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MACROMOLECULAR CHEMISTRY AND POLYMERIC MATERIALS

Synthesis, Structure, Composition, and Properties of Rolivsans

B. A. Zaitsev, G. I. Khramova, and T. S. Tsygankova

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

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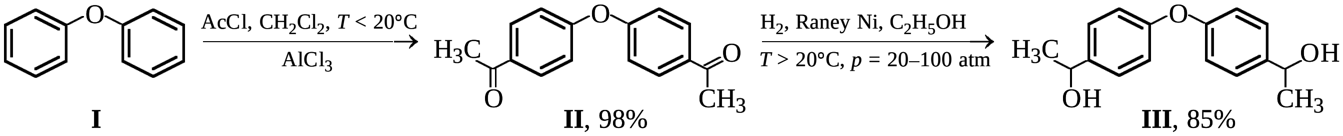
Abstract—Novel thermosetting resins Rolivsans were prepared, and their structure, composition, and properties were studied. The structural parameters of Rolivsans as influenced by the synthesis conditions were determined.

Novel thermosetting liquid (solvent-free) resins named Rolivsans are used for preparing polymeric and composite materials with enhanced resistance to heat and to the most aggressive agents [1–12]. They are used in various branches of engineering. Rolivsans have been prepared by acid-catalyzed reactions of bis[4-(1-hydroxyethyl)phenyl] ether with methacrylic acid [13–15].

The goals of this study were to analyze in detail the synthesis conditions, elucidate the composition and structure of Rolivsans, and reveal correlations between their structural characteristics and properties. The starting compound in the synthesis is diphenyl ether **I**, which is quantitatively converted to di(4-acetylphenyl) ether **II** by the Friedel–Crafts acylation. Compound **II** is subsequently hydrogenated in the presence of Raney nickel to obtain bis[4-(1-hydroxyethyl)phenyl] ether **III**, which is then refluxed with methacrylic acid **IV** in an aromatic solvent in the presence of an acid catalyst (e.g., *p*-toluenesulfonic acid) and a polymerization inhibitor (e.g., hydroquinone):



I **II**, 98% **III**, 85%

$$\xrightarrow{CH_2{=}C(CH_3)CO_2H\ (\mathbf{IV}),\ H^+,\ T = 70\text{–}145°C} \text{Rolivsans.}$$

(M1 + M2 + M3 + OL + AO), 95%

where M1–M3 are monomers, OL is an oligomer, and AO denotes antioxidants (products of alkylation of phenolic compounds with monomers M1 and M2 and with oligomer OL).

Comprehensive studies have shown that a one-pot process resembling the synthesis of oligoether acrylates and performed in the course of one or several hours at 70–110°C involves the following successive-parallel reactions: polycondensation of diol **III** [15, 16]; esterification with methacrylic acid of this diol and oligoethers containing terminal hydroxy groups and formed by polycondensation (formation of monomeric and oligomeric methacrylates [13–15]); dehydration of diol **III** and oligoethers [15, 17, 18]; cleavage of (di)methacrylates to (di)vinyl-substituted aromatic compound and methacrylic acid [13–15, 19, 20]; stepwise (co)polymerization of (di)vinyl-substituted aromatic compounds by the polyaddition mechanism with proton transfer (oligomerization) [13–15, 18, 21–23]; and alkylation of dihydric phenols (e.g., hydroquinone) with unsaturated aromatic compounds [24].

Each of these reactions was studied separately with model compounds and Rolivsan components; also, separate stages of the synthesis of Rolivsan as a system of monomers and oligomers were examined. The composition and structure of Rolivsans were studied by exclusion liquid chromatography (ELC) (Figs. 1, 2), IR and ^1H NMR spectroscopy, elemental analysis, and analysis for functional groups (ester and bromine numbers, ozonolysis). The IR and ^1H NMR

