

# Synthesis of Unsaturated Polyesters of Increased Solubility in Styrene

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**ABSTRACT:** The present study presents the synthesis of unsaturated polyester resins using only one glycol i.e., ethylene glycol. Polyesters of inorganic solubility in styrene were prepared. Properties of the resins in the noncrosslinked state in the process of crosslinking and after curing were

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**Key words:** isomer/isomerization; resins; polyesters; thermal properties; synthesis

## INTRODUCTION

Unsaturated polyester resins are prepared as a result of unsaturated polyesters dissolution in a crosslinking monomer. Unsaturated polyesters are obtained by polycondensation of dicarboxylic acids with glycols, whereby one of the starting components must have a double bond.<sup>1</sup> Maleic and fumaric acids are the most frequently used. Isomerization of maleate (cis) to fumarate (trans) polyesters takes place during polycondensation at about 200°C. This is a desirable phenomenon, as fumarate bonds are more reactive in copolymerization with styrene that has a favorable effect on thermal and mechanical resistance of the products. Suitably chosen mixtures of ethylene, diethylene, and propylene glycols are typical glycol components. Styrene is a crosslinking monomer in most cases.<sup>2</sup>

The number and position of double bonds is an important factor responsible for the properties of unsaturated polyesters. The most frequently obtained polyesters are those in which, besides the radicals of maleic acid, there are also radicals of other dicarboxylic acids (e.g., phthalic acid). Polyesters can be synthesized when the molar excess of acids or glycols reaches up to 20%. With the molar excess of glycols, polycondensation proceeds slowly, and the obtained resin is characterized by lower reactivity than that predicted from the number of unsaturated bonds. With the predominance of acid contents, polycondensation proceeds much more quickly, but the obtained polyester is characterized by a large acid number.

Styrene solution of acidic polyester is less stable in time and can induce package corrosion. After curing, resin is characterized by larger hardness and thermal resistance. One of the ways to increase resin stability is locking the terminal acid groups, e.g., by means of dicyclopentadiene.<sup>3</sup>

Unbranched glycols like ethylene or diethylene glycols used in the synthesis cause limited solubility in styrene of the prepared polyester. Polyesters prepared from the branched glycols like 1,2-propylene or 1,3-butylene are characterized by better solubility in styrene. The obtained solutions possess significantly smaller viscosity.<sup>3</sup>

Unsaturated polyesters used as construction materials are usually prepared from maleic, phthalic anhydrides, and 1,2-propylene glycol, with close to equimolar ratio of both acid anhydrides.<sup>4</sup>

The present study presents the synthesis of new unsaturated polyester resins for construction application. The resins were synthesized from two acid anhydrides used in nonequimolar quantitative ratios and only one glycol, i.e., ethylene glycol. Isopropyl alcohol was used to terminate polyester chains with hydrophobic groups and to decrease the number of functional groups. The suitably scheduled synthesis of polyesters allows to prepare resins of inorganic styrene content as a result of polyester chain termination with ester groups.

## EXPERIMENTAL

### Materials

- Maleic anhydride (ZA "Kędzierzyn")
- Phthalic anhydride (ZA "Kędzierzyn")
- Ethylene glycol (POCh Gliwice)

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TABLE I  
Composition of the Reaction Mixture

Raw material (g)	Resin no.					
	1	2	3	4	5	6
Maleic anhydride	182.8	130.6	168.2	142.1	153.3	153.5
Phthalic anhydride	236.6	236.6	253.3	214.7	270.5	192.3
Isopropyl alcohol	32.0	—	31.7	—	31.4	—
Acid monoester	—	84.2	—	96.6	—	108.7
Ethylene glycol	198.5	198.5	196.7	196.5	194.5	194.5
Styrene	350.0	350.0	350.0	350.0	350.0	350.0
Hydroquinone	0.1	0.1	0.1	0.1	0.1	0.1

