Hydroxyalkyl Derivatives of Phenyldiamine as Modifiers for Unsaturated Polyester Resins, Part 1: Derivatives of Phenyl-1,4-Diamine

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ABSTRACT: The results are presented on the synthesis of new modifiers and functioning of amine modifiers for unsaturated polyester resins, obtained by reacting ethylene oxide or propylene oxide with phenyl-1,4-diamine. Also the effect of the modifiers and cobalt accelerator on the reactivity of resins was studied. When used in the amount of up to 2 wt %, the amine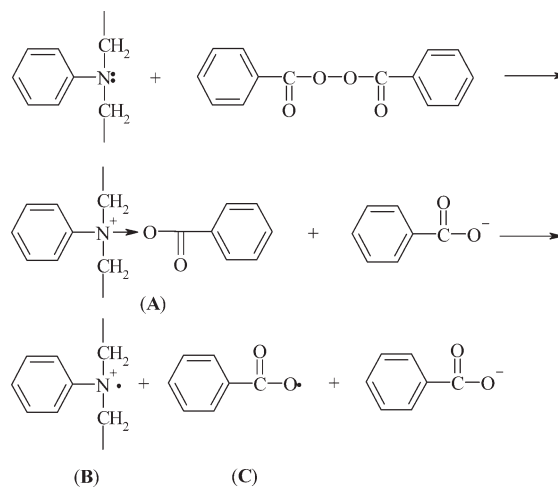s substantially (several times) reduced the gelation time of modified unsaturated polyesters. The reactivity of resins, however, improved in expense of their stability. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 120: 311–321, 2011

Key words: unsaturated polyester resins; amine modifiers; modification of polyester resins; hydroxyalkyl derivates of *p*-phenydiamine

INTRODUCTION

Unsaturated polyester resins (UP) are usually cured in the system consisting of a resin itself, i.e., styrene solution of an unsaturated alkyd, and a radical producing initiator, such as benzoyl peroxide or ketone peroxides with some metal salts. Some compounds reduce the activation energy of peroxide decomposition and hence allow for a low-temperature initiation of the curing system. These accelerators can selectively react with certain groups of initiators. In low-temperature curing of unsaturated polyester resins, cobalt or vanadium salts as well as tertiary amines are most often used. In the presence of cobalt salts, the curing takes place at 20–100°C when 1–12 wt % solutions of cobalt(II) octanate or naphthenate in dioctyl phtalate, styrene or mineral spirits is used or the vanadium accelerators are used for fast room temperature curing.[1] Manganese accelerators with ketone peroxides yield unsaturated poliester resins compositions of long life time, but cure quickly at 60–100°C.[1] Tertiary amines are used in unsaturated polyester resins compositions with benzoyl peroxide for room-temperature curing.[2] The most widely reported industrial formulations are the three-component systems consisting of the polyester dissolved in styrene, peroxy initiator, and a tertiary amine.[3–9] These compositions are very reactive even in temperature as low as 5°C[1] and the system: benzoyl peroxide-amine is often mentioned as the amine-curing system of unsaturated polyester resins.

Among the amines, the most frequently used are aromatic ones, such as *N*,*N*-dimethyl-aniline, *N*,*N*-diethylaniline, or *N*,*N*-dimethyl-*p*-toluidine. Unfortunately, unsaturated polyester resins with amine dissolved in it have a poor stability. Somewhat better stability have the formu-lations where amine is chemically incorporated into polyester chains, already at the stage of its synthesis. Then, the activator is very uniformly distributed over the bulk. This is possible when the amine has two or more functional groups capable of reacting with carboxylic acids (or acid anhydrides) or with diols. The easiest solution is when amine contains hydroxyl groups.[10–14] Incorporation of such an amine into resin structure may significantly accelerate gelation of the resin because of formation of active RO• radicals that initiate polymerization [(eqs. (1)]:[15]


$$\text{(1)}$$

TABLE I
Compounds Used and Their Suppliers

Compound	Supplier
Accelerator Co-1 (1.0 wt % solution of cobalt(II) octenate in styrene),	ORGANIKA-SARZYNA, Nowa Sarzyna, Poland
Benzyltriethylammonium chloride,	Prepared from trietylamine and benzyl chloride, University of Technology, Faculty of Chemistry
Hydroquinone, pa,	POCH, Gliwice, Poland
Luperox K-1, (50 wt % solution of peroxide of butanone in dibutyl phtalate),	ATOCHEM GmbH, Germany
Interox BP-50-P1, 50 wt % solution of benzoyl peroxide in dibutyl phtalate,	Peroxid Chemie GmbH, Germany
Phtalic anhydride, pure,	NITROGEN PLANTS, Kędzierzyn, Poland
Maleic anhydride, pure,	NITROGEN PLANTS, Kędzierzyn, Poland
3-Oxapentane-1,5-diol (diethylene glycol), pure,	OIL REFINERY, Płock, Poland
Propane-1,2-diol (propylene glycol), pure	OIL REFINERY, Płock, Poland
Ethylene oxide, pure	FLUKA, Buchs, Switzerland
(±)Propylene oxide, pure	FLUKA, Buchs, Switzerland
Phenyl-1,4-diamine, pure	FLUKA, Buchs, Switzerland
Styrene, pure	FLUKA, Buchs, Switzerland
Dioxane, pure	POCH, Gliwice, Poland

Initiating complex (Formula **A**) is formed in the first stage from amine and benzoyl peroxide. The complex then decomposes to a cation radical (Formula **B**) and benzoyl radical (Formula **C**).[16]

Unsaturated poliester resins are very frequently cured with the use of metal containing accelerators of hydroperoxide decomposition. The most popular is cobalt(II) naphthenate added in the amount of 0.002–0.03 wt %.[17] It is often referred to as the cobalt-curing system. The most effective accelerating systems consist of metal and amine both built into polyester structure.[18,19] The promoting effect of amine both incorporated chemically or physically added to unsaturated poliester resins in the cobalt-curing system has been explained by Jada[18] and Kharash,[19] what is shown in eqs. (2) and (3), where ROOH is a hydroperoxide:

$$Co^{2+} + ROOH \longrightarrow Co^{3+} + RO\bullet + OH \qquad (2)$$

$$(3)$$
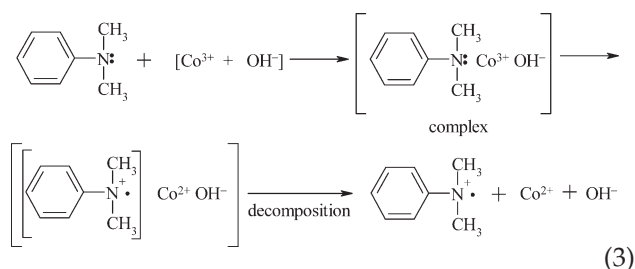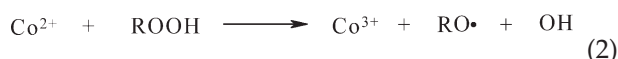
As mentioned in[18,19] the amine does not just act by complexing Co^{3+} and its reduction to Co^{2+}, but it can initiate decomposition of hydroperoxide.[18,19]

Hence, introduction of a cobalt(II) salt to a unsaturated polyester resins modified with an aromatic tertiary amine containing reactive hydroxyl groups

results in a substantial reduction of gelation time. $Cobalt^{3+}$ ions formed in the reaction of hydroperoxide with Co^{2+} are first complexed and then reduced thus leading to formation of active $RO\bullet$ radicals that initiate curing; or amine itself can decompose hydroperoxide and add up to the curing process.[18,19]

Quarternary ammonium salts are added in order to improve storage stability of unsaturated polyester resins. Their effect can be explained in terms of reduced rate of aging of unsaturated polyester resins by capturing $RO\bullet$ radicals.