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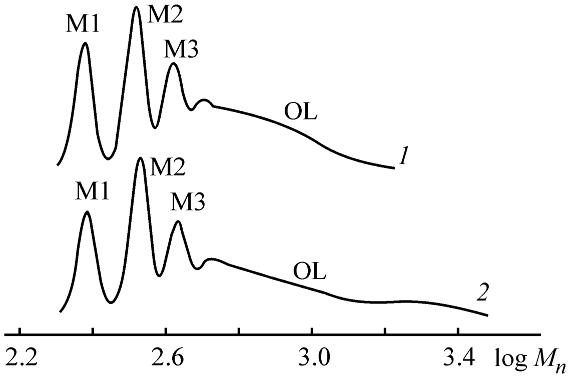


Fig. 1. Gel chromatograms of sample K (Table 2), obtained at 20°C with (*1*) one column and (*2*) six series-connected columns. Eluent tetrahydrofuran. ($\overline{M}_n$) Number-average molecular weight; the same for Fig. 3.

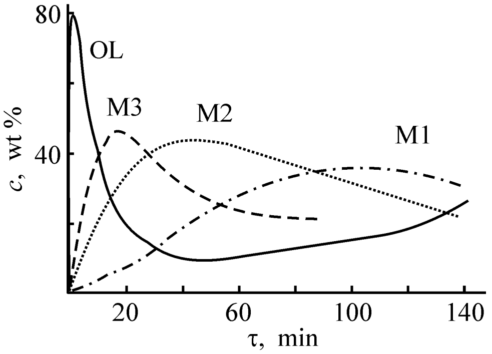


Fig. 2. Composition of Rolivsan vs. synthesis time τ (benzene, 13.5 mM sulfo acid **V**, 80°C). (*c*) Content of components.

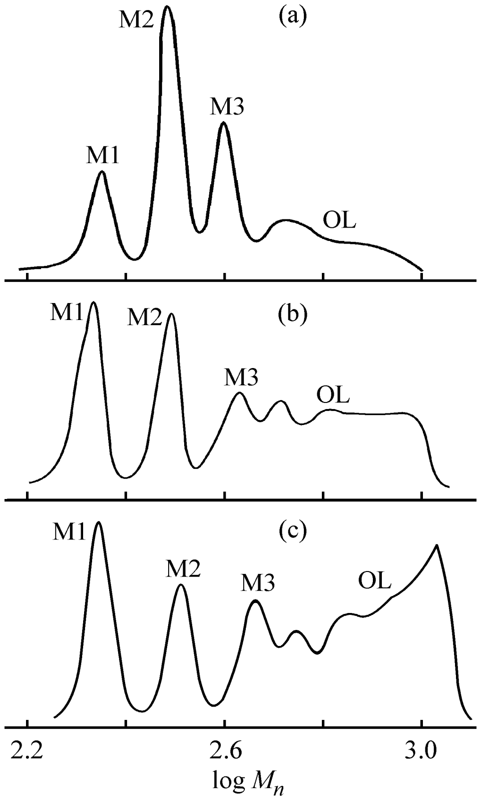


Fig. 3. Gel chromatograms of Rolivsans prepared in benzene at the ratio diol **III** : acid **IV** = 1 : 2.5. Initial concentration of sulfo acid **V** 13.5 mM. Samples were taken (a) 45, (b) 90, and (c) 120 min after the beginning of the synthesis.

spectra of model compounds and separate Rolivsan components M1, M2, M3, and OL have been discussed previously [15, 22–25]. Naturally, the spectra of Rolivsan as a system of monomers and oligomers contain a much greater number of absorption bands associated with various functional groups than the spectra of the components taken separately.

A typical IR spectrum of Rolivsan contains absorption bands of unsaturated and aromatic groups at 3080, 3060, 3030, 2975, 1630, 1600, 1500, 985, 965, 940, and 905 cm^{-1}, and also bands of methyl and methylene groups at 2960, 2925, 2870, and 2850 cm^{-1} and methine groups at 2900 cm^{-1}. The IR spectrum also contains strong absorption bands related to carbonyl groups in methacrylates (1715 cm^{-1}) and to aromatic ether groups (1240 cm^{-1}), and to other absorption bands (1170, 1100, 1060 cm^{-1}, etc.) assignable to stretching vibrations of ester and ether groups.