- Isopropyl alcohol (POCh Gliwice)
- Hydroquinone (Z.Ch. "Chemiform")
- Styrene (Z.Ch. "Oświęcim")
- Xylene (POCh Gliwice)
- Luperox GZN—50% ethylmethyl ketone hydroperoxide solution in dimethyl phthalate (Elf Atochem GmbH)
- Cobalt (II) octoate—styrene solution containing 1% Co (Department of Polymer Chemistry and Technology, M.C. Skłodowska University)
- Monoester of maleate or phthalate acid (Department of Polymer Chemistry and Technology, M.C. Skłodowska University)

### Synthesis of unsaturated polyester resins

#### One-stage method

In the reactor equipped with stirrer, toppiece for separation of azeotrope, reflux condenser, and heating jacket, maleic anhydride, phthalate anhydride, and isopropyl alcohol were placed in the amounts given in Table I (resins 1, 3, and 5). For preliminary reaction of raw material, the whole amount was heated at 130–140°C for 2 h. When the addition reaction was completed, ethylene glycol and xylene were added and subjected to polycondensation. The process of polycondensation was carried out in the temperature range of 150–220°C in the solvent—xylene (in the amount 5–10% in relation to the condensed mixture) with simultaneous azeotropic removal of condensation water from the reaction medium. The course of the process was controlled obtaining <sup>1</sup>H NMR spectra and determining the acid number. The drop of acid number of the reaction mixture compared to the assumed value 30–32 mg KOH/g and content of fumaric units being over 90% were taken as the indicator of the process completion (Figs. 1 and 2). The obtained unsaturated polyesters whose structure confirmed by the chromatographic analysis of condensate (Fig. 3) were cooled to 100–120°C and dissolved in styrene stabilized with hydroquinone giving resins of the crosslinking monomer contents 35, 40, 45, and 50% (Table II).

#### Two-stage method

In the reactor, maleic anhydride, phthalate anhydride, and ethylene glycol were placed in the amounts given in Table I (resins 2, 4, and 6) and subjected to the reaction as in one-stage method. Monoester of the corresponding acid or their mixture was added to the preliminarily reacted substrates, and polycondensation was carried out as in the one-stage reaction. The obtained polyesters were dissolved in styrene stabilized with hydroquinone obtaining resins of the crosslinking monomer contents 35, 40, 45, and 50% (Table II). The composition of the reaction mixture used in this study is given in Table I.

The resins of 35% styrene contents were subjected for further studies due to processing properties of resins. The composition of synthesized unsaturated polyester resins and their properties in the non-crosslinked condition are presented in Tables I and III.