The aim of this work was to obtain novel ternary amines that can be used as modifiers and preaccelerators for unsaturated polyester resins. They are prepared in reactions of ethylene oxide or propylene oxide with phenyl-1,4-diamine. Preliminary results of a study on their effect on gelation behavior and stability of unsaturated polyester resins is also reported.

EXPERIMENTAL

Materials

Table I presents a list of the materials used and their suppliers.

Syntheses

Synthesis of benzene-1,4-diamine-N,N,N′,N′-tetraethane-2,2′,2″,2‴-tetraole (modifier A) and benzene-1,4-diamine-N,N,N′,N′-tetrapropane-2,2′,2″,2‴-tetraole (modifier B)

To a three-necked 250 cm³ flask equipped with a reflux condenser adopted to work with highly volatile liquids and thermometer 27.04 g (0.25 moles) of phenyl-1,4-diamine was placed together with 51.70 g
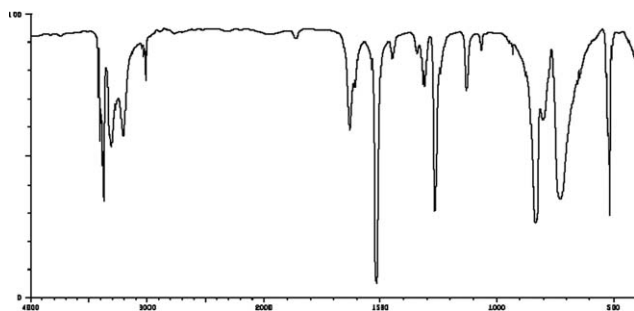
Figure 1 IR spectrum of phenyl-1,4-diamine.

(50.0 cm^3, 0.57 mole) of dioxane and 44.05 g (50.7 cm^3, 1.0 mole) of ethylene oxide. P-phenyldiamine was also reacted with 58.08 g (69.98 cm^3, 1.0 mole) of propylene oxide. The content was brought to boiling (ca. 30°C—with ethylene oxide or ca. 40°C—with propylene oxide) while stirring. The temperature slightly increased as the reaction progressed. It was halted when temperature reached dioxane boiling point (102°C). The product was isolated by distilling dioxane off. It had the form of dark brown resin. The yields of products were: 89.1 and 88.2%, respectively.

The spectra of the substrates used in the reaction of phenyl-1,4-diamine and those of ethylene oxide or propylene oxide are presented in Figures 1 through 6, and the description of adsorption IR spectra and resonance signals from ^{1}H NMR are presented in Tables III and IV.

The product of reaction of phenyl-1,4-diamine with ethylene oxide or propylene oxide were crystalline solid of sharp melting points:

a. benzene-1,4-diamine-N,N,N',N'-tetraethane-2,2', 2'',2'''- tetraole $t_{m,found} = 70.8°C$,
b. benzene-1,4-diamine-N,N,N',N'-tetrapropane-2,2', 2'',2'''-tetraole $t_{m,found} = 89.5°C$.

The chemical structure of products was confirmed by elemental analysis (Table II) and by using spec-

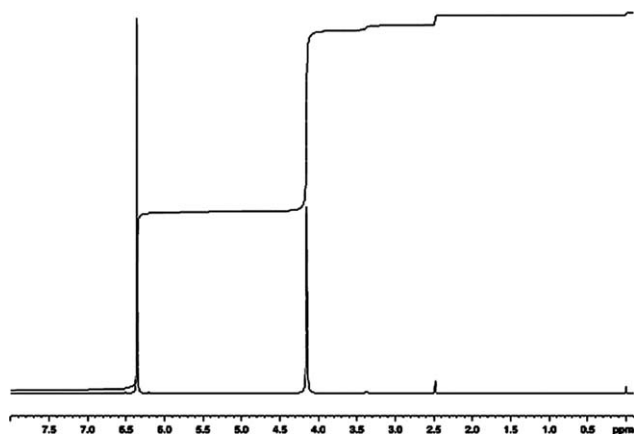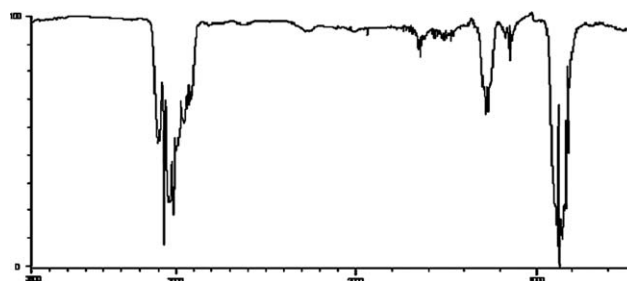troscopic methods: FT-IR (Table III, Figs. 7 and 9) and ^{1}H NMR (Table IV, Figs. 8 and 10).

Synthesis of modified unsaturated polyester resins

To a three-necked 500 cm^3 flask equipped with a mechanical stirrer, inlet to inert gas (nitrogen), thermometer, Liebig condenser and calibrated distillate collector, 76.1 g (0.5 mole) of phtalic anhydride, 49.0 g (0.5 mole) of maleic anhydride, 41.0 g (0.43 mole) of diethylene glycol, 42–44 cm^3 (0.57–0.60 mole) of propylene glycol (depending on the amount of amine-glycol modifier added), and the modifier itself up to 6.4 g (2.0 wt % with respect to the total mass of all substrates) were introduced. The flask was purged with nitrogen for 15 min before heating was switched on. Then 0.18 cm^3 (ca. 12 mg) of 10% solution of hydroquinone in acetone was added and the content heated at 165–200°C under nitrogen for 9–12 h, until the acid number of the mixture has dropped down to below 50 mg KOH per g of resin.[20] The mixture was then cooled down to 90–100°C and diluted with 125 cm^3 of styrene stabilized with hydroquinine.

Curing of unsaturated polyester resins

By using normalized procedures, time of gelation at 25°C (time until air bubble was arrested in the test tube filled with resin containing initiator)[21] and
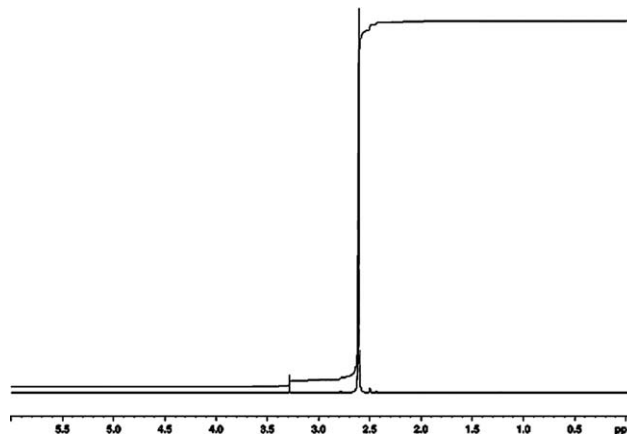

Figure 3 IR spectrum of ethylene oxide.

