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MACROMOLECULAR COMPOUNDS AND POLYMERIC MATERIALS

Divinyl Aromatic Compounds and Di(methacrylates) Prepared by Acid-Catalyzed Transformations of Bis[4-(1-hydroxyethyl)phenyl]alkanes

B. A. Zaitsev and I. D. Shvabskaya

Institute of Macromolecular Compounds, Russian Academy of Sciences, St. Petersburg, Russia

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Abstract—The mechanism of formation of divinyl aromatic monomers including *p,p*'-divinyldiphenylmethane and 1,2-*p,p*'-divinyldiphenylethane and of their dimerization via terminal vinyl groups was studied. The factors affecting the structure, composition, and properties of thermosetting resins of a new class, Rolivsans, containing methacrylates of secondary aromatic alcohols (diols) and divinyl aromatic compounds with methylene bridges between benzene rings were examined.

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Divinylbenzenes and dimethacrylates of diols are common monomers and cross-linking agents widely used for preparing ion-exchange resins, sorbents, polymeric compounds, and binders for reinforced plastics and coatings [1–3]. Thermosetting resins containing diphenyl ethers and biphenyls with terminal vinyl and methacrylate groups (Rolivsans) have been developed [4–10]. They form heat-resistant thickly cross-linked polymers which are widely used in electrical engineering and electronics as insulating materials intended for operation in aggressive media [11–13].

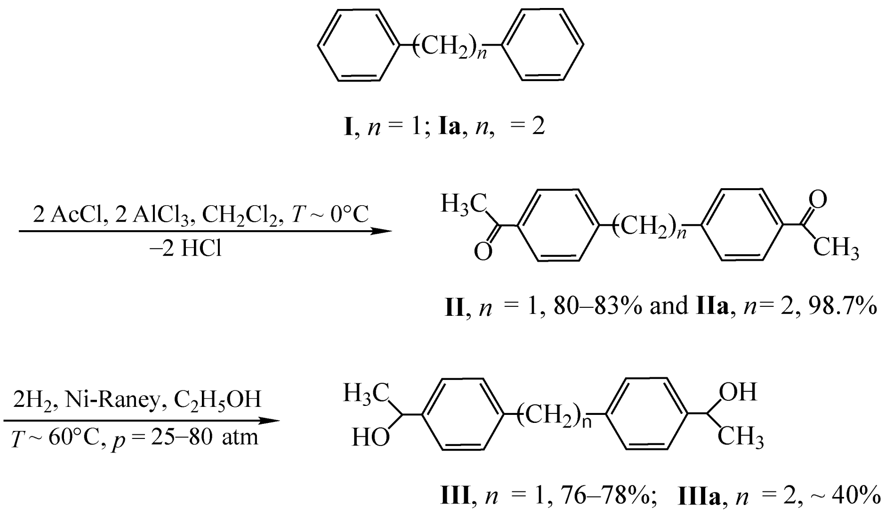
The raw materials for preparing new polyfunctional compounds are diverse aromatic compounds and unsaturated carboxylic acids [4–8]. A heat-resistant insulating compound, Rolivsan MV-1, was developed and found practical use. Its synthesis is based on transformations of methacrylic acid and bis[4-(1-hydroxyethyl)phenyl] ether (BHPE), catalyzed by strong acids, with diphenyl ether (diphenyl oxide) used as the starting compound [4–7, 13, 14].

The use of toxic and volatile divinylbenzenes (55–80% mixture of isomers and ethylvinylbenzenes) can be reduced if more accessible procedures for preparing divinyl aromatic compounds and Rolivsan-type formulations, involving the use of less toxic compounds, will be developed. This will allow enhancement of the heat resistance and physicomechanical properties of the polymeric materials and improvement of the sanitary and hygienic conditions of their production.

The goal of this study was to examine in detail the synthesis conditions, structure, and properties of divinyl aromatic compounds with methylene bridges between benzene rings and of monomer–oligomer formulations and resins based on them. Diphenylalkanes and their fluoro derivatives have low dielectric permittivity [15, 16], and diphenylmethane groups are incorporated in the structure of a number of heat-resistant polymers [17, 18]. An important problem is the development of dielectrics for interlayer insulation with a low dielectric constant, capable to enhance the integration of microcircuits [19]. Therefore, heat-resistant network polymers exhibiting the required characteristic and prepared by curing of unsaturated monomers and oligomers containing diphenylalkane groups (in the form of films, compounds, adhesives, and coatings) may be of interest for micro- and nanoelectronics.

The preparation methods and molecular design of Rolivsans [4–8] governed the choice of appropriate disecondary aromatic diols (DADs), namely, of bis[4-(1-hydroxyethyl)phenyl]methane and 1,2-bis[4-

(1-hydroxyethyl)phenyl]ethane as key precursors. They were prepared by a two-step method. Bis(4-acetylphenyl)methane (4,4'-diacetyldiphenylmethane) **II** [4, 20, 21] and 1,2-bis(4-acetylphenyl)ethane (4,4'-diacetyldiphenylethane, 4,4'-diacetylbibenzyl) **IIa** were synthesized in high yield by Friedel–Crafts acetylation of diphenylmethane **I** and diphenylethane Ia, respectively [20, 21]. The products were subjected to catalytic hydrogenation on Raney nickel to obtain bis[4-(1-hydroxyethyl)phenyl]methane **III** and 1,2-bis[4-(1-hydroxyethyl)phenyl]ethane **IIIa** [20, 21]:

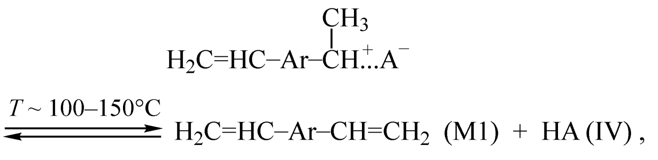


I, $n = 1$; **Ia**, n, $= 2$

II, $n = 1$, 80–83% and **IIa**, $n = 2$, 98.7%

III, $n = 1$, 76–78%; **IIIa**, $n = 2$, ~ 40%

Previously [4, 10, 22–24] we studied acid-catalyzed transformations of DADs, e.g., of BHPE and 4,4'-di(1-hydroxyethyl)biphenyl. We found that the process involves the following consecutive-parallel reactions: (a) polycondensation of DAD to form oligoether (OE), (b) dehydration of DAD and OE to form p,p'-divinyl aromatic compounds M1, and (c) oligomerization of M1 via a sequence of acid-catalyzed reactions (similar to styrene dimerization) of terminal CH_2=CH–Ar groups (polyaddition mechanism with proton transfer) [10, 22–24]. We expected that acid-catalyzed transformations of diols **III** and **IIIa** would occur similarly. Indeed, by reversed-phase high-performance liquid chromatography (HPLC), IR spectroscopy, and elemental and chemical analysis we showed that transformations of diols **III** and **IIIa** yield mixtures consisting of 4,4'-divinyldiphenylalkane M1, its unsaturated dimer, trimer, tetramer, and oligomers of higher molecular weight and follow Scheme I. The product composition strongly depends on the synthesis conditions. In addition to our previous data concerning acid-catalyzed transformations of disecondary diols derived from diphenyl oxide (BHPE) [10, 22–24] and biphenyl [4, 8], it can be noted that, with diols **III** and **IIIa** also, the high-temperature interval (100–150°C) determined by the boiling points of toluene and *o*-xylene (and their azeotropic mixtures with the released water), in combination with the relatively low concentration of the catalyst, *p*-toluenesulfonic acid monohydrate **IV**, appeared to be optimal for preparing monomers M1 in high yields (Table 1). The choice of elevated temperatures for performing this cationic process is not occasional. High temperatures are unfavorable for the dimerization of divinyl aromatic compounds, considered below. At a high temperature, the equilibrium process of the formation and subsequent deprotonation of the styrene-like carbocation in the initial step (initiation) of cationic polymerization appeared to be strongly shifted toward the initial monomer M1. This implies immediate regeneration of the catalyst HA (IV), caused by the proton transfer to the counterion:



$$H_2C{=}HC{-}Ar{-}\overset{\displaystyle CH_3}{\overset{|}{C}}\overset{+}{H}\ldots A^{-} \xrightleftharpoons{T \sim 100–150°C} H_2C{=}HC{-}Ar{-}CH{=}CH_2\ (M1) + HA\,(IV),$$

Therefore, divinyl aromatic monomer M1 formed by high-temperature transformations of DAD in a nonpolar medium in the presence of **IV** can undergo dimerization by the cationic mechanism only to a low extent (Table 1).

Experiments show that further elevation of the reaction temperature (above 140–150°C) is not appropriate because of initiation of side reactions of aralkylation of M1 with the nonpolar aromatic solvent [23, 25]. The side reaction of three-dimensional radical polymerization (cross-linking) of M1 under these conditions also becomes possible, despite the presence of the inhibitor. If the process is performed in the presence of oxygen (air) and sulfonic acids, it can yield saturated (cyclic) and oxidized products.

Thus, heating of diols **III** and **IIIa** in a nonpolar solvent with a high boiling point (*o*-xylene, $T_b > 144°C$) in the presence of small amounts (1–5 mM) of catalyst **IV**, with the removal of the released water by azeotropic distillation, gives (according to size-exclusion liquid chromatography and reversed-phase HPLC) monomers M1 in almost quantitative yield (Table 1). Pure monomers M1 can be readily isolated from the product by sublimation or recrystallization from ethanol.

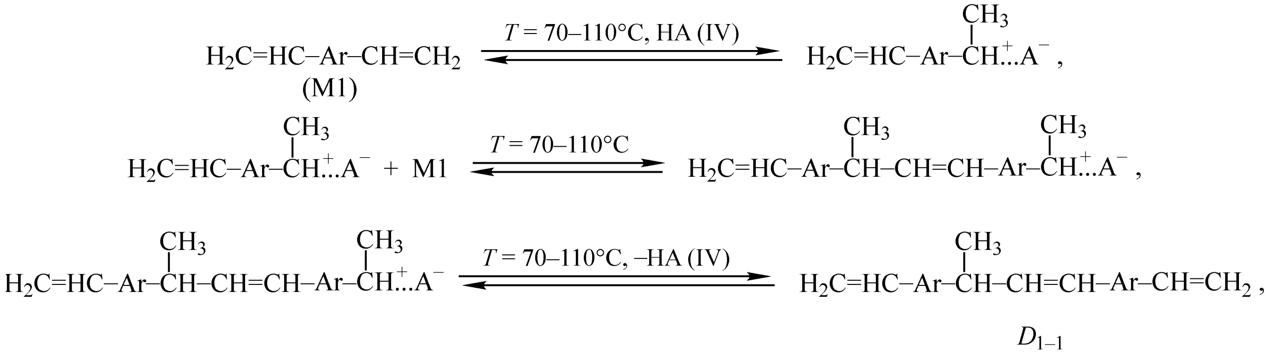
The IR spectra of 4,4'-divinyldiphenylalkanes contain absorption bands of unsaturated, aromatic, and methylene groups at 3080 (CH stretching vibrations in $=CH_2$); 3015 (CH stretching vibrations in =CH); 2975, 2910, and 2845 (CH stretching vibrations in $–CH_2–$); 1630 (–C=C–); 1600 (Ar); 1495 (Ar); 1465–1420 (CH_2 bending vibrations [26]); 990 and 905 cm^{-1} (H–C= out-of-plane bending vibrations) [27].

