenyl)phthalide
§ Determined by Kebner’s method (see the Experimental section)
The new resol-type phthalide-containing polymers synthesised are of interest not only for the creation of valuable heat-resistant materials of traditional designation but also as new valuable "smart" polymers, for example polymers exhibiting the effect of switching of electric current as a result of external effects.

**EXPERIMENTAL**

Phenol distilled at $T_{boil}$ 181°C and thionyl chloride distilled at $T_{boil}$ 76°C were used.

-o-Benzoylbenzoic acid was purified in the following way: an aqueous solution of Na salt of o-benzoylbenzoic acid was filtered out from insoluble impurities and was decolourised by treatment with activated carbon, and, after filtration to remove the activated carbon, a solution of hydrochloric acid was added to the filtrate to a pH of 5–6. The precipitated o-benzoylbenzoic acid was filtered out, washed with water to remove residues of hydrochloric acid, and dried at 100°C, $T_m$ 125–126°C.

Dioxane was dried over molecular sieves of grade NaA and distilled, $T_{boil}$ 100–101°C.

Reagent-grade ACS anhydrous ZnCl$_2$ (Fluka) was used as the catalyst without additional purification.

Phthalide-containing monophenol (I) was obtained by the condensation of o-benzoylbenzoic acid chloride with phenol in solution in 1,4-dioxane in the presence of anhydrous ZnCl$_2$ catalyst by the procedure described earlier [8, 9] and modified by the present authors. Yield 76.8%, $T_m$ 168–169°C (according to published data, 168–169°C). Content of elements, found (calculated), %: C 79.47 (79.57); H 4.68 (4.64).

$^1$H NMR (acetone-d$_6$, $\delta$, ppm, $J$/Hz): 8.67, s, 1H, H$_2$; 7.91, d, 1H, H$_2$; 7.61, ddd, 1H, H$_8$; 7.30–7.43, m, 5H, H$_6$, H$_{10}$, H$_{11}$, H$_{12}$, 6.89, td, 2H, H$_{11,15}$; 6.72–7.79, m, 12H, H$_{16}$, H$_{17}$, H$_{18}$, H$_{19}$, H$_{20}$, 6.39, (acetone-d$_6$, $\delta$, ppm): 169.19 (C5), 157.83 (C13), 152.55 (C3), 141.83 (C16), 134.58 (C7), 132.09 (C10), 129.66 (CH8), 128.93 (CH11, 15), 128.63 (CH17, 21), 126.80 (CH18, 20), 125.58 (CH9), 125.41 (C4), 124.63 (C6), 115.42 (CH12, 14), 91.47 (C2).

**Synthesis of resol-type phenol–formaldehyde cooligomer based on a mixture of phthalide-containing monophenol (I) and phenol in a weight ratio of 40:60 (cooligomer Ille)**

Into a three-necked flask equipped with a stirrer and a reflux water condenser was charged 4.8 g (0.05 mol) of phenol, 3.1 g (0.01 mol) of compound I, 5.3 mL of 36% Formalin formaldehyde solution containing 2.1 g (0.07 mol) of formaldehyde (molar ratio of formaldehyde and phenols 1.2:1), and 0.2 mL of a 25% aqueous solution of ammonia. The reaction mass was heated in a boiling water bath during constant stirring until the clear separation of the reaction mass into two layers (resin and water). The water layer was decanted, and the resin was repeatedly washed with hot water and dried initially in air and then in an oven at 50–60°C. The resin was purified by reprecipitation from acetone solution into water. Cooligomer yield 80.0%, $T_{soft}$ 120–122°C, content of oxymethyl groups 10.3%, content of elements, %: C 75.7, H 5.1; curing time at 180°C, 3 min 20 s.

Cooligomers Ille to IId were obtained in a similar way. Their main characteristics are given in Table 1.

**Synthesis of a resol-type phenol–formaldehyde cooligomer based on a mixture of phthalide-containing monophenol (I) and phenol in a weight ratio of 50:50 (cooligomer Ilff)**

In a round-bottomed flask with a reflux water condenser, 3.0 g (0.01 mol) of compound I was dissolved at 60–70°C in 15 mL of dioxane, and 3.0 g (0.03 mol) of phenol, 4.1 mL of 32% Formalin containing 1.4 g (0.048 mol) of formaldehyde, and 0.2 mL of

<table>
<thead>
<tr>
<th>Cooligomer</th>
<th>Physicomechanical properties</th>
<th>Content of acetone-soluble low-molecular-weight substances, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bending stress causing failure, MPa</td>
<td>Specific impact strength, kJ/m$^2$</td>
</tr>
<tr>
<td>Ille</td>
<td>42.4</td>
<td>1.6</td>
</tr>
<tr>
<td>Ilb</td>
<td>49.0</td>
<td>1.6</td>
</tr>
<tr>
<td>Ile</td>
<td>47.0</td>
<td>1.7</td>
</tr>
<tr>
<td>Ild</td>
<td>41.7</td>
<td>1.9</td>
</tr>
<tr>
<td>IIe</td>
<td>36.3</td>
<td>1.2</td>
</tr>
<tr>
<td>III</td>
<td>31.5</td>
<td>1.3</td>
</tr>
<tr>
<td>IVa</td>
<td>41.0</td>
<td>1.0</td>
</tr>
<tr>
<td>IVb</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 2. Physicomechanical properties of cured cooligomers based on monophenol (I)
a 25% aqueous solution of ammonia were added to the solution obtained. The reaction mass was heated in a glycerin bath at 110–120°C for 6 h. The cooled reaction mass was precipitated into a tenfold (by volume) quantity of water. The precipitated tacky resin was removed by decanting, repeatedly washed with hot water, and dried initially in air and then in an oven at 50–60°C. Yield 70.3%, T_{soft} 90–92°C, content of hydroxymethyl groups 6.3%, content of elements, %: C 70.25, H 5.7.

**Synthesis of a resol-type phenol–formaldehyde homooligomer based on phthalide-containing monophenol (homooligomer IIg)**

In a round-bottomed flask with a reflux condenser, 4.5 g (0.015 mol) of compound I was dissolved at 60–70°C in 10 mL of dioxane, and 3.1 mL of 27% Formalin containing 0.9 g (0.03 mol) of formaldehyde and 0.1 mL of a 25% aqueous solution of ammonia were added to the solution obtained. The reaction mass was heated in a glycerin bath at 110–120°C for 10 h. The cooled reaction mass was precipitated in a tenfold (by volume) quantity of water. The precipitate was filtered out, repeatedly washed with hot water, and dried initially in air and then in an oven at 50–60°C. Yield 83.9%, T_{soft} 97–99°C, content of hydroxymethyl groups 10.3%, content of elements, %: C 74.3, H 5.2.

IR spectra were recorded on a Nicolet Magna-780 IR Fourier spectrometer. The spectra were processed using IBM PC software. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AV-400 instrument with a working frequency of 400.13 and 100.16 MHz respectively in acetone-$d_6$.

The content of hydroxymethyl groups was determined by Kebner’s method [10] by the condensation of resols with excess phenol in a strongly acidic medium with subsequent titration of the excess phenol by the iodometric method.

To determine the physicomechanical properties by hot pressing, standard specimens were obtained for tests in the form of pellets measuring 10 x 15 x 4 mm. Pressing conditions: temperature 180°C, pressing time 1 h, pressure 10 MPa. The physicomechanical characteristics of the cured polymers were measured on a Dinstat instrument using standard procedures.

The percentage of acetone-soluble low-molecular-weight substances was determined by extraction in a Soxhlet apparatus over a 3 h period.

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**REFERENCES**