Figure 2 ^{1}H NMR spectrum of phenyl-1,4-diamine.

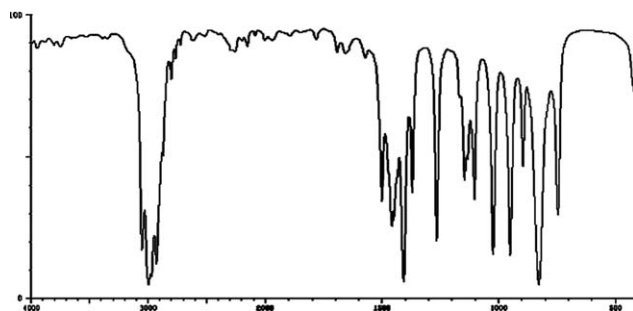**Figure 4** ^{1}H NMR spectrum of ethylene oxide.

Figure 5 IR spectrum of propylene oxide.

stability of resins at 70°C (time until air bubble was arrested in the test tube filled with resin containing no initiator)[22] were determined for all unsaturated polyester resins. The time of gelation was measured for the so-called amine-curing system, i.e., with benzoyl peroxide as initiator, for cobalt-curing system consisting of butanone peroxide initiator and cobalt(II) octanate accelerator. A series of curing experiments with cobalt curing system was performed with an addition of 0.3 wt % of benzyltriethylammonium chloride.

Analytical methods

The reaction of amine addition to oxiranes was followed by determining the epoxy number of the reaction mixture using hydrochloric acid solution in dioxane.[23] ^{1}H NMR spectra of the products were recorded at 25°C in solvent d_6-dimethyl sulfoxide and a hexamethyldisiloxane internal standard on a FT 80 MHz Tesla BS 587A spectrometer (Brno, Czechoslovakia) and Bruker AM 500 MHz (Germany). IR spectra were recorded from a KBr pellets on a Perkin–Elmer PARAGON 1000 FT spectrometer (Wellesley, MA). Elemental analysis were mada on a Fisons EA 1108 apparatus (Carlo-Erba, Stanford, Valencia, CA).

The polycondensation leading to unsaturated polyester resins was followed by measuring the amount of water released from the system and, at the end of reaction, by measuring the acid number (AN) of reaction mixture. The reaction was ended when AN was smaller than $\sim$ 50 mg KOH per g of resin.[20] Hydroxyl numbers (HN) of alkyds used for preparing unsaturated poliester resins were also measured according to the standard procedures.[24]
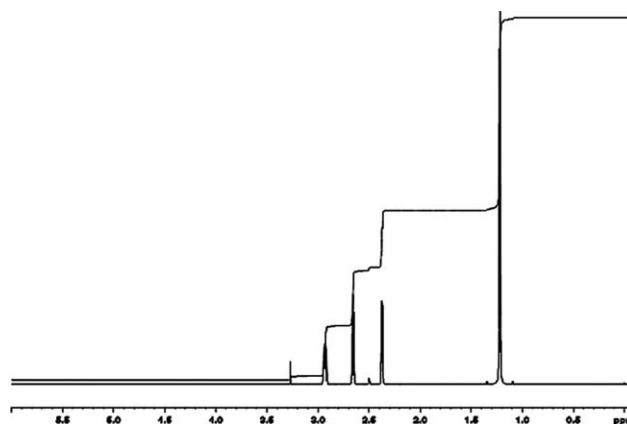

Figure 6 ^{1}H NMR spectrum of propylene oxide.

RESULTS AND DISCUSSION

Synthesis of modifiers A and B

The amine-glycol modifiers for unsaturated polyester resins were obtained in one step reaction between 1 mole of phenyl-1,4-diamine and 4 mole of ethylene oxide or 4 mole propylene oxide and obtain tetrahydroxy alcohols containing tertiary amino groups with nitrogen atoms linked directly to aromatic ring. The reaction schemes are:
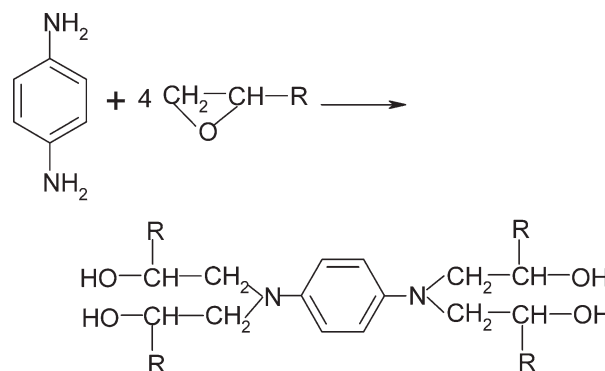
where: R = —H or —CH$_3$

In the reaction of one mole of phenyl-1,4-diamine with four moles of oxirane one obtains an alcohol with four hydroxyl groups and two tertiary nitrogen atoms. The course of reaction confirm the vanishing IR absorption bands at $\sim$ 3400 cm^{-1} and at 1343 and 1320 cm^{-1} due to stretching and deformational vibrations of amino groups and appearing new broad bands due to hydroxyl groups at 3246 and 3292 cm^{-1} (associated hydroxyl groups) and bands

TABLE II
Elemental Analysis of Modifiers
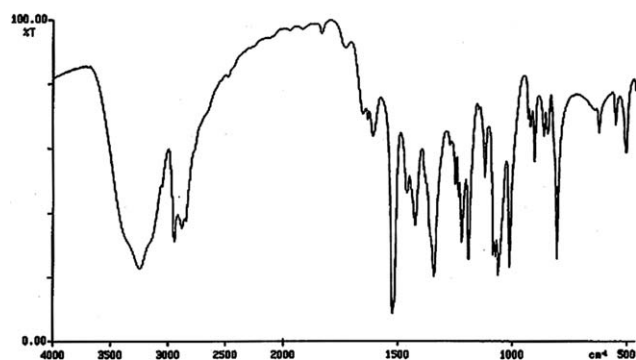
Compound	%C		%H		%N	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
Modifier A	59.14	58.75	8.51	8.43	9.85	9.73
Modifier B	64.26	63.84	8.39	8.17	8.33	7.98