The suggested procedure for the synthesis of vinyl and divinyl aromatic compounds is simple and reliable. It is performed under relatively mild conditions and is characterized by high yields of monomers M1. This fact distinguishes it from the well-known alternative procedures described, e.g., in [28], in which high-temperature (at 150–300°C and above) dehydration of arylmethylcarbinols in the presence of such typical catalysts as $KHSO_4$, Al_2O_3, and P_2O_5 is performed with vacuum distillation of the vinyl monomer to avoid its polymerization. In addition, a decrease in the process temperature (from 100–150 to 0°C and below) and an increase in the concentration of the acid catalyst can lead to the typical cationic polymerization (common temperature interval 0 ± 30°C) of the vinyl monomer (e.g., styrene) [29, 30], and in the case of divinyl aromatic monomer M1 or oligomer, to its three-dimensional cationic polymerization. To exclude the formation of the cross-linked polymer, it is necessary to find such conditions for dimerization (or oligomerization) of M1 at which the step of the cationic polymerization initiation should either be immediately completed by the chain transfer to the counterion (A) or be restricted to the addition of only one monomeric unit M1 with the subsequent termination, i.e., with the catalyst regeneration. With this mechanism of chain propagation restriction, only a linear (unsaturated) dimer with terminal CH_2=CH groups can be formed. Terminal vinyl groups of the dimer of M1 (D_{1-1}) and monomer M1 (in contrast to styrene forming an inactive unsaturated dimer [29, 30]) are capable of further dimerization, with an increase in the molecular weight of the oligomer [4, 10, 22–24].

We found that, in contrast to the synthesis of divinyl aromatic monomers M1, the optimal conditions for the formation of linear unsaturated dimers D_{1-1} are as follows: temperature interval 50–100°C, increased (by a factor of 5–10) concentration of the acid catalyst, and longer (2–7 h) synthesis time. We found that the composition, molecular-weight distribution of the components, and properties of the unsaturated product (Table 2) can be conveniently controlled by varying the conditions: temperature (70–90°C), concentration of catalyst **IV** (35 ± 20 mM), and time of recurrent reactions of dimerization via terminal CH_2=CH groups (2–7 h). Thus, our results show that, in cationic polymerization of M1 in a nonpolar medium at 70–90°C, the chain propagation reactions appear to be practically suppressed owing to proton elimination (i.e., chain termination) already in the initiation step or after the very first elementary event of the monomer addition. This leads to the formation of linear unsaturated oligomers by the mechanism of successive dimerization of M1 via terminal vinyl groups (Scheme I).

It should be noted that the preparation of linear unsaturated oligomers of increased molecular weight (2500–3500 g mol^{-1}) is a stepwise and long process. As seen from Table 2, the formation of monomers M1 (by transformations of the corresponding DADs) and their subsequent oligomerization can be performed as separate processes or combined in a one-pot two-step process. Its first step involves the formation of monomer M1 and water (removed by azeotropic distillation) and is due to the above-indicated polyreactions which can be presented in total as dehydration of diol **III** or **IIIa**. The completion of the first step can be judged by cessation of the water release and by the composition of the monomer–oligomer mixture, determined by size-exclusion liquid chromatography, reversed-phase HPLC, vapor osmometry, IR spectroscopy, and refractometry. To perform the second step, oligomerization of M1, it is

Scheme I.



Ar = p,p'-$C_6H_4(CH_2)_n$–C_6H_4, HA is catalyst **IV**, and D_{1-1} is the dimer of monomer M1.

necessary to decrease the reaction temperature (e.g., to ~70°C), to introduce an additional portion of the catalyst, and to continue heating, taking samples for determining (monitoring) the composition and molecular weight. Both monomers M1 and low-melting divinyl aromatic monomer–oligomer mixtures (Tables 1, 2) are readily compounded with the known thermosetting resins and are of interest as heat- and chemically resistant cross-linking agents, and also for the preparation of films, coatings, and compounds.

In the presence of methacrylic acid **V**, the above-considered mechanism of DAD transformations becomes substantially more complex. As seen from the HPLC (Fig. 1) and IR data, the refluxing of diols **III** and **IIIa** with methacrylic acid **V** in an aromatic solvent in the presence of catalyst **IV**, with the removal of the released water, yields unsaturated monomer–oligomer mixtures of the Rolivsan type, whose composition strongly depends on the synthesis conditions (Table 3). Our experiments confirm the mechanism of the formation of such systems, studied previously for the reactions of BHPE with methacrylic acid **V** as example [4, 5–7, 10, 22–24]. This mechanism, which can now be applied to transformations of bis[4-(1-hydroxyethyl)phenyl]alkanes also, involves consecutive-parallel reactions (Scheme II): (a) polycondensation of diols **III** and **IIIa**; (b) esterification of diols **III** and **IIIa** and of the polyethers formed; (c) acidolysis and dehydration of the polyethers with the formation of bis(4-vinylphenyl)alkanes M1, alcohol monomethacrylate M2, and diol dimethacrylate M3; (d) cleavage of methacrylates; and (e) successive dimerization of M1 and M2 via terminal CH_2=CH groups.