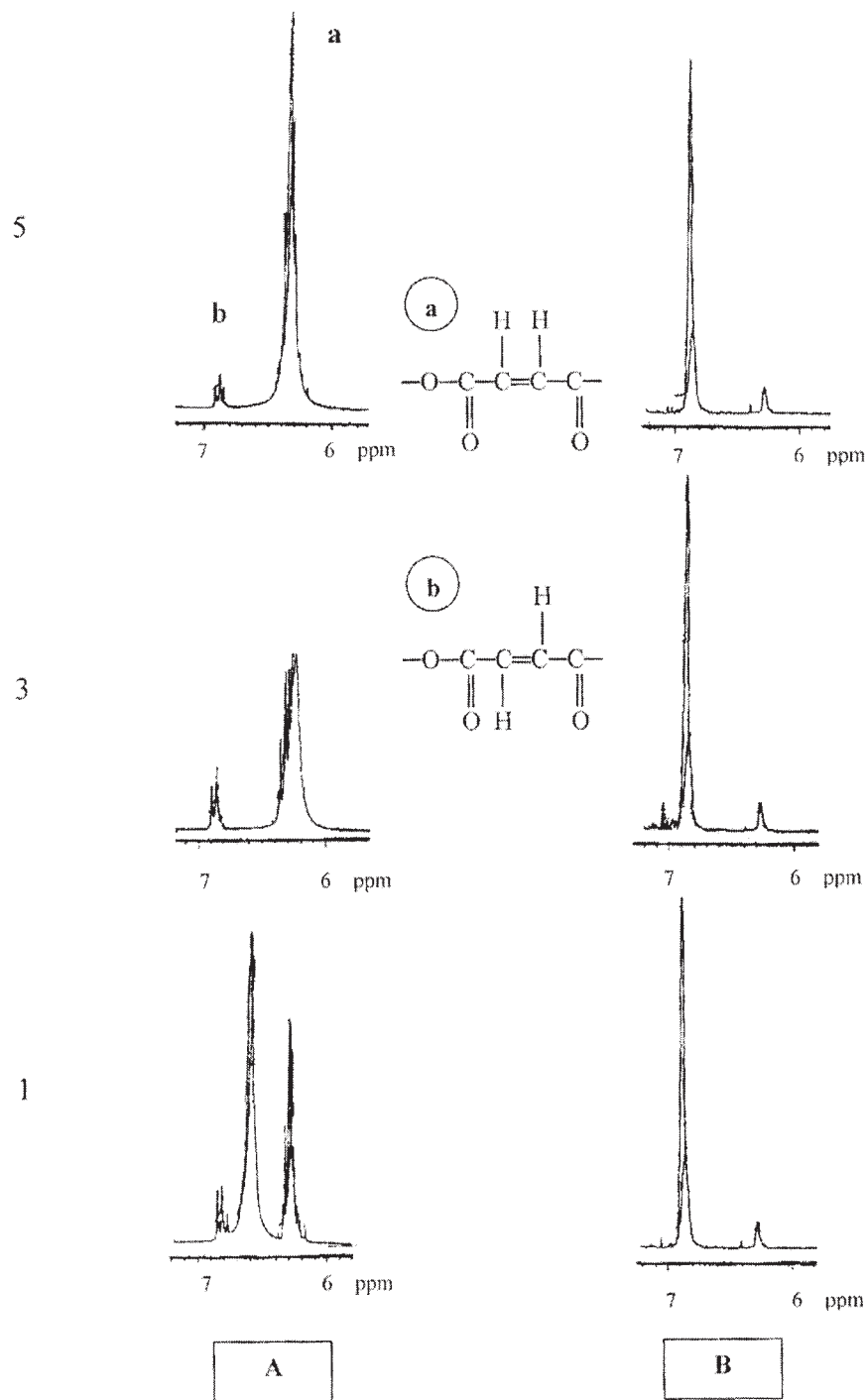
#### Resin curing

The obtained unsaturated polyester resins were cured with a typical system: initiator/accelerator consisting of two parts of ethylmethylketone hydroperoxide mass and 0.2 part of cobalt (II) octoate mass containing 1% metal. The resins were cured at 25°C and then additionally cured in two stages: first, heating at 60°C for 24 h, and then, at 120°C for 2 h.

#### Methodology

<sup>1</sup>H NMR spectra were obtained using the NMR spectrometer model 567A (Tesla, Czechoslovakia). Chemical changes were determined in reference to the standard tetramethylsilane. The samples for analysis were taken about 2 h after ethylene glycol addition (140°C), during the synthesis (at about 200–220°C), and after water condensation and xylene distillation from the syntheses.

The chromatographic analysis of azeotropically distilled condensate for the presence of isopropyl