Type of vibrations and functional group	Band location [cm^{-1}]				
	Phenyl-1, 4-diamine	Ethylene oxide	Propylene oxide	Modifier A	Modifier B
ν_{NH_2}	3400, 3398	–	–	–	–
ν_{OH}	–	–	–	3246	3292
ν_{C-H} in aromatic ring	3043, 3013	–	–	3052	3057
ν_{CH_3}, ν_{CH_2}	–	3105, 3050, 3030, 3000, 2985^a	3051, 2997, 2972, 2951, 2874, 2801	2944, 2878, 2858 ^{a}	2965, 2893
$\nu_{C=C}$, aromatic ring vibrations	1630, 1621, 1539	–	–	1652, 1632, 1609, 1522	1656, 1612, 1521
δ_{CH_3}, δ_{CH_2}	–	1620, 1250^a	1675, 1601, 1457, 1446, 1408, 1370, 1260, 1145	1457, 1423, 1340, 1234, 1220 ^{a}	1458, 1424, 1371, 1351, 1226, 1233
δ_{NH_2}	1343, 1320	–	–	–	–
δ_{OH}	–	–	–	1190, 1118	1195, 1135
ν_{C-O}, in first or second order alcohol	–	–	–	1082, 1072, 1060	1068
$\delta_{out\ of\ plane}$, aromatic ring vibrations	992, 965, 953, 840	–	–	1011, 903, 862, 846, 805	1015, 994, 948, 936, 907, 833
ν_{C-O-C}, asymetric vibration of oxide ring	–	955, 835, 830, 822	1105, 1024, 961, 896, 824, 747	–	–

^{a} No bands for ν_{CH_3} or δ_{CH_3} are observed for this compound.

in the range 1080–1060 cm^{-1} corresponding to stretching vibrations of C—O bonds in primary and secondary alcohols, as well as those at 1190 and 1195 cm^{-1} due to deformational vibrations of hydroxyl groups (Figs. 7 and 9). Similarly, in ^{1}H-NMR spectra (Figs. 8 and 10), the signal at 5.52 ppm from amine protons disappears and appears instead a signal at 4.40 ppm from hydroxyl protons in 2-hydroxyethyl groups (modifier A) or two signals at 4.50 and 4.90 ppm from OH protons in 2-hydroxypropyl groups (modifier B). These two last signals are related to configuration at the chiral carbon atom in the hydroxypropyl group. In case of modifier A, a signal from methylene protons appears in the range from 2.90 to 3.70 ppm, whereas for modifier B three extra peaks from methyl protons are seen in the spectra at 1.00 ppm, beside methylene protons signal at 2.70–3.40 ppm, as well as from methine proton at 3.60–4.00 ppm. The difference between resonance

positions of signals from methylene and methine protons in modifier B is a result of strongly electronegative character of the hydroxyl group oxygen, which is stronger than that from the nitrogen at aromatic ring. The signals at 6.30–6.80 ppm due to aromatic protons appear in stectra of both modifier A and B.
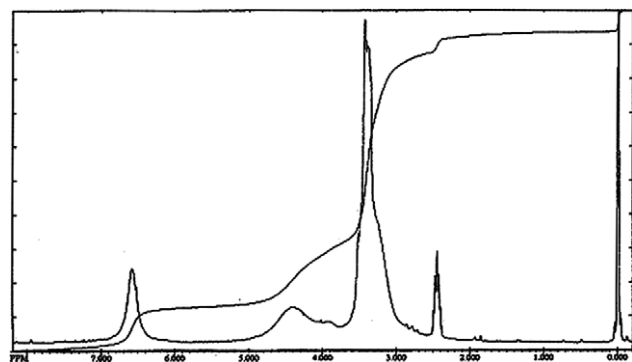
Gelation time for modified unsaturated polyester resins

The modifiers A and B prepared as described above:
Modifier A - benzene-1,4-diamine-N,N,N',N'-tetraethane-2,2',2'',2'''-tetraole,

TABLE IV
Chemical Shifts of Protons in ^{1}H NMR Spectra of Phenyl-1,4-diamine, Ethylene Oxide, Propylene Oxide, and Products of Reaction

Name of chemical compound	Chemical shifts [δ ppm]	Group
Phenyl-1,4-diamine	4.15	—NH$_2$
	6.36	aromatic protons
Ethylene oxide	2.61	—CH$_2$—
Propylene oxide	1.22	—CH$_3$
	2.37 and 2.65	—CH$_2$—
	2.92	>CH—
Benzene-1,4-diamine-N, N,N',N'-tetraethane-2, 2',2'',2'''-tetraole (modifier A)	2.90–3.70	>N—CH$_2$—CH$_2$—O—
	4.40	—OH
	6.30 – 6.80	aromatic protons
Benzene-1,4-diamine-N, N,N',N'-tetrapropane-2, 2',2'',2'''-tetraole (modifier B)	1.00	—CH$_3$
	2.70–3.40	>N—CH$_2$—
	3.60–4.00	—O—CH<
	4.50 and 4.90	—OH
	6.30–6.80	Aromatic protons

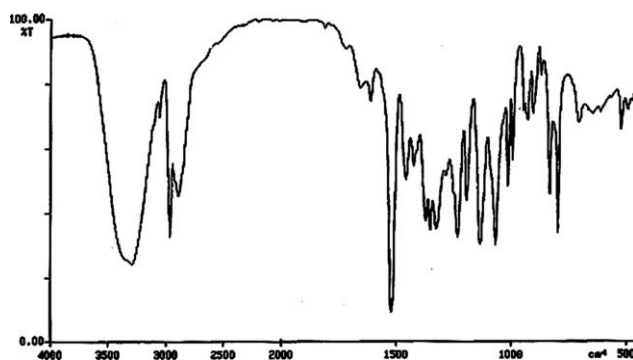**Figure 7** IR spectrum of benzene-1,4-diamine-N,N,N',N'-tetraethane-2,2',2'',2'''-tetraole (modifier A).

Figure 8 ^{1}H NMR spectrum of benzene-1,4-diamine-
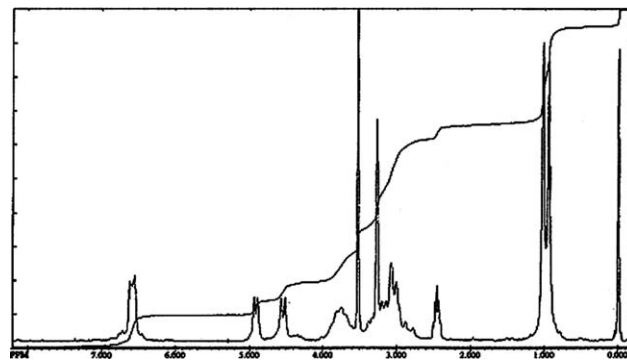N,N,N′,N′-tetraethane-2,2′,2″,2‴-tetraole (modifier A).

Modifier B - benzene-1,4-diamine-N,N,N′,N′-tetra-
propane-2,2′,2″,2‴-tetraole

were built into the structure of an unsaturated
polyester resins and their effects on gelation time and
stability of the resin was observed. The reference
resin was prepared by condensation of phtalic and
maleic anhydride with propane-1,2-diol (propylene
glycol) and 3-oxapentane-1,5-diol (diethylene gly-
col).[2] This is a typical construction resin with 3-oxa-
pentane-1,5-diol (diethylene glycol) used as a mono-
mer reducing stiffness of the polyester segments.
Modified resins were obtained by replacing a part of
propylene glycol with one of the modifiers. The upper
proportion of the modifier was established in prelimi-
nary experiment not to exceed 2 mol %. This was suf-
ficiently small quantity so that no gelation at polyest-
erification stage was observed in the presence of both
multifunctional modifiers. As the amount of modifiers
increased, the color of modified resins became darker
and darker, from yellow at the concentration of modi-
fiers A and B equal about 0.01 to 0.02 wt % to dark
brown at the concentration 1.75 to 2.0 wt %.

