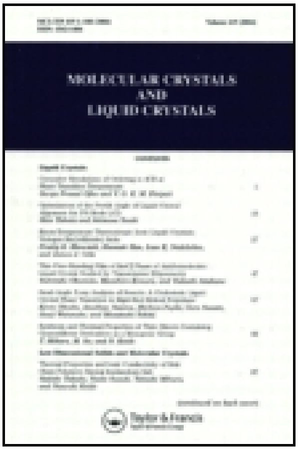

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New Acrylic Esters, Derivatives of Some Diglycidyl Ethers as Main Components of Lacquer Compositions

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UV-curable compositions consist of the new diacrylates and dimethacrylates of diglycidyl ethers of Bisphenols: P(1,1-bis-(4-hydroxyphenyl)-cyclopentane), C(1,1-bis-(4-hydroxyphenyl)-cyclohexane), H(1,1-bis-(4-hydroxyphenyl)-cycloheptane) reactive diluents and with photoinitiator Irgacure 651.

Keywords: UV-cured epoxyacrylates; protective coatings

INTRODUCTION

The use of high intensity radiation, and especially the ultraviolet (UV) to the process of polymerization and hardening of various kinds of monomers and oligomers provoked during the last twenty years a quantitative increase and range of application in many important technological branch of industry. Oligomers containing the highly reactive acrylic groups at both of their ends are mainly used in the industry. The materials hardened with the help of the UV radiation are used for example as protective coatings for metals, plastic materials, optical fibres, magnetic apparatus, as the materials in electrotechnics and in lithography1,2,3. Our interest is connected with the application of diacrylates as the main components of the UV hardened compositions for the protective coatings of optical fibres. The protective coatings should protect the optical fibres against mechanical damage, effect of atmospheric factors and at the same time meet optical requirements.

In practice, depending on the application three kinds of protective coatings are used: inner soft, outer hard and in some cases only one of intermediate properties. Materials used for these kinds of covers have to possess suitable but differentiated physicochemical properties before and after curing.

The materials used for this aim should possess low surface viscosity to secure adhesion with the cable walls,

- high Young's modulus giving resistance to external forces, causing optical fibre deformation,
- resistance to such factors as water, acids and bases as well as high glassing temperature.

There were worked out the ways of the above mentioned acrylates preparation and there were prepared the lacquer compositions which one of the very good this purpose there proved to be acrylic or methacrylic esters of the diglycidyl ether bisphenols.

In this report the results of research concerning synthesis of diacrylate and dimethylacrylate of diglicydyl ethers of bisphenols: P(1,1-bis-(4-hydroxyphenyl)-cyclopentane), C(1,1- bis-(4-hydroxyphenyl)-cyclohexane), H(1,1- bis-(4-hydroxyphenyl)-cycloheptane) and also lacquer compositions made of these components are given. Glycidyl ethers were prepared in the reaction of bisphenols with epichlorohydrin in the two phase liquid/liquid system including the organic and aqueous phases. Esterification of the above diglycidyl ether was carried out with the use of acrylic and methacrylic acid in the presence of TEBAC (triethylbenzylammonium chloride) as a catalyst at the higher temperature.

EXPERIMENTAL

Synthesis of bisphenols

In 500 ml of three-necked round-bottom flask equipped with mechanical stirrer and thermometer, 0.5 mol of cyclic ketones, 2 moles of phenol, 125 g of concentrated hydrochloric acid, and 2.5 g of (-mercaptopropionic acid was stirred at 25-50 (C for 30 hours. The lower aqueous layer was decanted from the upper semisolid organic layer. The organic layer was washed twice with 500 ml of hot water (70-80 (C) to remove the excess phenol.

The crude of bisphenols yield about 80 %. They were purified by crystallisation from isopropanol, methanol or tetrachloroethane.