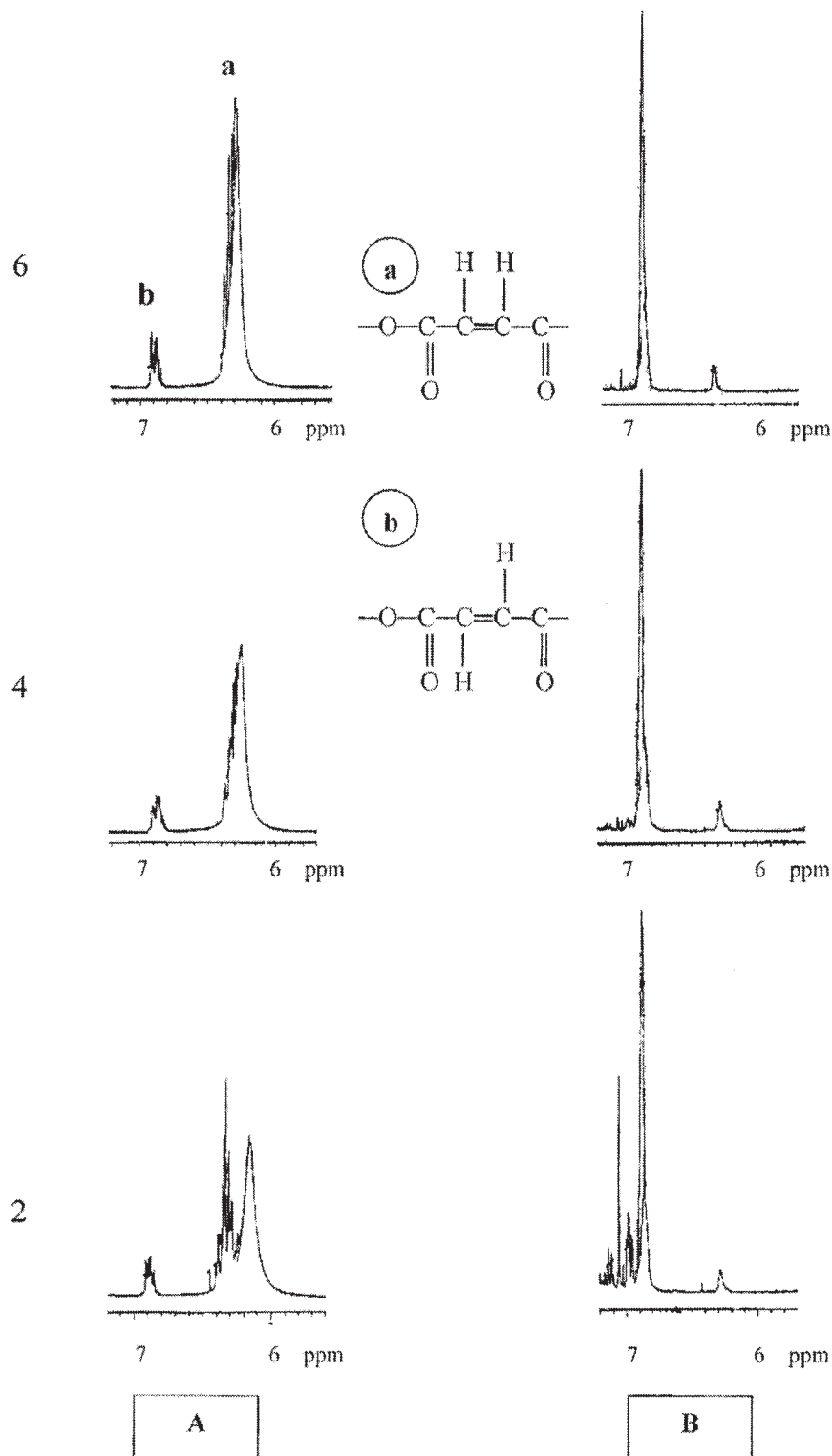


**Figure 1**  $^1\text{H}$  NMR analysis of unsaturated polyester samples taken at  $140^\circ\text{C}$  (A) and  $200^\circ\text{C}$  (B) for one-step syntheses nos. 1, 3, and 5. Maleate bonds at  $\delta = 6.4$  ppm (A), fumarate bonds at  $\delta = 6.9$  ppm (B).

alcohol was made by means of gas chromatograph DANI, GC 1000. Three samples were taken from the whole amount of distilled condensate for studies.