The standard initiator for the cobalt-curing of un-
saturated polyester resins was used. Namely, the sys-
tem consisted of cobalt(II) octenate as accelerator and
butanone peroxide initiator dispersed in dibutyl phta-
late (Luperox K-1). The attempt of using benzoyl per-

Figure 9 IR spectrum of benzene-1,4-diamine-N,N,N′,N′-
tetrapropane-2,2′,2″,2‴-tetraole (Modifier B).

Figure 10 ^{1}H NMR spectrum of benzene-1,4-diamine-
N,N,N′,N′-tetrapropane-2,2′,2″,2‴-tetraole (Modifier B).

oxide dispersed in dibutyl phtalate (Interox BP-50-P1)
was unsuccessful for too long gelation times.

The unsaturated polyester resins were synthesized
by carrying condensation of the components at 165–
200°C under nitrogen until the acid number of reac-
tion mixture dropped down below 50 mg KOH per
g of resin.[20] The results of stability tests are pre-
sented in Table V.

The shelf stability of the modified resins reduced
with the increasing amount of modifiers A or B
added to polycondensation. This is a result of the
presence of tertiary amino groups built into polyes-
ter, the groups that are known for their significant
reduction of threshold energy of double bond
decomposition or cleavage. The resin, even in ab-
sence of initiator, gelled when heated to 70°C. The ge-
lation was the more rapid the higher was the modi-
fier contents. In general, the modifiers containing 2-
hydroxyethyl substituents at nitrogen atom (such as
modifier A) are less active in reducing shelf stability
than those with 2-hydroxypropyl substituents (modi-
fier B). The factor by which the shelf-life of the resin
reduced for the resin containing the smallest (0.01 wt
%) and the highest (2.0 wt %) content of modifier A
was 15 times, while that for modifier B was 25 times.
Such a high reduction of the shelf stability of the res-
ins seems to be related to the donor character of
methyl group in 2-hydroxypropyl groups.

Gelation times for the modified resins are shown
in Figures 11 and 12. The plots were constructed after
measuring the gelation times of the modified resins
with each point corresponding to an average value
from three measurements. In Figures 13 and 14 the
dependence of gelation time is plotted against the
amount of cobalt accelerator for resins prepared with
different amounts of modifiers A and B. The reactiv-
ity and stability measurements were carried out by
changing: the content of modifiers built into the struc-
ture of unsaturated polyester resins (Figs. 11 and 12)
the amount of cobalt accelerator (Figs. 13 and 14).

In Figures 11 and 12 one can observe two ranges
of gelation times, one where gelation times of

TABLE V
Properties of Unsaturated Polyester Resins with Amine Modifiers Incorporated into Their Chemical Structure
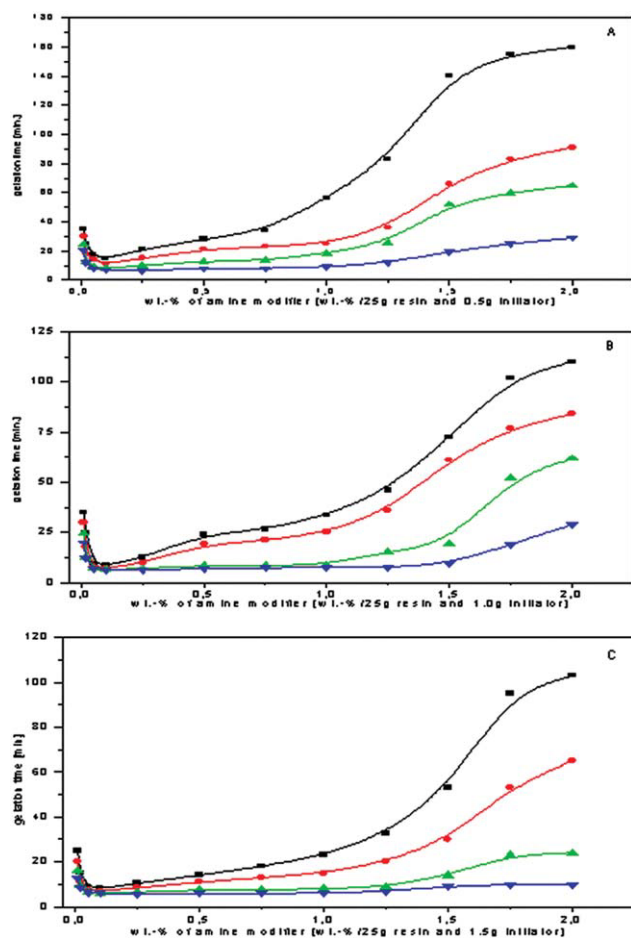
Kind of modifier[a]	Number of resin	Mole of amine acce-lerating groups/kg resin [× 10^{-3}]	Wt % of modifier	Acid number [mg/KOH/g]	Hydroxyl number [mg KOH/g]	Stability of resins at 70°C		Color
						Without ammonium salt [hours]	With ammonium salt [hours]	
1	2	3	4	5	6	7	8	
None	1	0.000	0.00	45.23	55.18	825	2658	Colorless
	2	0.113	0.01	39.58	47.49	555	1554	Yellowish
	3	0.226	0.02	45.13	54.56	450	1350	Yellowish
	4	0.565	0.05	49.05	58.36	318	927	Yellow
	5	1.130	0.10	46.03	55.22	256	498	Yellow
Modifier A	6	2.825	0.25	38.94	46.99	18	156	Dark yellow
	7	5.651	0.50	42.97	52.03	15	138	Dark yellow
	8	8.477	0.75	39.46	47.99	15	126	Light brown
	9	11.302	1.00	44.48	54.18	15	120	Light brown
	10	14.128	1.25	40.31	48.77	15	114	Brown
	11	16.954	1.50	40.66	49.09	15	108	Brown
	12	19.779	1.75	47.91	58.49	15	105	Dark brown
	13	22.605	2.00	38.35	47.22	15	105	Dark brown
	14	0.094	0.01	38.79	46.55	147	1032	Yellowish
	15	0.189	0.02	40.08	48.09	126	864	Yellowish
	16	0.472	0.05	43.81	53.07	105	762	Yellow
	17	0.944	0.10	38.75	46.50	63	681	Yellow
Modifier B	18	2.360	0.25	43.95	52.94	27	330	Dark yellow
	19	4.720	0.50	47.92	57.95	21	117	Dark yellow
	20	7.080	0.75	37.16	45.09	18	90	Light brown
	21	9.440	1.00	45.79	55.24	18	75	Light brown
	22	11.800	1.25	36.12	44.34	18	63	Brown
	23	14.160	1.50	43.99	53.28	18	51	Brown
	24	16.520	1.75	40.72	49.46	18	48	Dark brown
	25	18.880	2.00	42.00	51.24	15	48	Dark brown

[a] modifier A—benzene-1,4-diamine-N,N,N′,N′-tetraethane-2,2′,2″,2‴-tetraole, modifier B—benzene-1,4-diamine-N,N,N′, N′-tetrapropane-2,2′,2″,2‴-tetraole.