The ^{1}H NMR spectrum of Rolivsan contains signals typical of such related compounds as styrene, its unsaturated dimer *trans*-1,3-diphenyl-1-butene [24], and methacrylates. Protons of the substituted phenylene group give an *AA*'*BB*' pattern centered at δ = 7.25 ppm. Protons of the unsaturated groups appear as a set of signals (ppm) at δ = 6.7–5.2, namely, at 6.66 (CH= in CH_2=CH), 6.21 and 5.75 [CH_2= in CH_2=C(CH_3)], doublets at 5.63 (5.60 and 5.66; CH_2= in CH_2=CH) abd 5.23 (5.20 and 5.26; CH_2= in CH_2=CH), and a doublet of doublets at 6.45. The signal at 6.21 ppm also belongs to the *trans*-CH=CH protons, since similar signals of the internal double bond (δ 6.19, 6.24 ppm) are observed in the ^{1}H NMR spectrum of the related compound, unsaturated styrene dimer [PhCH=CHCH(CH_3)Ph]. The *tert*-H proton in the >CHPh group appears as a broad ill-resolved multiplet at 3.67 ppm and a multiplet at 4.32 ppm (PhCHPh). The methyl and methylene groups give signals at 2.01 and 1.45 (MeC=CH_2), 1.61 and 1.64 (MeCHAr), and 2.59 ppm (CH_2Ar). The ^{1}H NMR spectrum contains no signals at 2.3 ppm, which are characteristic of toluene methyl protons. This fact suggests that, under the conditions of Rolivsan synthesis, acid-catalyzed aralkylation of the solvent (toluene) with M1, M2, and OL does not occur.

Table 1. Influence of the synthesis time τ on the composition and properties of Rolivsans

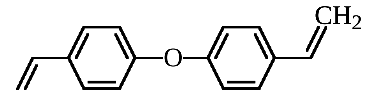
τ, min	Resin composition, wt %					Unsaturation, mol >C=C</100 g product	Ester number, mg KOH/g product	n_D (T, °C)
	M1	M2	M3	OL	AO			
45	14	37	30	18	1	0.559	190	1.577 (20)
90	20	24	21	34	1	0.592	160	1.597 (40)
120	16	20	15	48	1	0.610	135	1.609 (40)

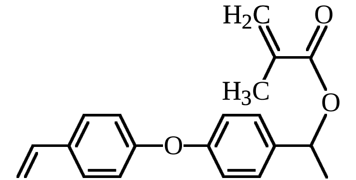
Table 2. Characteristics of Rolivsan M1

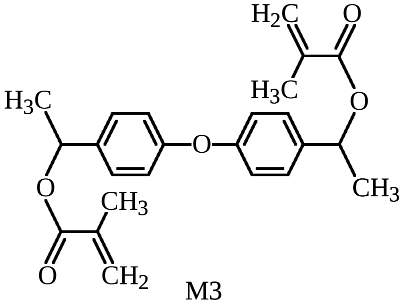
Grade	Component content, wt %					Unsaturation, mol >C=C</100 g product	$\overline{M}_n$	n_D^{20}	η^{25}, cP	d^{20}, g cm^{-3}
	M1	M2	M3	OL	Ar(OH)$_n$					
K	14	27	25	32	2	0.58	420	1.590	1620	1.09
S	12	22	18	46	2	0.55	480	1.600	3500	1.10

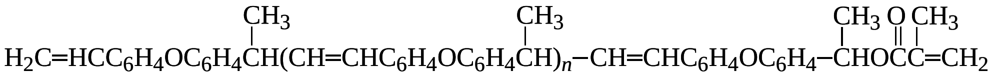
Figures 2 and 3 show how the composition and molecular-weight distribution (MWD, found by ELC) depend on the synthesis conditions. Initially, refluxing in benzene or toluene results in fast polycondensation of diol **III**, which results in the formation of an oligoether with terminal hydroxy groups [15, 16]. The competing reactions are esterification of the oligoether of diol **III** with methacrylic acid [15, 16] and dehydration; these reactions yield oligomeric methacrylates (OL), monomer M1 [15, 18], and water removed by azeotropic distillation. Acidolysis of the oligoether and oligomeric methacrylates yields monomeric methacrylates M2 and M3 [13–15].