During examination of polyesters and resins in the uncured state and during crosslinking, the acid number according to the standard (PN-87/C-89082/11); viscosity at  $25^\circ\text{C}$  according to the standard (PN-86/C-89082/04) by means of a digital viscometer

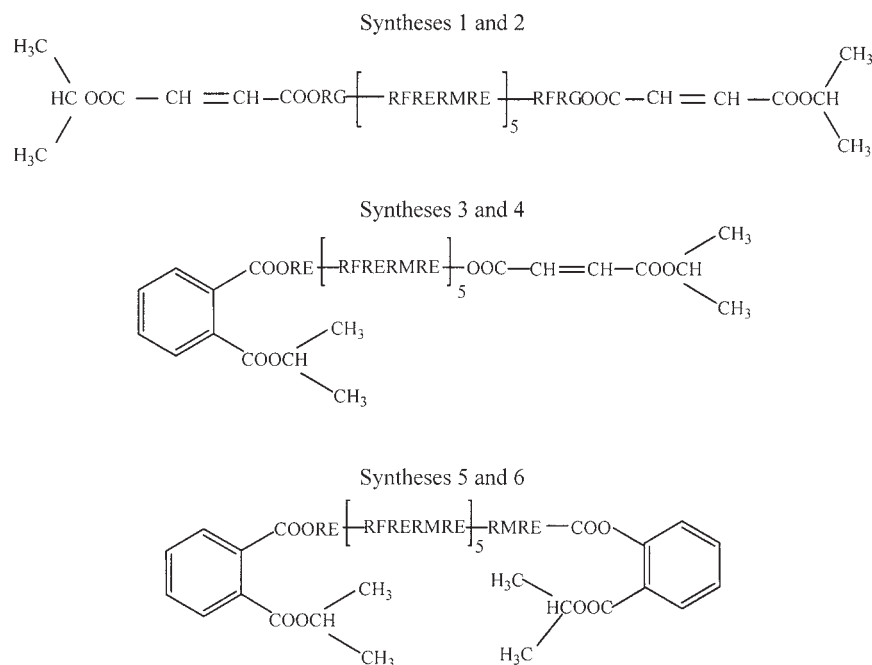
DF-III Brookfield of cone/plate type with 5 rpm with a spindle 52; density at  $25^\circ\text{C}$  according to the standard (PN-86/C-89082/03); gelation time at  $25^\circ\text{C}$  according to the standard (PN-87/C-89082/15); peak exotherm temperature at  $25^\circ\text{C}$  according to the standard (PN-86/C-89082/14); and softening temperature using the method "ring-ball" according to the standard (PN/C-04020) were determined.



**Figure 2**  $^1\text{H}$  NMR analysis of unsaturated polyester samples taken at  $140^\circ\text{C}$  (A) and  $200^\circ\text{C}$  (B) for two-step syntheses nos. 2, 4, and 6. Maleate bonds at  $\delta = 6.4$  ppm (A), fumarate bonds at  $\delta = 6.9$  ppm (B).

After crosslinking of resins, the following properties were studied: Barcol hardness; heat resistance (HDT) according to (ISO 75-1/-2) with loading 1.8 MPa and jaw spacing 64 mm; and softening temperature after

Vicat (ISO 306) under loading 10 N with the temperature increase rate  $50^\circ\text{C}/\text{h}$ . Thermal stability was examined by means of derivatograph MOM (Budapest, Hungary) in the temperature range of  $20\text{--}1000^\circ\text{C}$ ,



**Figure 3** Chemical structure of obtained unsaturated polyesters.

with the sample heating rate at 10°C/min. The glass-transition temperatures were determined by means of differential scanning calorimeter DSC 204 produced by Netzsch in two heating runs 20–200°C, with the temperature increase rate 10°C/min in nitrogen atmosphere. The T<sub>g</sub> values were read from the second heating run.

Mechanical properties, i.e., flexural strength according to the standard (PN-79/C-89027), flexural elastic

modulus according to the standard (PN-82/C-89051); tensile strength according to the standard (PN-81/C-89034), were determined using the strength machine Zwick/Roell Z010 (Zwick, Germany).

## RESULTS AND DISCUSSION

The present study presents the synthesis of new unsaturated polyester resins for construction purposes.