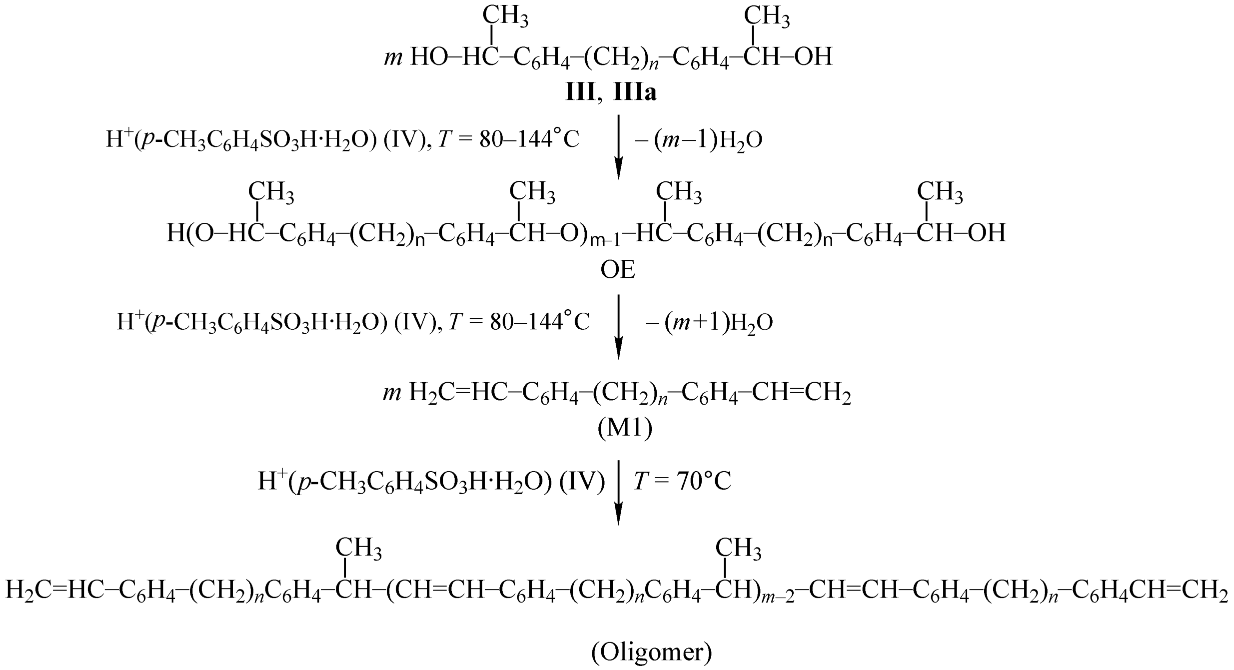
In the IR spectra of Rolivsans, there are bands of methyl and methylene groups at 2960, 2925, 2870, and 2850 cm^{-1} and of methine groups at 2900 cm^{-1}, and also strong bands of stretching vibrations of the carbonyl group, characteristic of methacrylates, at 1710 cm^{-1} [4, 31]. The band of out-of-plane H–C= bending vibrations in –CH=CH- (*trans*) groups at 965 cm^{-1} grows in intensity, as the concentration of these groups increases in the course of successive reactions of dimerization (cationic polyaddition) of vinyl aromatic compounds. At a relatively low concentration (3.3–7.3 mM) of catalyst **IV**, mixtures with a high content of monomers M1 and M2 (70–80%) are formed (Fig. 1). Only a considerable increase in the concentration of catalyst **IV** to 16–27 mM, in combination with heating of the reaction mixture at 70°C for an additional time, leads to appreciable changes in the product composition (Fig. 1).

EXPERIMENTAL

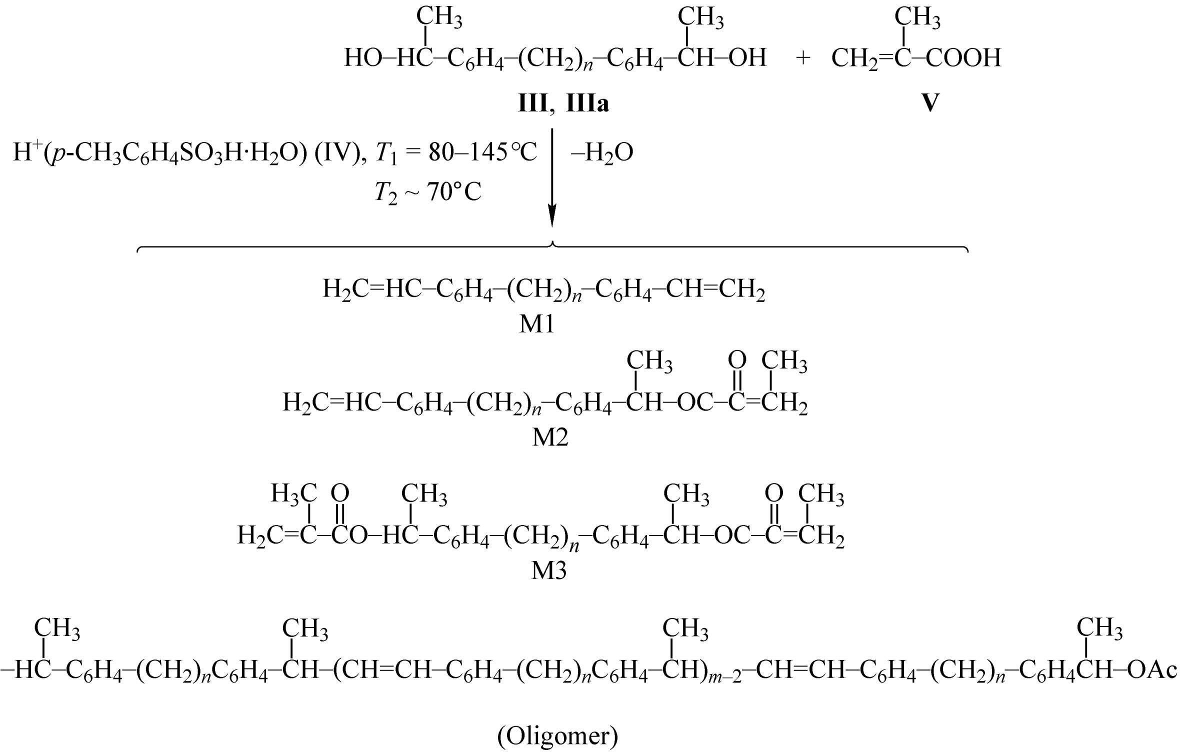
The IR spectra were recorded with a Specord 75-IR device from thin films and $CHCl_3$ solutions. The monomer–oligomer composition of the products was determined by reversed-phase chromatography (Separon Si C18 sorbent, eluent toluene, elution rate 0.1 ml min^{-1}, refractometric detector). The number-average molecular weight of the products (oligomers) was calculated from the content of terminal vinyl groups, determined from the intensity of the H–C= absorption band at 900 cm^{-1} in the IR spectra, and also from the results of chromatographic analysis. Aromatic diketones **II** and **IIa** were synthesized by Friedel–Crafts acetylation of diphenylmethane **I** and diphenylethane **Ia** [32, 33] by the following modified procedure (Schemes I, II).

