

Hydroxyalkyl Derivatives of Phenyldiamine as Modifiers for Unsaturated Polyester Resins. II. Derivatives of Phenyl-1,3-diamine

Jerzy Duliban

Faculty of Chemistry, Department of Organic Chemistry, Rzeszów University of Technology, 35-959 Rzeszów, Poland

Received 8 January 2011; accepted 30 December 2011

DOI 10.1002/app.36721

Published online in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: The results are presented on the synthesis of new modifiers and on functioning of these modifiers in unsaturated polyester (UP) resins. The modifiers were obtained by reacting ethylene oxide or propylene oxide with phenyl-1,3-diamine. The effect of the modifiers and cobalt accelerator on the reactivity of resins was studied. When used in the amount of up to 1.50 wt %, the amines substantially (several times)

reduced the gelation time of modified UPs. The reactivity of resins, however, improved in expense of their stability. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: unsaturated polyester resins; amine modifiers; modification of polyester resins; hydroxyalkyl derivatives of *m*-phenyldiamine

INTRODUCTION

Unsaturated polyester (UP) resins, i.e., styrene solutions of an unsaturated alkyd, are usually cured by the system consisting of a radical producing initiator, such as benzoyl peroxide or ketone peroxides with some metal salts, as accelerators. Tertiary aromatic amines also reduce the activation energy of peroxide decomposition and hence allow for a low-temperature initiation of the curing system. These amines are used in UP resins compositions with benzoyl peroxide for room-temperature curing.¹ The most widely reported industrial formulations are the three-component systems consisting of the polyester dissolved in styrene, peroxy initiator, and a tertiary amine.^{2–8} These compositions are very reactive even at temperature as low as 5°C.⁹ The benzoyl peroxide-amine system is often mentioned as the amine-curing system of UP resins.

Accelerators can selectively react with some groups of initiators. In low-temperature curing of UP 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) octanoate or naphthenate in dioctyl phthalate, styrene or mineral spirits is used. Vanadium accelerators are used for fast room temperature curing.⁹

The accelerators most frequently used, however, are aromatic amines, such as *N,N*-dimethylaniline, *N,N*-

diethylaniline, *N,N*-dimethyl-*p*-toluidine, or other aromatic amines. UP resins with dissolved amine have, unfortunately, poor shelf stability, so they should preferably be prepared immediately before use. The formulations where amine is chemically incorporated into polyester chains, already at the stage of its synthesis have somewhat better stability. Then, the activator is uniformly distributed over the bulk. The best possible situation is when the amine has two functional groups capable of reacting with carboxylic acids or anhydrides or with diols. The most convenient situation is to use hydroxyalkylamine groups,^{10–15} preferably with more than two hydroxyalkylamine functional groups capable of being built into polyester.^{15–17} 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.¹⁸ Initiating complex is formed in the first stage from amine and benzoyl peroxide. The complex then decomposes to a cation radical and benzoyl radical.^{19–21}

The aim of this work was to obtain novel ternary amines that can be used as modifiers and preaccelerators for UP resins. They are prepared in reactions of ethylene oxide or propylene oxide with phenyl-1,3-diamine. Preliminary results of a study on their effect on gelation behavior and stability of UP resins are also reported.

EXPERIMENTAL

Materials

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

Correspondence to: J. Duliban (jduliban@prz.rzeszow.pl).

TABLE I
Compounds Used and Their Suppliers

Compound	Supplier
Accelerator co-1 (1.0 wt % solution of co-balt(II) octanate in styrene)	ORGANIKA-SARZYNA, Nowa Sarzyna, Poland
Benzyltriethylammonium chloride	Prepared from triethylamine and benzyl chloride, University of Technology, Faculty of Chemistry POCH, Gliwice, Poland
Hydroquinone, pa	ATOCHEM GmbH, Germany
Luperox K-1, (50 wt % solution of peroxide of butanone in dibutyl phthalate)	Peroxid Chemie GmbH, Germany
Interox BP-50-P1, 50 wt % solution of benzoyl peroxide in dibutyl phthalate	
Phthalic 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-1,3-diamine, pure	SIGMA-Aldrich Chemical, Germany
Styrene, pure	FLUKA, Buchs, Switzerland

Syntheses

Synthesis of benzene-1,3-diamine-*N,N,N',N'*-tetraethane-2,2',2'',2'''-tetraole (modifier A) and benzene-1,3-diamine-*N,N,N',N'*-tetrapropane-2,2',2'',2'''-tetraole (modifier B)

To a 100-mL pressure reactor equipped with a magnetic stirrer 16.20 g (0.15 mole) of phenylene-1,3-diamine was placed together with 26.45 g (44.05 cm³, 0.60 mole) of ethylene oxide or 34.85 g (42.0 cm³, 0.60 mole) of propylene oxide. The content was gradually heated to ca. 85°C while stirring. The temperature slightly increased as the reaction progressed. It was halted when temperature reached 100°C. The time of the process was ca. 60 h for the reaction with ethylene oxide or 110 h for that with propylene oxide. It was ended when the concentration of epoxide groups in the reaction mixture fell down to zero. The products of reaction were resinous substances of black color.