modified resins are shorter that those for unmodified ones and the second one where gelation times after modification become longer. These are determined by the combined actions of the built in amine and cobalt accelerator. The results suggest that the presence of modifiers A and B built into the resin in the amount of 0.01 to 1.25 wt % leads to a faster gelation of the resin as compared to unmodified one, whereas as its proportion in the resin ranges from 1.5 to 2.0 wt %, the gelation time becomes longer than for unmodified resin. A significant change is caused by an extra addition of cobalt accelerator (applied in the form of 1 wt % solution of cobalt(II) octaneate in styrene). Then, somewhat longer gelation time is observed as its content is small (0.10 or 0.15 cm^3 of cobalt accelerator per 25 g of resin). Fours series of experiments were made with cobalt solution content of 0.10, 0.15, 0.25, or 0.50 cm^3 per 25 g of resin. For unmodified resin the respective gelation times were, 92, 72, 50.5, or 42.5 min for the normative amount of initiator (2 wt %).[21] The plots of gelation times versus the amount of modifier built into resin structure at different amounts of cobalt accelerator are presented in Figures 11 and 12. The
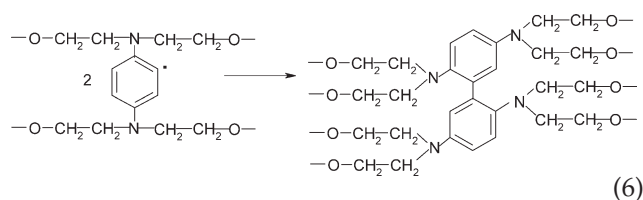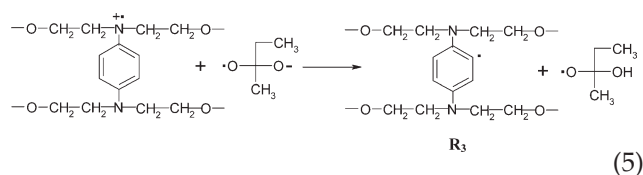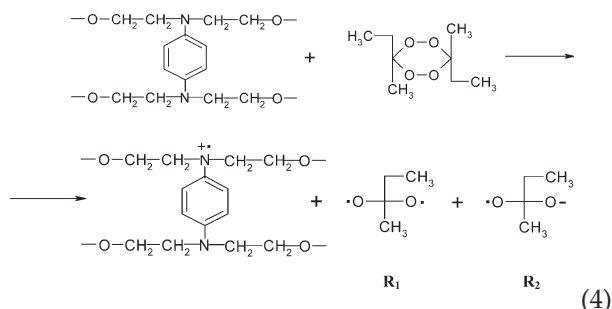
fastest to gel were the resins containing 0.05 to 0.15 wt % of modifier A or B. It was fount that doubling the amount of initiator relative to its normative portion[22] reduces gelation time by 30–50%. The reduction was the smaller, the more cobalt solution was used (cf. plots A and B in Figs. 11 and 12). With 0.25 and 0.50 cm^3 of cobalt(II) octanate the reduction of gelation time in the system containing both the normative (2 wt %) and higher (4 wt %) amount of initiator was higher than 12–17%. Still higher amount of initiator (6 wt %) reduced gelation time by 15% (in relation to the last system with 4 wt % of initiator). To summarize, one can say that by doubling the amount of initiator from 2–4 wt % one can increase the resin reactivity and reduce gelation time by up to 50%. Further increase of initiator amount to 6 wt % does not substantially improve the resin reactivity, anymore.

The presence in the resin structure more than 1.50 wt % of modifier A or 1.75 wt % of modifier B results in slower gelling of modified resins as compared with unmodified one. The reason might be the high concentration of amine. The modifier acts as a scavenger of radicals formed from initiator. As
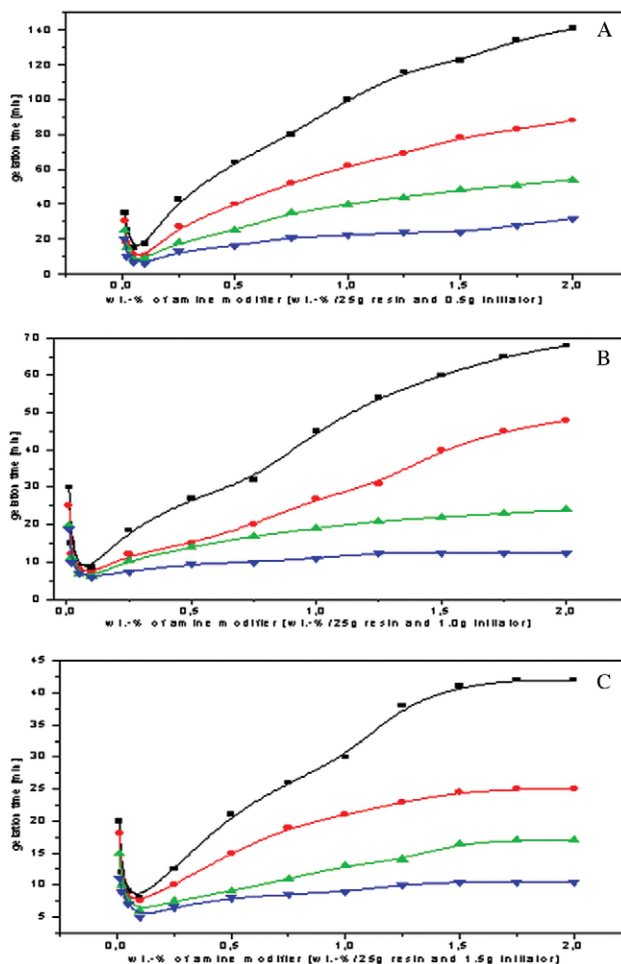
$$(5)$$

$$(6)$$

Incorporation of the tertiary aromatic amine into the structure of an unsaturated polyester resin results in a substantial reduction of the initiator decomposition threshold (Schemes 4 and 5). Hence, the faster curing of the resin. The free radicals

Figure 11 Gelation times of unsaturated polyester resins with various amount of chemically incorporated modifier A: To 25 g of resin, 0.5 g (plot A), 1.0 g (plot B) 1.5 g (plot C) of butanone peroxide initiator was added; the amounts of cobalt accelerator solution: (■): 0.10 cm^3; (●): 0.15 cm^3; (▲): 0.25 cm^3; (▼): 0.50 cm^3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

follows from literature data[16,25–28] amines may act not just as promoters of initiator decomposition, but also as stabilizers preventing radicals formed naturally to propagate into a chain reactions in organic systems. Also the amines built into resin may react with macroradicals thus reducing the rate of polymerization. The process may proceed according to the scheme [eqs. (4)–(6)]:

$$(4)$$

Figure 12 Gelation times of unsaturated polyester resins with various amount of chemically incorporated modifier B: To 25 g of resin, 0.5 g (plot A), 1.0 g (plot B) 1.5 g (plot C) of butanone peroxide initiator was added; the amounts of cobalt accelerator solution: (■): 0.10 cm^3; (●): 0.15 cm^3; (▲): 0.25 cm^3; (▼): 0.50 cm^3. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
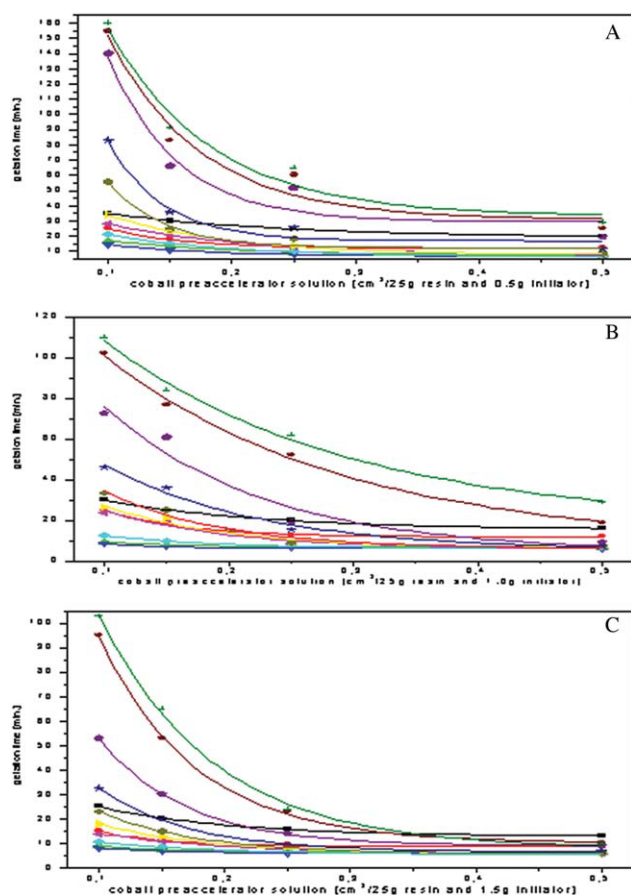
Figure 13 Gelation times of unsaturated polyester resins with various amount of cobalt accelerator solution and various amounts of chemically incorporated modifier A. To 25 g of resin, 0.5 g (plot A), 1.0 g (plot B) 1.5 g (plot C) of butanone peroxide initiator was added; the amounts of chemically incorporated modifier A: (■): 0.01 wt %; (●): 0.02 wt %; (▲): 0.05 wt %; (▼): 0.10 wt %; (◆): 0.25 wt %; (+): 0.50 wt %; (×): 0.75 wt %; (✱): 1.00 wt %; (◼): 1.25 wt %; (◧): 1.50 wt %; (□): 1.75 wt %; (◉): 2.00 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

formed from the initiator as well as the secondary ones formed from the aromatic amine can, in subsequent reactions, lead to the transfer of a radical to the main chain unsaturated bond or to the double bond in styrene (reaction Schemes 4 and 5 and 7 and 8).

$$R^{\bullet} + -CH_2-O-\overset{O}{\underset{}{C}}-\overset{H}{\underset{H}{C}}=\overset{H}{\underset{}{C}}-\overset{O}{\underset{O}{C}}-O-CH_2- \longrightarrow -CH_2-O-\overset{O}{\underset{}{C}}-\overset{H}{\underset{R}{C}}-\overset{\bullet}{\underset{H}{C}}-\overset{O}{\underset{O}{C}}-O-CH_2- \tag{7}$$

$$R^{\bullet} + \langle\!\!\!\!\bigcirc\!\!\!\!\rangle-CH=CH_2 \longrightarrow \langle\!\!\!\!\bigcirc\!\!\!\!\rangle-\overset{R}{\underset{}{CH}}-CH_2^{\bullet} \tag{8}$$
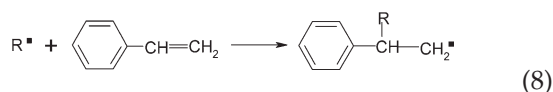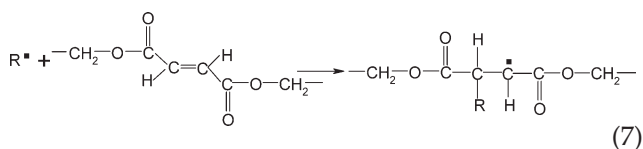
where $R^{\bullet} = R_1, R_2,$ or R_3

All these processes lead to a faster gelation of the polyester resin and, at the low concentration of

modifiers A and B (0.10 and 0.05 wt %, respectively) one observes a minimum on the relationship curing rate versus amount of modifier (Figs. 11 and 12). As the amount of radicals increases, the more radicals are formed that lead to an increase of their recombination probability, according to reaction Scheme 6. This competitive process increases the gelation time of the polyesters.

As the gelation times of resins modified with amines **A** and **B** used in the proportion 1.5 to 2.0 wt % and moderate amount of initiator are relatively long, the resins can be used as so called casting masses. The relative low reactivity is advantageous because of reduced stresses after curing at low temperature. The limited stability of resins measured according to standard procedures[22] (cf. Table V, Column 6) is a disadvantage of amine modifiers
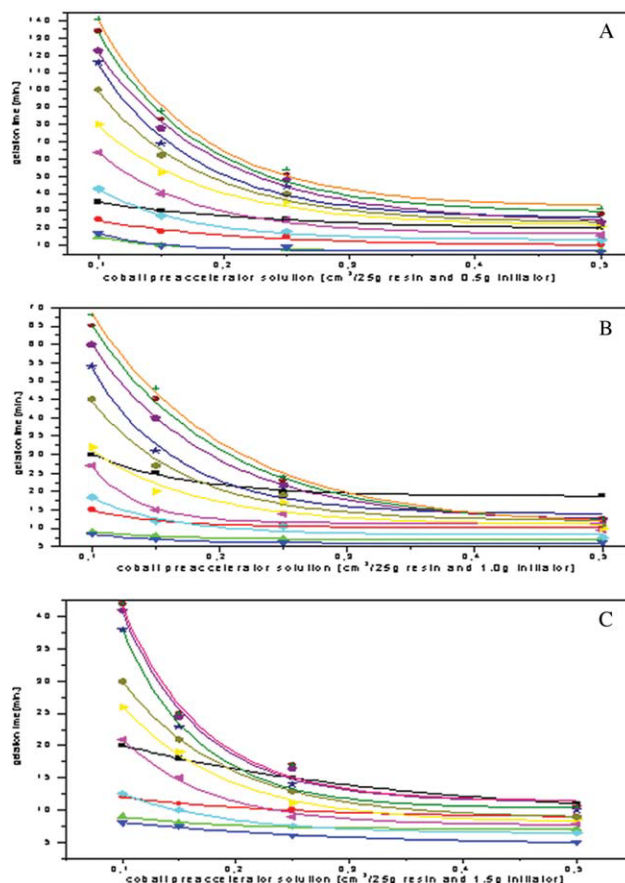
Figure 14 Gelation times of unsaturated polyester resins with various amounts of cobalt accelerator solution and various amounts of chemically incorporated modifier B. To 25 g of resin, 0.5 g (plot A), 1.0 g (plot B) 1.5 g (plot C) of butanone peroxide initiator was added; the amounts of chemically incorporated modifier B: (■): 0.01 wt %; (●): 0.02 wt %; (▲): 0.05 wt %; (▼): 0.10 wt %; (◆): 0.25 wt %; (+): 0.50 wt %; (×): 0.75 wt %; (✱): 1.00 wt %; (◼): 1.25 wt %; (◧): 1.50 butanone wt %; (□): 1.75 wt %; (◉): 2.00 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VI
Comparison of Gelation Times for Unsaturated Polyester Resins Containing or Not the Benzyltriethylammonium Chloride Stabilizer