Synthesis of epoxy resins

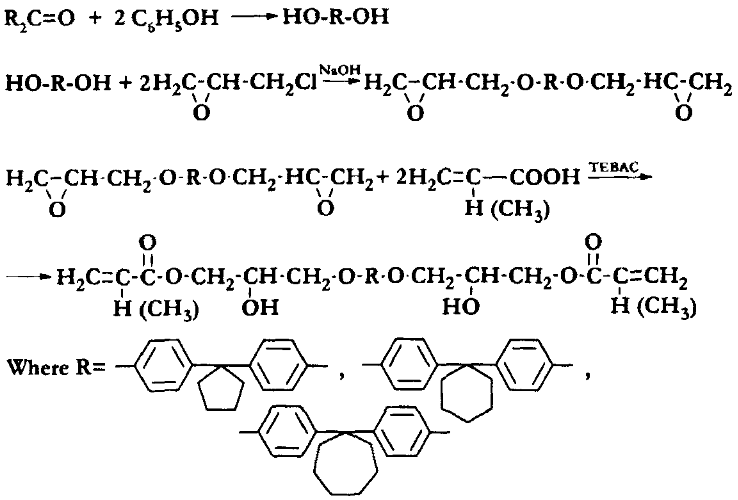
Into a four-necked flask of 750 ml volume, equipped with a mechanical stirrer, reflux condenser, thermometer and dropper 0.3 mol bisphenol, 277.5 g (3 moles) of epichlorohydrin and 126 g (2.1 moles) of isopropanol were placed. The mixture was heated in the water bath to 70 (C. The first portion 15 ml of 15 % solution of sodium hydroxide as an addition catalyst was dropped in very carefully. After 10 min. the second portion 195 ml of 15 % solution of sodium hydroxide was added for 5 min. and stirred for another 10 min.

The organic layer was separated in a distributor, the solvent and excess of epichlorohydrin were distilled under reduced pressure (1.6 kPa).The remains of epichlorohydrin were distilled azeotropically under reduced pressure adding 2x40 ml of toluene into resin and filtered. Yield about 90 %.

Synthesis of acrylic or methacrylic esters

Reactions between epoxy resins and acrylic acid were carried out at 90-110 (C. The mixture of epoxy resin 0.5 mol, acrylic acid or methacrylic acid (1 mol), hydroquinone 0.02 g was heated to reaction temperature and TEBAC 2 g was added to the mixture with stirring. After a certain time, the sample (0.1-2 g) of the reaction mixture was removed from the flask and titrated with a 0.1 N alcoholic KOH solution in acethone (50 ml). The final acid number was less than 3, indicating virtual complete reaction.

A general scheme of preparation of "epoxyacrylate" can be presented by the reaction:



$$R_2C{=}O + 2\,C_6H_5OH \longrightarrow HO\text{-}R\text{-}OH$$

$$HO\text{-}R\text{-}OH + 2H_2\underset{\setminus\,/\atop O}{C{-}CH}\text{-}CH_2Cl \xrightarrow{NaOH} H_2\underset{\setminus\,/\atop O}{C{-}CH}\text{-}CH_2\text{-}O\text{-}R\text{-}O\text{-}CH_2\text{-}\underset{\setminus\,/\atop O}{HC{-}CH_2}$$

$$H_2\underset{\setminus\,/\atop O}{C{-}CH}\text{-}CH_2\text{-}O\text{-}R\text{-}O\text{-}CH_2\text{-}\underset{\setminus\,/\atop O}{HC{-}CH_2} + 2H_2C{=}\underset{H\,(CH_3)}{C}{-}COOH \xrightarrow{TEBAC}$$

$$\longrightarrow H_2C{=}\underset{H\,(CH_3)}{C}\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2\text{-}\underset{OH}{CH}\text{-}CH_2\text{-}O\text{-}R\text{-}O\text{-}CH_2\text{-}\underset{HO}{CH}\text{-}CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}\underset{H\,(CH_3)}{C}{=}CH_2$$

Where R=

UV-curable compositions consist of the above mentioned acrylates, with reactive diluents and also with photopolymerization initiator 2,2-dimethoxy-2-phenyl-acetophenone (Irgacure 651) taken in amount of 2 percentage. Butyl acrylate, 2-ethylhexyl acrylate and styrene were used as diluents.

RESULTS AND DISCUSSION

For the obtained compositions were determined: density, viscosity, index of refraction before curing, glass temperature, Young's modulus, hardness, tensile strength, elongation and also thermal resistance after curing. It occured that the properties of the investigated compositions are dependent on their structure and content. It was stated that the maximum resistance properties of the cured compositions as well as Young's modulus were obtained with the content of about 10-30 percentage active diluent (Table I, II, III). All the obtained compositions meet requirements of the materials for the hard protective coatings of optical fibres.