**TABLE II**  
Physical Properties of Resin Solutions of Different Styrene Percentage Content

Styrene (%)	Properties	Resin no.					
		1	2	3	4	5	6
35	Acid number (mg KOH/g)	20.0	20.0	21.1	19.0	19.4	19.6
	Viscosity (mPa s)	1835	1650	1400	935	1425	1260
	Density (g/cm <sup>3</sup> )	1.14	1.14	1.14	1.14	1.14	1.14
	Refractive index	1.547	1.548	1.549	1.590	1.551	1.549
40	Acid number (mg KOH/g)	18.6	18.1	20.2	16.9	18.2	17.2
	Viscosity (mPa s)	1110	970	900	590	550	850
	Density (g/cm <sup>3</sup> )	1.13	1.13	1.12	1.13	1.13	1.13
	Refractive index	1.548	1.549	1.549	1.549	1.552	1.550
45	Acid number (mg KOH/g)	17.6	17.8	18.6	14.7	16.3	16.0
	Viscosity (mPa s)	740	590	590	370	504	630
	Density (g/cm <sup>3</sup> )	1.12	1.12	1.11	1.11	1.12	1.12
	Refractive index	1.549	1.549	1.548	1.550	1.552	1.550
50	Acid number (mg KOH/g)	16.1	16.1	17.1	13.4	14.6	14.7
	Viscosity (mPa s)	575	530	400	300	470	580
	Density (g/cm <sup>3</sup> )	1.11	1.09	1.10	1.10	1.11	1.10
	Refractive index	1.550	1.549	1.548	1.550	1.553	1.550

TABLE III  
Physical Properties of the Obtained Polyesters

Properties	Polyester no.					
	1	2	3	4	5	6
Acid number of polyester (mg KOH/g)	32.4	32.6	32.7	32.5	30.0	29.3
Softening temperature by the method "ring-ball" (°C)	59	58	59	60	59	61

The resins were prepared in one- (syntheses nos. 1, 3, and 5) or two- (syntheses nos. 2, 4, and 6) stage syntheses with the use of two acid anhydrides in the nonequimolar quantitative ratio and only one glycol, i.e., ethylene glycol. It was not certain if polyesters obtained using only ethylene glycol will form solutions of larger styrene content. The properly scheduled course of polyester synthesis allows to obtain a compound of complete miscibility with styrene. As we expected, we observed decreasing of the viscosity and density with styrene content. The increase in polyester solubility in styrene was achieved due to unsaturated polyester chain termination with ester groups (Table II, Fig. 4). The presence of ester groups on the molecule terminal ends of the obtained polyesters was confirmed by gas chromatography analysis (Table IV). As follows in the case of one- or two-stage syntheses, about 74–78% of isopropyl alcohol used at the begin-

ning are built into unsaturated polyester chains. The terminal ester groups cause the resins to be more durable in time due to a smaller content of carboxylic groups.

Another advantageous phenomenon in the syntheses of polyesters from maleic anhydride is isomerization of maleate (cis) polyesters to fumarate (trans) ones, as fumaric bonds are more reactive in copolymerization with styrene. This has an advantageous effect on thermal and mechanical resistance of the products. It is assumed that during synthesis of unsaturated polyesters almost complete maleate–fumarate isomerization takes place. It depends on condensation time, medium acidity (presence of acids or carboxylic groups), catalysts (e.g., piperidine and morpholine), type of glycol, and stereochemical agents. Addition of some modifying unsaturated acids particularly aromatic (e.g., phthalic acid) ones results