Wt % of modifier	Gelation time [min]			
	Modifier A		Modifier B	
	Without ammonium salt [min]	With ammonium salt [min]	Without ammonium salt [min]	With ammonium salt [min]
1	2	3	4	5
0.01	25.0	73.0	25.0	75.0
0.02	13.0	25.0	15.0	36.0
0.05	9.0	23.0	8.0	29.0
0.10	8.0	21.0	9.0	24.0
0.25	10.0	25.0	18.0	46.0
0.50	13.0	45.0	25.0	51.0
0.75	13.5	56.0	35.0	81.0
1.00	18.5	86.0	40.0	171.0
1.25	25.5	170.0	44.0	250.0
1.50	52.0	250.0	48.0	390.0
1.75	60.0	280.0	51.0	390.0
2.00	65.0	280.0	54.0	370.0

containing 0.25 to 2.0 wt % of **A** or **B**. It is well known that tertiary amines built into the structure of unsaturated polyester resins reduce the resin stability and hence shorten the shelf life. The stability figures show that the resins containing 0.01 to 0.05 wt % of modifier **A** and those with 0.01 to 0.05 wt % of modifier **B** can be classify as those of good stability, but the resins containing more amine modifiers have rather short shelf life. The stable resins had the normative stability time of 258 to 555 h. (modifier **A**) or 105 to 147 h. (modifier **B**). The normative stability time is the gelation time of resin kept without an initiator at 70°C. The unstable resins had the normative stability time of 15–27 h.

The stability of unsaturated polyester resin can be improved by using quaternary ammonium salt stabilizers.[29] The resins containing 0.3 wt % benzyltrimethylammonium chloride. The stability of resins at 70°C improved in the presence of the ammonium stabilizer, but to the extent again depending on the amount of amine modifier built into resin. In all cases the stability expressed in terms of normative time improved three through seven times and the improvement was the highest for resins containing less than 0.1 wt % of amine modifiers. The character of stability dependence on the amount of amine built into resin did not change in the presence of quaternary ammonium salt.

To summarize, for an unsaturated polyester resin modified with modifiers A and B it is possible to adjust the gelation times at considerably broad range. This parameter depends on three major factors: the amount of built-in modifier, the concentration of cobalt accelerator and the amount of initiator used for curing. Each of them influences the time gelation in its specific way. The most important is the amount of amine modifier. Somewhat less important

is the amount of cobalt accelerator. The amount of initiator modifies gelation time only when used in the amount 2–4 wt %. At the higher amount of 6 wt % of butanone peroxide the reactivity of resin expressed in terms of gelation time does not increase significantly, anymore. The gelation time of the compositions containing ammonium stabilizer with 2.0 wt % of initiator and 0.25 cm^3 of cobalt accelerator per 25 g of resin are listed in Table VI. The gelation time became longer that for compositions without ammonium salt to the extent dependent on the type of modifier.

CONCLUSIONS

1. Amine-modifiers with aromatic ring as modifiers for unsaturated polyester resins were obtained by reacting *p*-phenydiamine with oxirane: etylene and propylene oxide. The amines introduced into resins structure at the stage of polycondensation strong reduce the gelation time in the cobalt curing system.
2. The reduction of gelation time was observed in cobalt curing system in the presence of at most 1.25 wt % of the modifiers. For resins modified with 1.50 and 2.00 wt % of modifiers one observes an increase of gelation time as compared with that for unmodified resins. The most promising results with regard to the reactivity of resins and their storage stability were observed when 0.10 wt % of modifier **A** and 0.05 wt % of modifier **B** were used.
3. By using more than ∼ 0.30 cm^3 of cobalt accelerator per 25 g of resin does not improve the resin reactivity (i.e., reduces gelation time), irrespectively of the amount of initiator.
4. By introducing benzyltriethylammonium chloride stabilizer to the modified unsaturated polyester resins one can significantly increase their storage stability. For both modifiers the presence of ammonium salt changed the reactivity of composition by prolonging the gelation time. Again the reactivity depended on the amount of the built-in amine modifier.

References

1. Kłosowska-Wołkowicz, Z.; Królikowski, W.; Penczek, P. Polyester Resins and Laminates (in Polish); WNT: Warsaw, 1986.
2. Kłosowska-Wołkowicz, Z.; Jedlínski, Z. Polimery (Warsaw) 1970, 15, 1.
3. German pat. DE-227711 (1986); CA 1986, 104 208379d.
4. Japan pat. JP-2250025 (1987); Available at: www.derwent.com.
5. Japan pat. JP-1026653 (1989); Available at: www.derwent.com.
6. Ukrainian pat. SU-1467137 (1990); Available at: www.derwent.com.

7. German pat. DE-3345102 (1985); CA 1985, 103 196858y.
8. Attia, I. A.; Abdel-Halim, M. S.; Abdel-Azim, A.-A. A. Polym Bull (Berlin) 1995, 34, 377.
9. Penczek, P.; Kłosowska-Wołkowicz, Z. Polimery (Warsaw) 1997, 42, 294.
10. German pat. DE-3643788 (1988); CA 1989, 110, 39557b.
11. USA. pat. US-4775597 (1988); CA 1989, 110, 40630b.
12. Eur. pat. EP-271385 (1988); CA 1989, 110, 98628y.
13. Duliban, J. Macromol Mater Eng 2001, 286, 624.
14. Duliban, J. Polimery (Warsaw) (Warsaw) 2004, 49, 774.
15. Jada, S. S. Makromol Chem 1982, 183, 1763.
16. Horner, L.; Schloenk, E. Angew Chem 1949, 61, 711.
17. Porejko, S.; Fejgin, J.; Zakrzewski, L. Chemistry of Macromolecular Compounds (in Polish); WNT: Warszawa, 1972.
18. Jada, S. S. Ind Eng Chem Prod Res Dev 1983, 22, 14.
19. Kharash, M. M.; Pauson, P.; Nudenberg, W. J. J Org Chem 1953, 38, 322.
20. Polish Standard PN-87/C-89082/11 (Polish version of ISO 2114–1974).
21. Polish Standard PN-87/C-89082/15 (Polish version of ISO 2535–1974).
22. Polish Standard PN-86/C-89082/09.
23. Brojer, Z.; Hertz, Z.; Penczek, P. "Epoxy resins" (in Polish), PWN, Warszawa 1972, p. 462.
24. Polish Standard PN-87/C-89082/12.
25. Pat. USA, US-2 195,362 (1936)
26. Pat. USA, US-2 255,313 (1941)
27. Noller, D.; Stengel, S.; Mageli, O. Mod Plast 1962, 39, 147.
28. Siedow, L. N. Plast Massy 1962, 12, 16.
29. Oleksy, M.; Galina, H. Polimery (Warsaw) 2000, 45, 541.