It is known that the components of Rolivsans are M1, M2, M3, OL, and AO. The composition and properties of Rolivsans can be varied widely by ensuring a greater extent of oligomerization of M1 and M2 in the presence of *p*-toluenesulfonic acid **V** by the step (dimerization) addition mechanism with proton transfer to the monomer and formation of, first, dimers, then trimers [13–15, 21–23], etc. Methacrylates M2 and M3 are gradually cleaved to form acid **IV** and, respectively, monomers M1 and M2 (Table 1):


M1


M2


M3



$$H_2C{=}HCC_6H_4OC_6H_4\overset{CH_3}{CH}(CH{=}CHC_6H_4OC_6H_4\overset{CH_3}{CH})_n{-}CH{=}CHC_6H_4OC_6H_4{-}\overset{CH_3}{CH}O\overset{O}{C}\overset{CH_3}{C}{=}CH_2$$

OL

$$M3 \xrightarrow{80–110°C,\ [H^+]_V} M2 + \mathbf{IV} \xrightarrow{80–110°C,\ [H^+]_V} M1 + 2\mathbf{IV} \xrightarrow{80–110°C,\ [H^+]_V} m_2 - [m_1]_n - m_2$$

$$\xrightarrow[-\mathbf{IV}]{80–110°C,\ [H^+]_V} \underset{OL}{H{-}[m_1]_{n-1}CH{=}CH{-}X{-}CH{=}CH_2}$$

m_1 = CH=CH–X–CH(CH_3), m_2 = $H_2C{=}CMeCO_2MeHC{-}X{-}CHMe$, X = $C_6H_4OC_6H_4$.

Tables 1 and 2 show that, at relatively low conversions, when the concentrations of methacrylates M2 and M3 are relatively high and the content of oligomers (mainly dimers) is low, the refractive index n_D^{20} and viscosity η^{25} of the resin are comparatively low (1.56 and 450 cP, respectively).

Oligomerization leads to lower content of M2 and M3 and higher content of linear unsaturated oligomers with increased molecular weights (mainly dimers to pentamers); as a result, the refractive index and viscosity grow substantially (to n_D^{20} = 1.60–1.62 and η^{25} = 2500–4000 cP).

Thus, the composition and properties of Rolivsans, molecular-weight distribution of oligomeric components, and distribution of functional groups can be varied within prescribed limits by changing the synthesis conditions.

EXPERIMENTAL

The IR spectra were measured on a Specord 75-IR spectrophotometer (thin films), and the ^{1}H NMR spectra, on a JEOL C-60 HL spectrometer (60 MHz, $CDCl_3$, internal reference TMS). The ELC analysis of Rolivsans and their components was performed using a Waters gel-permeation chromatograph with columns packed with Ultrastyrogel (500 Å) at 20°C; eluent THF, $CHCl_3$, or toluene. The number-average molecular weight $\overline{M}_n$ was determined with a Hitachi–Perkin–Elmer 115 vapor osmometer. The content of unsaturated bonds was found by ozonation (ADS-3 ozonizer, 0°C, solvent CCl_4) and by the bromide–bromate method (determination of the bromine number, followed by recalculation to the iodine number). The ester number was found by dissolving the resin sample in dioxane purified by distillation from KOH and Na, adding 0.1 N solution of KOH in ethanol–dioxane, refluxing for 7 h (the reflux condenser was equipped with a tube packed with soda lime), and titrating with 0.1 N HCl.

CONCLUSIONS

(1) The mechanism of formation of Rolivsans, novel thermosetting resins whose curing yields heat-resistant network polymers, was elucidated.

(2) The composition and structure of Rolivsans were determined by IR and ^{1}H NMR spectroscopy, vapor osmometry, elemental and functional analysis, and exclusion liquid chromatography.

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