The spectra of the substrate of phenyl-1,3-diamine are presented in Figures 1 and 2, and the description of adsorption IR spectra and resonance signals from ¹H-NMR are presented in Tables II and III.

The chemical structure of the products was confirmed by elemental analysis (Table IV) and by spectroscopic methods: FTIR (Table II, Fig. 1) and ¹H-NMR (Table III, Fig. 2).

Synthesis of modified UP resins

The syntheses of UP resins modified with benzene-1,3-diamine-*N,N,N',N'*-tetraethane-2,2',2'',2'''-tetraole or benzene-1,3-diamine-*N,N,N',N'*-tetrapropane-2,2',2'',2'''-tetraole were carried out as described previously.²²

Curing of UP resins

Description of the gelation process and measurement stability of UP resins measured at 70°C is given in the publication.²²

Analytical methods

The addition reaction of amine to oxiranes was followed by determining the epoxy number of the reaction mixture using hydrochloric acid solution in dioxane.²³ ¹H-NMR spectra of the products were recorded at 25°C in solvent *d*₆-dimethyl sulfoxide and a hexamethyldisiloxane internal standard on a Bruker AM 500 MHz Germany. IR spectra were recorded from a KBr pellets on a PerkinElmer PARAGON 1000 FT spectrometer (Wellesley, MA). Elemental analyses were made on a Fisons EA 1108 apparatus (Carlo-Erba, Stanford, Valencia, CA).

The process of polycondensation leading to UP 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 ca. 50-mg KOH per gram of resin.²⁴ Hydroxyl numbers (HNs) of the alkyds used for preparing UP resins were also measured according to the standard procedures.²⁵

RESULTS AND DISCUSSION

Synthesis of modifiers A and B

The amine-glycol modifiers for UP resins were obtained in one step reaction between one mole of phenylene-1,3-diamine and four moles of ethylene oxide or four moles propylene oxide and obtain tetrahydroxy alcohols containing tertiary amino groups