Bis(4-acetylphenyl)methane II. To a mixture of 80 ml of CH_2Cl_2 and 80.10 g (0.600 mol) of anhydrous $AlCl_3$, cooled to approximately 0°C, we added with

Scheme II.



Scheme III.



stirring 41.45 g (0.528 mol) of acetyl chloride over a period of 15–20 min. To the resulting acetylating complex, we gradually added over a period of 1 h with vigorous stirring at 0 ± 5°C a solution of 40.80 g of diphenylmethane **I** in 28 ml of CH_2Cl_2. The released HCl was absorbed with an alkali solution. Then the reaction mixture was stirred at ~0°C for an additional 2.5 h, and diketone **II** was isolated by decomposing the complex of

the acetylated product with $AlCl_3$ using a mixture of 900 g of finely crushed ice, 2 l of distilled water, and 1.2 l of 20% HCl, washing the diketone with water, and drying at 60–70°C. After the recrystallization of the crude product from ethanol, we obtained 50.80 g (83% of theoretical yield) of bis(4-acetylphenyl)methane **II**, T_m 93–94°C (published data [33]: 92–93°C).

1,2-Bis(4-acetylphenyl)ethane IIa. To a mixture of 170 ml of CH_2Cl_2 and 133.4 g (1.00 mol) of anhydrous $AlCl_3$, we gradually added over a period of 15–20 min with stirring at ~0°C 85.20 g (1.080 mol) of acetyl chloride. To the acetylating complex, we similarly added over a period of 70 min with vigorous stirring at 0 ± 5°C a solution of 72.80 g (0.400 mol) of 1,2-diphenylethane Ia (T_m 51–52°C) in 30 ml of CH_2Cl_2. The reaction mixture was stirred at 35–40°C for an additional 2 h, and the acetylated product was isolated as described above. Yield of diketone **IIa** 105.0 g (98.7% of theoretical yield), T_m 163–166°C. For additional purification, 50.0 g of the product was dissolved in 1350 ml of ethanol at ~75°C. After the recrystallization, we obtained 45.50 g of 1,2-bis(4-acetylphenyl)ethane **IIa**, T_m 164–166°C. Found, %: C 81.10, H 6.80. $C_{18}H_{18}O_2$. Calculated, %: C 81.20, H 6.77.

Disecondary aromatic diols **III** and **IIIa** were prepared by catalytic hydrogenation of the diketones on Raney nickel [34] using the modified procedure.

Bis[4-(1-hydroxyethyl)phenyl]methane III. A mixture of 500 ml of ethanol, 12.0 g of Raney nickel catalyst, and 110.0 g (0.436 mol) of diketone **II** was heated in a pressure vessel at 60–80°C with vigorous stirring at the initial hydrogen pressure of 77 atm, which decreased to ~25 atm in the course of 40–50 min owing to hydrogen uptake. The catalyst was separated by centrifugation (at 4000 rpm) and filtration, and the ethanol was removed at reduced pressure. The residue (about 121.7 g) was recrystallized from a 1 : 2 (by volume) mixture of hexane or petroleum ether with toluene to obtain 87.5 g (78.3% of theoretical yield) of diol **III**, T_m 83–87.5 and 84.5–86.5°C (after repeated recrystallization) (published data [28]: 85–86°C). Found, %: C 80.2, H 7.96. $C_{17}H_{20}O_2$. Calculated, %: C 79.7, H 7.86. Content of OH groups Found, %: 13.1. Calculated, %: 13.3.