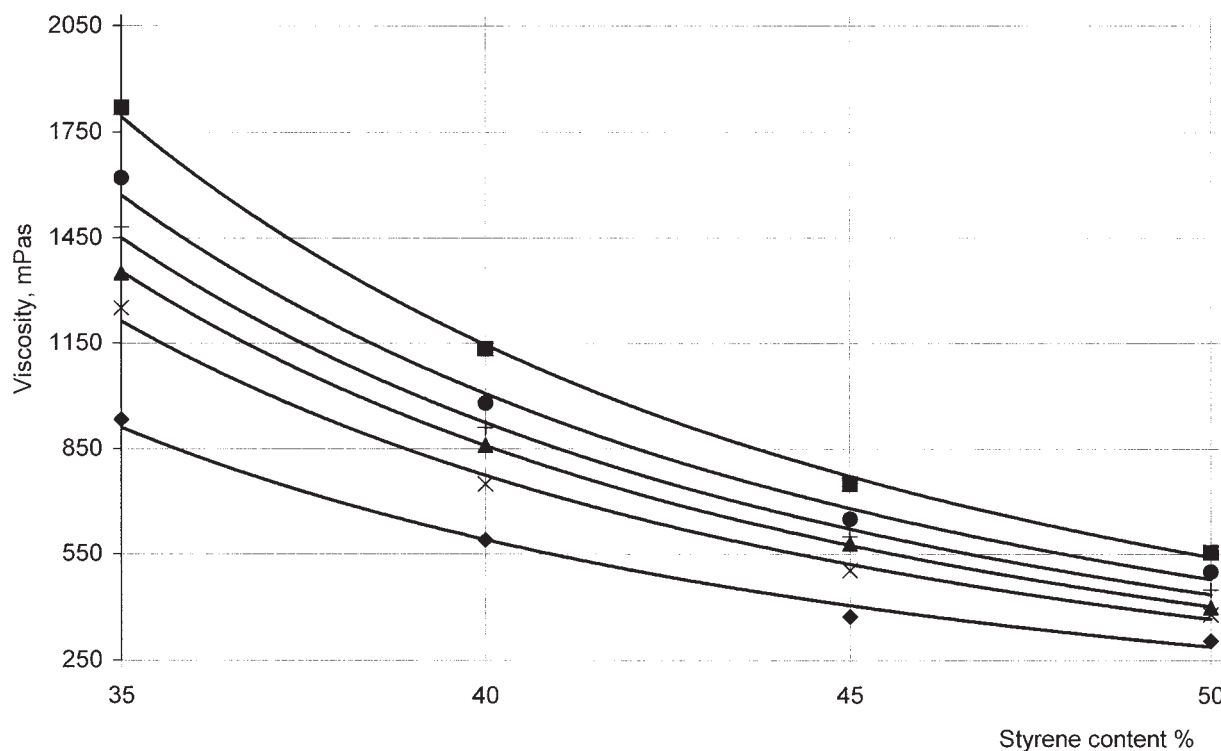


Figure 4 Dependence of unsaturated polyester resins viscosity on the percentage contents of styrene No 1 (■); No 2 (●); No 3 (+); No 4 (◆); No 5 (×); No 6 (▲).

TABLE IV  
Losses During Polyester Synthesis

Raw material (g)	Polyester no.					
	1	2	3	4	5	6
Water	84.1	84.9	82.2	82.1	84.1	83.4
Isopropyl alcohol	12.2	11.4	12.8	12.9	10.9	11.5
Ethylene glycol	3.7	3.7	5.0	5.0	5.0	5.1

in increased rate and maximum degree of isomerization.<sup>3</sup> The analysis of <sup>1</sup>H NMR spectra of the obtained unsaturated polyesters shows the presence of maleate bonds at  $\delta = 6.4$  ppm at 140°C, i.e., in the initial stage of synthesis of unsaturated polyester (addition of ethylene glycol to a suitable acid anhydride) in one- or two-stage syntheses (Figs. 1 and 2). In the second step of synthesis (azeotropic distilling off of condensation water at 200°C), disappearance of maleate bonds and appearance of fumarate bonds at  $\delta = 6.9$  ppm are observed (Figs. 1 and 2).