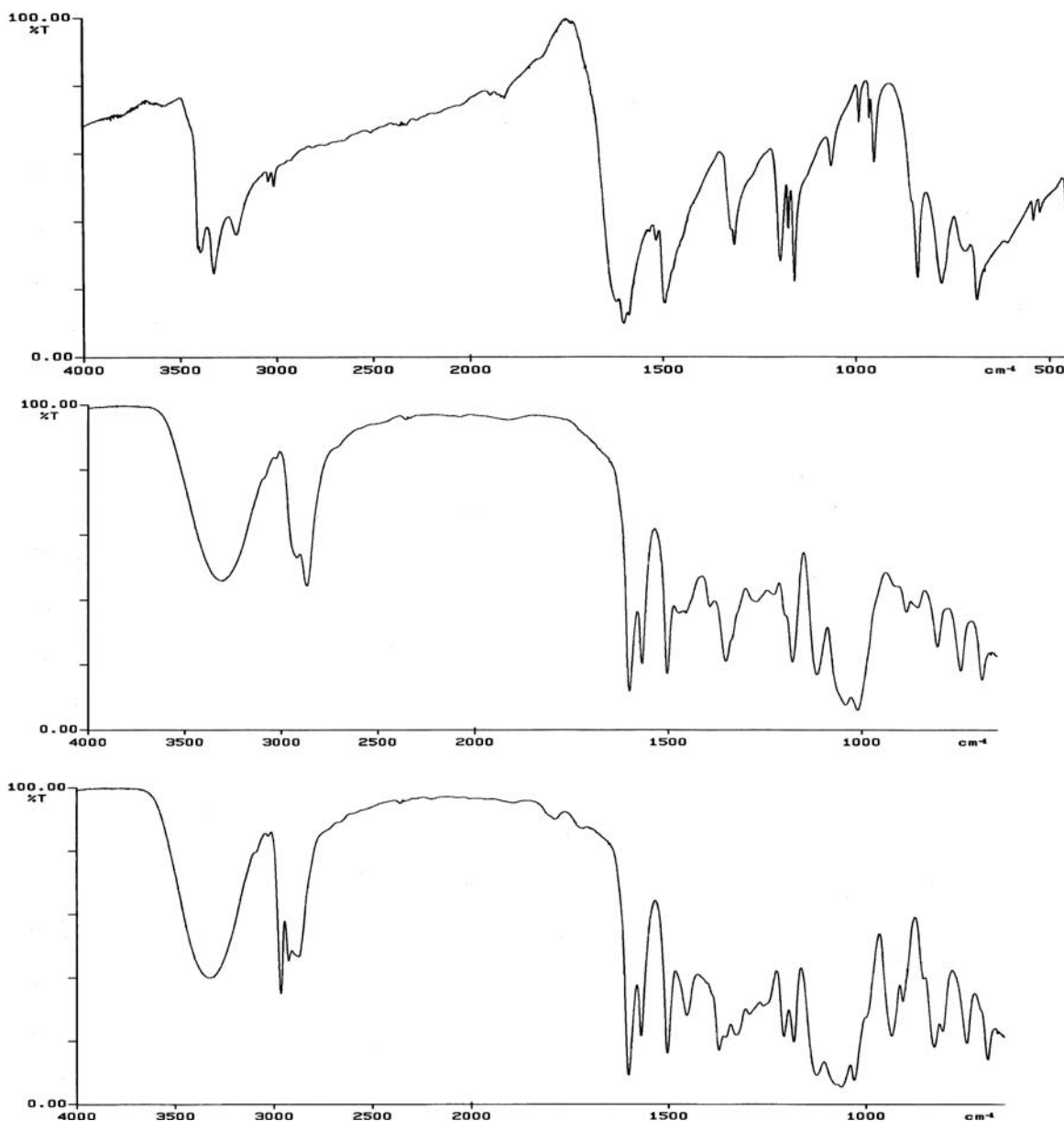
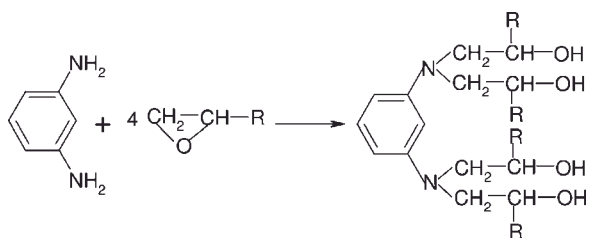


Figure 1 IR spectra of phenyl-1,3-diamine (the upper spectrum), benzene-1,3-diamine-*N,N,N',N'*-tetraethane-2,2',2'',2'''-tetraole (modifier A) (the middle spectrum), and benzene-1,3-diamine-*N,N,N',N'*-tetrapropane-2,2',2'',2'''-tetraole (modifier B) (the lower spectrum).

with nitrogen atoms linked directly to the aromatic ring. The reaction schemes are:



where $R = -H$ or $-CH_3$.

In the reaction of one mole of phenyl-1,3-diamine with four moles of oxirane one obtains an alcohol

with four hydroxyl groups and also two tertiary nitrogen atoms by aromatic ring. The course of reaction confirmed the vanishing IR absorption bands at 3398, 3326, and 3208 cm^{-1} due to stretching vibrations and at 1496 (vibrations in plane), 1323, and 1316 cm^{-1} (vibrations out of plane) due to deformational vibrations of amino groups and appearing new broad bands due to hydroxyl groups at 3509 and 3327 cm^{-1} (associated hydroxyl groups) and bands at 1041 and 1011 cm^{-1} (modifier A) and in the range 1078–1030 cm^{-1} (modifier B) corresponding to stretching vibrations of C–O bonds in primary and secondary alcohols, as well as those at 1179 and 1183 cm^{-1} due to deformational vibrations of