Applicability of the obtained compositions for optical fibre coatings was tested in technological process of optical fibre preparation in the Optical Fibre Laboratory, Maria Curie-Skłodowska University, Lublin.

TABLE I Optimal properties of lacquer composition

Kind of composition	Properties		
	Density (g/cm^3)	Viscosity at 20°C (mPa s)	Refraction index n_D^{20}
A-DGDP+AB(10:1)	1,1638	33538	1,5425
A-DGDP+S(10:3)	1,1171	1415	1,5550
A-DGDC+AB(10:3)	1,1043	2070	1,5273
A-DGDC+AEH(10:3)	1,0867	12650	1,5308
A-DGDH+AB(10:2)	1,1412	20777	1,5290
A-DGDH+S(10:3)	1,1116	4564	1,5551
M-DGDP+AB(10:1)	1,1527	12200	1,5358
M-DGDC+AB(10:3)	1,1011	1485	1,5165
M-DGDC+AEH(10:3)	1,0905	5180	1,5190
M-DGDH+AB(10:2)	1,0933	5645	1,5224
M-DGDH+S(10:3)	1,0996	1345	1,5491

TABLE II Optimal properties of cured lacquer compositions

Kind of composition	Properties			
	Young's modulus (Mpa)	Breaking stress (MPa)	Relative elongat. at break, (%)	Shore's hardness D
A-DGDP+AB(10:1)	1507	60,3	4,15	81,2
A-DGDP+S(10:3)	2350	70,6	4,12	82,0
A-DGDC+AB(10:3)	1514	49,7	3,9	81,5
A-DGDC+AEH(10:3)	1278	42,4	4	81,0
A-DGDH+AB(10:2)	1801	54,8	3,5	78,0
A-DGDH+S(10:3)	1918	77,0	5,6	77,0
M-DGDP+AB(10:1)	1697	65,3	3,84	83,1
M-DGDC+AB(10:3)	1663	59,5	3,9	77,0
M-DGDC+AEH(10:3)	1579	47,1	3,2	77,0
M-DGDH+AB(10:2)	1600	61,0	3,3	80,0
M-DGDH+S(10:3)	1780	77,0	5,7	80,0

TABLE III Thermogravimetric analysis of cured lacquer compositions

Kind of composition	T_1(°C)	T_2(°C)	Mass loss in the temperature (°C)			
			5%	30%	60%	90%
A-DGDP+AB(10:1)	220	450	370	435	470	680
A-DGDP+S(10:3)	240	445	375	435	455	665
A-DGDC+AB(10:3)	200	445	340	435	460	630
A-DGDC+AEH(10:3)	180	440	320	440	465	640
A-DGDH+AB(10:2)	220	450	350	440	470	650
A-DGDH+S(10:3)	260	440	365	440	450	620
M-DGDP+AB(10:1)	200	440	335	430	450	630
M-DGDC+AB(10:3)	200	445	340	435	460	620
M-DGDC+AEH(10:3)	190	440	330	440	460	630
M-DGDH+AB(10:2)	220	440	360	430	460	620
M-DGDH+S(10:3)	260	450	365	440	455	610

Reagents

A-DGDP – 1,1-bis[4-(3-acryloyloxy-2-hydroxypropoxy)phenyl] cyclopentane

M-DGDP – 1,1-bis[4-(3-methaacryloyloxy-2-hydroxypropoxy)phenyl] cyclopentane

A-DGDC – 1,1-bis[4-(3-acryloyloxy-2-hydroxypropoxy)phenyl] cyclohexane

M-DGDC – 1,1-bis[4-(3-mathacryloyloxy-2-hydroxypropoxy)phenyl] cyclohexane

A-DGDH – 1,1-bis[4-(3-acryloyloxy-2-hydroxypropoxy)phenyl] cycloheptane

M-DGDH – 1,1-bis[4-(3-methacryloyloxy-2-hydroxypropoxy)phenyl] cycloheptane

AB – butyl acrylate

AEH – 2-ethylhexyl acrylate

S - styrene

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