1,2-Bis[4-(1-hydroxyethyl)phenyl]ethane IIIa. A mixture of 250 ml of ethanol, 10.0 g of Raney nickel catalyst, and 47.0 g (0.1767 mol) of diketone **IIa** was heated in a pressure vessel at 62–88°C with vigorous stirring at the initial hydrogen pressure of 77 atm, which decreased to ~42 atm in the course of 1.5 h owing to hydrogen uptake. The catalyst and ethanol were removed as described above, and the residue (white powder) was dried at ~70°C in a vacuum oven, T_m 128–131°C. After the recrystallization of 19.4 g of the crude product from toluene, we obtained 17.4 g of diol **IIIa**, T_m 131–134 and 133–136°C (after repeated recrystallization).

Unsaturated mixtures (product nos. 1–10, Table 1) were synthesized by DAD dehydration as follows. To prepare product no. 1, a mixture of 10.02 g ($M = 256.35$, 0.0391 mol, 0.3004 M) of diol **III**, T_m 84.5–86.5°C, 0.0100 g of 4-*tert*-butylcatechol, 0.125 g (5.050 mM) of catalyst **IV**, and 120 ml of *o*-xylene was heated at the boiling point (~144°C) with stirring for 2.0 h, with the removal of the released water by azeotropic distillation. The resulting mixture was cooled, washed in succession with distilled water, 5% $NaHCO_3$ solution, and again water, and dried over $CaCl_2$, after which it was passed through a 2–3-cm bed of Al_2O_3, and the solvent was distilled off at reduced pressure (1–2 mm Hg) at 36–38°C in the presence of 0.0017 g (0.02 wt %) of 4-*tert*-butylcatechol. Yield of the unsaturated product 7.59 g (88% of theoretical yield.). After sublimation of 0.50 g of the product at 130°C for 40–60 min in a vacuum (~0.5 mm Hg), we obtained approximately 0.28 g of bis(4-vinylphenyl)methane, purity >99%, T_m 36–38°C (published data [28, 33]: 32°C). By a similar procedure, we prepared 7.9 g (91.9% of theoretical yield) of product no. 2 and 19.57 g of product no. 3 from 10 and 25 g of diol **III**, respectively.

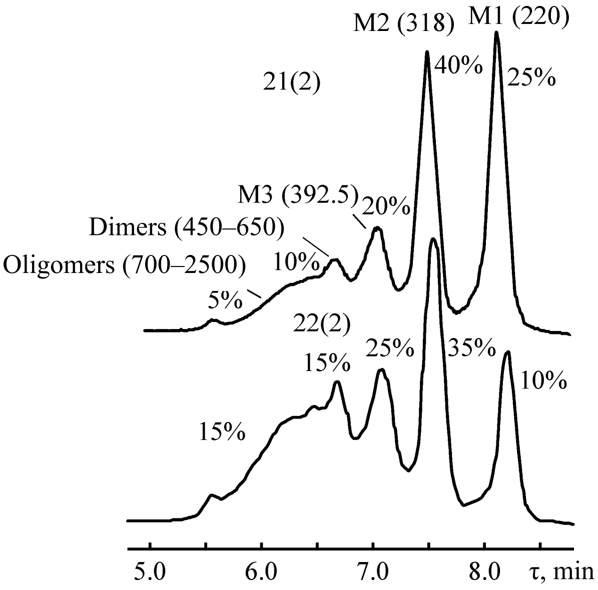
To obtain product no. 4, a mixture of 16.2004 g (0.05992 mol, 0.2774 M) of 1,2-bis[4-(1-hydroxyethyl) phenyl]ethane (diol **IIIa**, T_m 131–134°C), 0.0162 g of 4-*tert*-butylcatechol, 0.2024 g (4.93 mM) of catalyst **IV**, and 200 ml of *o*-xylene was heated at the boiling point with stirring for 1 h 50 min. In the process, more than 1.7 ml of water was removed by azeotropic distillation. After that, the first sample was taken (80 ml of the reaction mixture). The temperature was decreased to 70°C, 0.5100 g of catalyst **IV** was added (the total concentration of **IV** reached 24.75 mM), and the mixture was additionally stirred for 1 h. After working up the reaction mixture samples as described above, we obtained 5.1 g of product no. 4 (1) and 5.6 g of the remainder [product no. 4 (2)]. After sublimation of 2.0 g of product no. 4 (1) at 120–140°C for 20 min in a vacuum (~3 mm Hg), we obtained 1.45 g of 1,2-bis(4-vinylphenyl)ethane, T_m 91–93°C. Product no. 5 (14.2 g) was prepared from

16.2 g of diol **IIIa** similarly to product no. 4 (1).

To prepare product no. 6, a mixture of 8.1004 g (0.02996 mol, 0.2873 M) of diol **IIIa**, 0.0081 g of 4-*tert*-butylcatechol, 0.1013 g (4.92 mM) of catalyst **IV,** and 100 ml of *o*-xylene was heated at the boiling point with stirring for 2 h. In the process, more than 0.8 ml of water was removed by azeotropic distillation. After that, sample no. 6 (1) was taken (40 ml of the reaction mixture). The temperature was decreased to 70°C, and 0.2551 g of catalyst **IV** was added. The total concentration of **IV** reached 24.58 mM. The mixture was additionally stirred for 2, 3, and 3.5 h, and sample nos. 6 (2), 6 (3), and 6 (4), respectively, were taken and worked up as described above.

Product no. 7 (3.8 g) was prepared from 5.0 g of 4,4'-di(1-hydroxyethyl)biphenyl similarly to product no. 1. After the sublimation of 0.500 g of the product at the residual pressure of 1–2 mm Hg and bath temperature of 160°C for 7–10 min, 0.33 g of pure 4,4'-divinylbiphenyl M1 was obtained, T_m 152–154°C (published data [33]: 152.5–153°C). Product nos. 8, 9, and 10, enriched in bis(4-vinylphenyl) ether, were prepared from bis[4-(1-hydroxyethyl)phenyl] ether similarly to product no. 1. After the recrystallization from ethanol, the purity of bis(4-vinylphenyl) ether (4,4’-divinyldiphenyl oxide) M1 was 98 (T_m 85–87°C) and 99% (T_m 87–89°C).