The factors responsible for properties of unsaturated polyesters are the number and position of double bonds. The most frequently obtained polyesters are those in which, besides the maleate acid radical, other dicarboxylic (e.g., phthalic acid) radicals are found. In this study, the syntheses proceed in such a way that the prepared polyesters differ in double-bond contents due to application of various molar amounts of maleic anhydride in relation to phthalic anhydride. The obtained unsaturated polyester resins of differentiated molar composition of maleic anhydride in relation to phthalic anhydride are characterized by different physical properties in the noncrosslinked condition (Table V), and thermal and mechanical properties in the crosslinked condition (Table VI). Higher content of unsaturated bonds takes part in polymerization leading to the products characterized by higher reactivity, higher degree of crosslinking, and more mechanical stability. Two-stage syntheses lead to the resins characterized by higher copolymerization peaks by 40–50°C compared to the one-step syntheses (Table V). As for one- and two-stage unsaturated polyester

resins, Barcol hardness decreases with increasing amounts of phthalic anhydride and with decreasing amount of maleic anhydride.

However, hardness for the two-stage resins is higher by 2–3 units than that for those obtained in the one-step syntheses. Thermal resistance according to HDT is very similar in the range of 69–73°C. However, their values for the two-stage syntheses are about 8–9°C higher than those for the one-stage syntheses. With the increasing molar amount of phthalic anhydride, thermal resistance according to HDT assumes smaller values. Derivatographic analysis also showed that the temperatures of initial decomposition of unsaturated polyester resins obtained in the two-stage syntheses are larger by about 10–15°C than those obtained in a one-stage process. The largest initial decomposition temperatures are observed for unsaturated polyester resins including molar excess of maleic anhydride. The glass-transition temperatures determined by differential scanning calorimeter proceed in the same order. In the case of two-stage syntheses, they are about 25–30°C larger than for one-stage syntheses and also for those obtained with a larger amount of unsaturated acid anhydride. Mechanical properties of resins, i.e., flexural strength, changes in the same way; however, the values of tensile strength are similar (Table VI).

## CONCLUSIONS

On the basis of the obtained results, it should be stated that using only one glycol in unsaturated polyester synthesis does not restrict its solubility with styrene.

TABLE V  
Physical Properties of Uncured Resins

Properties	Resin no.					
	1	2	3	4	5	6
Acid number of the resin (mg KOH/g)	20.0	20.0	21.2	19.0	19.4	19.6
Viscosity (mPa s)	1835	1650	1400	935	1425	1260
Density (g/cm <sup>3</sup> )	1.14	1.14	1.14	1.14	1.14	1.14
Refractive index	1.547	1.548	1.54	1.548	1.551	1.549
Gelation time (min)	9	9	7	9.3	8	7.3
Peak exotherm temperature (°C)	106	161	105	158	122	156



TABLE VI  
Thermal and Mechanical Properties of Cured Resins

Properties	Resin no.					
	1	2	3	4	5	6
Barcol hardness	79.2	82.1	77.5	79.9	77.1	79.8
Glass-transition temperature (°C)	85.8	111.4	75.9	105.4	63.5	93.1
Thermal resistance HDT (°C)	76.0	84.8	73.0	81.9	69.2	76.5
Initial decomposition temperature (°C)	225	240	220	235	200	210
Final decomposition temperature (°C)	620	620	618	610	615	600
Flexural strength (MPa)	129.6	143.3	115.7	138.2	111.5	122.5
Flexural elastic modulus (GPa)	4.46	4.50	4.31	4.42	4.19	4.41
Maximal force at break $F_{\max}$ (N)	212.3	252.2	185.6	215.8	173.0	191.2
Elongation at break (%)	3.35	4.20	3.24	3.67	3.06	3.08
Tensile strength (MPa)	63.8	61.8	66.7	68.4	64.2	61.9
Tensile modulus (GPa)	4.3	4.4	4.2	4.43	4.2	4.37
Tensile lengthening (%)	1.1	1.6	1.9	1.8	1.0	1.6

The properly scheduled synthesis of polyester allows to obtain resins differing in the number of double bonds responsible for thermal and mechanical properties.

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