Unsaturated oligomer nos. 11–15 (Table 2) were synthesized as follows. To prepare oligomer no. 11, a mixture of 10.00 g (0.03901 mol, 0.3000 M) of diol **III** (T_m 84.5–86.5°C), 0.010 g of 4-*tert*-butylcatechol, 0.0502 g (2.03 mM) of catalyst **IV**, and 120 ml of *o*-xylene was heated at the boiling point with stirring for 2 h. In the process, approximately 0.95 ml of water was removed by azeotropic distillation. After working up the reaction mixture, we obtained 8.92 g of the product containing (according to the IR data) appreciable amounts of the incompletely cleaved polyether, initial product of polycondensation of diol **III** with –$(CH_3)CH$–O–$CH(CH_3)$– groups, which is due to low concentration of catalyst **IV**. Therefore, to bring the cleavage (dehydration) of the polyether and oligomerization of monomer M1 to completion, a mixture of 8.34 g of the product formed in this step, 0.0083 g of 4-*tert*-butylcatechol, 0.2080 g (10.07 mM) of catalyst **IV**, and 100 ml of toluene was repeatedly heated at the boiling point with stirring for 40 min. In the process, 0.40 ml of water was released and removed. Then the temperature was decreased to 70°C, 0.2082 g of catalyst **IV** (total concentration of **IV** 19.23 mM) and 5 ml of toluene were added, and the mixture was heated at 70°C with stirring for an additional 3 h. After working up the mixture, we obtained 7.5 g of the product. To prepare oligomer no. 12, a mixture of 25.00 g (0.0975 mol, 0.2991 M) of diol **III** (T_m 88–91°C), 0.0255 g of 4-*tert*-butylcatechol, 1.0031 g (16.176 mM) of catalyst **IV**, and 300 ml of toluene was heated at the boiling point with stirring for 40 min. In the process, more than 3.2 ml of water was removed by azeotropic distillation. Then the temperature was decreased to 70°C, and 1.5000 g of catalyst **IV** (total concentration of **IV** 40.176 mM) and 25 ml of toluene were added. After 1 h 40 min, sample no. 12 (1) was taken, and the remainder was heated for an additional 5 h. After working up sample no. 12 (1) and remainder no. 12 (2), we obtained 3.57 g of oligomer no. 12 (1) and 15.24 g of oligomer no. 12 (2). Oligomer nos. 13–15 were prepared from diol **III** similarly to oligomer no. 12.



Reversed-phase HPLC patterns of monomer–oligomer sample nos. 21 (2) and 22 (2) (Table 3). (τ) Component retention time. The molecular weights of the components are indicated in parentheses.

Unsaturated Rolivsan product nos. 16–22 (Table 3) were synthesized as follows. To prepare product no. 16, a mixture of 10.0020 g (0.0413 mol, 0.3591 M) of diol **III**, 0.0205 g of 4-*tert*-butylcatechol, 100 ml of toluene, 5.0344 g (0.05848 mol, 0.5085 M) of freshly distilled methacrylic acid **V**, and 0.073 g (3.34 mM) of catalyst **IV** was refluxed at 102–111°C with stirring for 2.5 h. After working up the reaction mixture, we obtained 9.5 g of the product. Product nos. 17–22 were prepared similarly.

Table 1. Influence of the synthesis conditions[a] on the composition and properties of unsaturated mixtures enriched in divinyl aromatic monomers (M1)

Product no.	–Ar– in disecondary diol 4,4'-HO(H_3C)HCArCH(CH_3)OH	c_{diol}, M	$c_{\text{cat IV}}$, mM	Time, min	Component content, wt %				M_n	T_m, °C	n_D^t
		M			M1	dimer	trimer	oligomer			
1	–C_6H_4–CH_2–C_6H_4– (III)	0.300	5.050	120	79	16.5	4	0.5	280 ± 10	30–33	1.603^{40}
2	–C_6H_4–CH_2–C_6H_4– (III)	0.300	4.130	120	87	10.5	2	0.5	260 ± 10	31–34	1.604^{40}
3	–C_6H_4–CH_2–C_6H_4– (III)	0.300	5.071	105	–	–	–	–	300 ± 25	29–35	$1.616^{28.5}$
4 (1)	–C_6H_4–CH_2–CH_2–C_6H_4– (IIIa)	0.2774	4.930	110	–	–	–	–	250 ± 20	82–87	–
4 (2)	–C_6H_4–CH_2–CH_2–C_6H_4– (IIIa)	0.2774	24.750	60	–	–	–	–	250 ± 20	82–90	–
5	–C_6H_4–CH_2–CH_2–C_6H_4– (IIIa)	0.2774	4.930	110	–	–	–	–	250 ± 20	85–89	–
6 (1)	–C_6H_4–CH_2–CH_2–C_6H_4– (IIIa)	0.2873	4.920	120	–	–	–	–	230 ± 10	–	–
7	–C_6H_4–C_6H_4– [8]	0.2577	4.870	50	75	–	–	–	–	135–145	–
8	–C_6H_4–O–C_6H_4– [4, 20–24]	0.2977	1.011	80	95	5	0.5	–	–	85–87	–
9[b]	–C_6H_4–O–C_6H_4– [4, 20–24]	0.2981	1.981	140	90	~9	~0.5	~0.5	–	84–86	–
10	–C_6H_4–O–C_6H_4– [20–24]	0.9977	1.977	180	80	~18	1.5	~0.5	–	82–86	–

[a] c_{diol} and $c_{\text{cat IV}}$ denote the concentrations of the diol and catalyst **IV**; heating in *o*-xylene at boiling point (~144°C); M_n is the number-average molecular weight; n^t_D is the refractive index determined at indicated temperature *t*, °C.

[b] Refluxing in toluene (~110°C).

Table 2. Influence of the synthesis conditions[a] on the composition and properties of the unsaturated oligomers

Oligomer no.	Concentration of diol **III**, M	$c_{1\ \mathrm{cat\ IV}}$, mM	T_1, °C	τ_1, h	Solvent	$c_{2\ \mathrm{cat\ IV}}$, mM	τ_2, h	Solvent	M_n	T_m, °C	n_D^t
6 (2)	0.2873	4.920	144	2	*o*-Xylene	24.58	2	*o*-Xylene	1700 ± 200	–	–
6 (3)	0.2873	4.920	144	2	"	24.58	3	"	2200 ± 300	–	–
6 (4)	0.2873	4.920	144	2	"	24.58	3.5	"	2700 ± 500	–	–
11	0.3000	2.03 (10.07)	144 –	2 0.7	*o*-Xylene Toluene	– 19.23	– 3.0	– Toluene	– 750 ± 100	– 65–75	– –
12 (1)	0.2991	16.176	110	0.7	Toluene	40.176	1.7	"	800 ± 200	–	–
12 (2)	0.2991	16.176	110	0.7	"	40.176	5	"	1200 ± 200	69–76	1.6185^{84}
13 (1)	0.2991	16.176	110	0.7	"	37.390	3	"	700 ± 200	38–46	1.6158^{79}
13 (2)	0.2991	16.176	110	0.7	"	37.390	7	"	1000 ± 200	58–63	1.6140^{79}
14 (1)	0.2429	19.640	110	1	"	36.320	5	"	2300 ± 500	–	–
14 (2)	0.2429	19.640	110	1	"	36.320	7	"	3500 ± 500	135–170	–
15	0.2429	19.640	110	1	"	36.320	5.75	"	2500 ± 500	100–140	–

Notes: $c_{1\ \mathrm{cat\ IV}}$ and $c_{2\ \mathrm{cat\ IV}}$ are the concentrations of catalyst IV, and T_1, τ_1, $T_2 = 70$°C, and τ_2 are the temperatures and times for the first and second synthesis steps, respectively.

Table 3. Influence of the synthesis conditions[a] on the composition and properties of Rolivsans containing compounds with diphenylalkane groups

Product no.	$c_{\text{diol III}}$, M	c_V, M	$c_{\text{cat IV}}$, M	T, °C	τ, h	Component content, wt %				n_D^{20}
						M1	M2	M3	oligomer	
16	0.3591	0.5085	3.340	110	2.5	25	58	6	11	1.5748
17 (1)	0.3591	0.5085	7.320	110	3.75	–	–	–	–	–
17 (2)	0.3591	0.5085	7.320	70	1.0	20	51	17	12	1.5728
18 (1) 14	0.3383	0.5072	13.730	110	2.7	–	–	–	–	–
18 (2) 14	0.3383	0.5072	13.730	70	1.0	7	62	25	6	1.6010
19 (1) 15	0.3360	0.5853	13.65	110	0.5	–	–	–	–	1.5750
19 (2) 15	0.3360	0.5853	13.65	110	1.0	–	–	–	–	1.5965
20 (1) 16	0.3363	0.5853	11.37	110	0.7	–	–	–	–	–
20 (2) 16	0.3363	0.5853	27.131	70	2.7	–	–	–	–	1.5823
21 (1) 17	0.3386	0.5076	9.186	110	1.8	–	–	–	–	–
21 (2) 17	0.3386	0.5076	13.736	110	3.8	25	42	20	13	1.5808
22 (1) 18	0.3378	0.5063	6.868	110	1.7	–	–	–	–	–
22 (2) 18	0.3378	0.5063	16.089	70	4.0	10	38	27	25	1.5750

[a] Solvent toluene.

CONCLUSIONS

(1) Dehydration of disecondary aromatic diols, e.g., of bis[4-(1-hydroxyethyl)phenyl]alkanes, performed by refluxing them at 100–150°C in a nonpolar aromatic solvent in the presence of 1–5 mM of *p*-toluenesulfonic acid monohydrate, gives *p,p*'-divinyl aromatic compounds, e.g., bis(4-vinylphenyl)methane and 1,2-bis(4-vinylphenyl)ethane, in quantitative yield.

(2) Heating of divinyl aromatic monomers M1, e.g., of bis(4-vinylphenyl)methane and 1,2-bis(4-vinylphenyl) ethane, for 2–7 h at 70–110°C in a nonpolar aromatic solvent at a concentration of catalyst **IV** of 35 ± 20 mM gives linear unsaturated oligomers in high yields.

(3) Acid-catalyzed reactions of bis[4-(1-hydroxyethyl) phenyl]alkanes with methacrylic acid yield products consisting of (di)vinyl aromatic compounds and (di) methacrylates. Their structure, composition, and properties can be controlled by varying the reaction temperature (70–144°C) and time, and also the concentration (3.3–27 mM) of the catalylst, *p*-toluenesulfonic acid monohydrate.

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