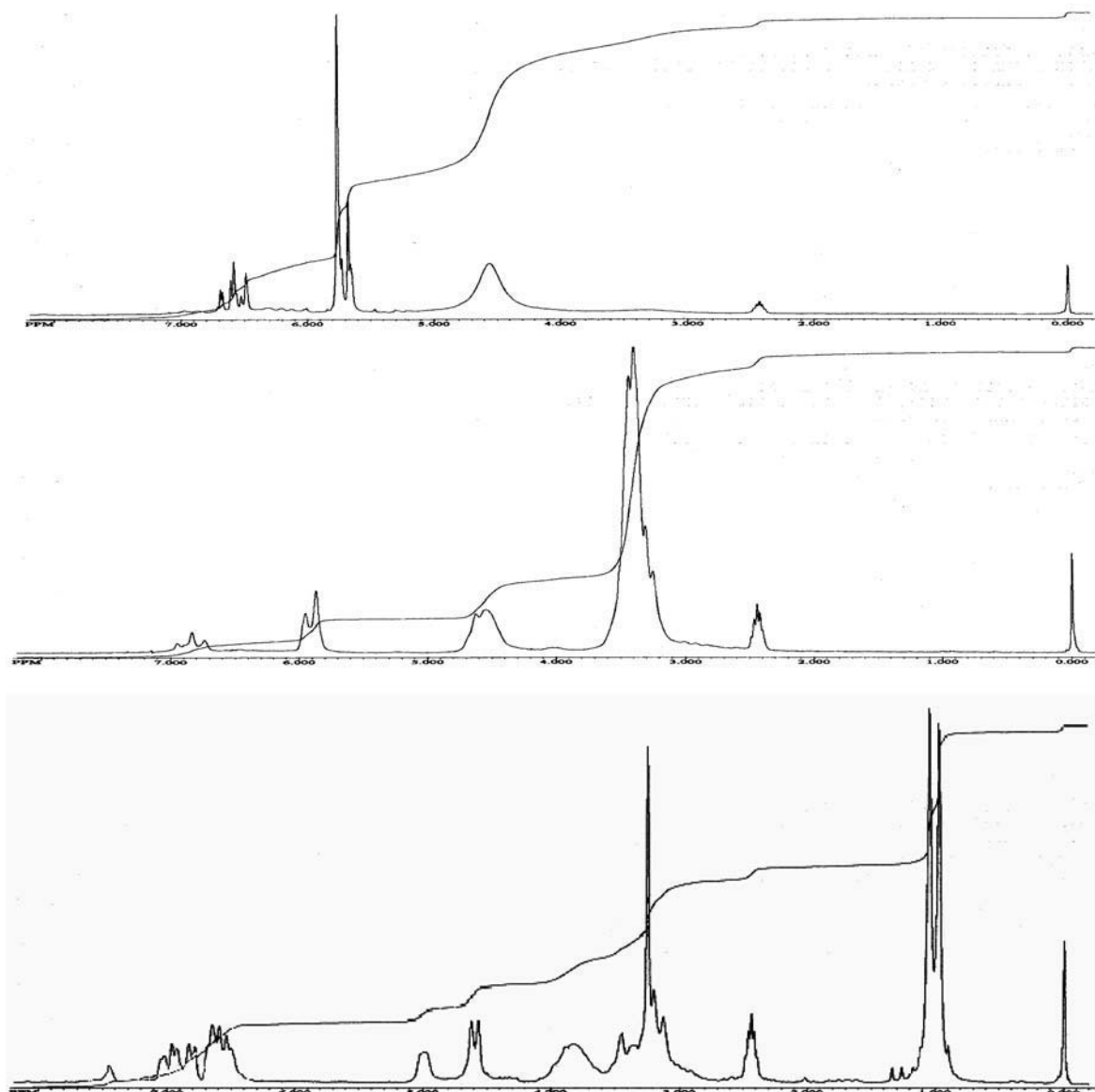


Figure 2 $^1\text{H-NMR}$ spectra of phenyl-1,3-diamine (the upper spectrum), benzene-1,3-diamine- N,N,N',N' -tetraethane-2,2',2'',2'''-tetraole (modifier A) (the middle spectrum), and benzene-1,3-diamine- N,N,N',N' -tetrapropane-2,2',2'',2'''-tetraole (modifier B) (the lower spectrum).

TABLE II
Absorption Bands in IR Spectra of Phenyl-1,3-diamine and Modifiers

Type of vibrations and functional group	Band location (cm^{-1})		
	Phenyl-1,3-diamine	Modifier A	Modifier B
ν_{NH_2}	3398, 3326, 3208	—	—
ν_{OH}	—	3509	3327
$\nu_{\text{C-H}}$ in aromatic ring	3043, 3013	3031	3032
$\nu_{\text{CH}_3}, \nu_{\text{CH}_2}$	—	2921, 2870 ^a	2966, 2927, 2876
$\nu_{\text{C=C}}$, aromatic ring vibrations	1621, 1601, 1589	1601, 1568, 1503	1602, 1570, 1504
$\delta_{\text{CH}_3}, \delta_{\text{CH}_2}$	—	1472, 1456, 1352 ^a	1456, 1373, 1357, 1330
δ_{NH_2}	1496, 1323, 1316	—	—
δ_{OH}	—	1179	1183
$\nu_{\text{C-O}}$, in first or second order alcohol	—	1041, 1011	1078, 1064, 1030
$\delta_{\text{out of plane}}$, aromatic ring vibrations	954, 841, 779, 688	886, 857, 805, 745	936, 908, 820, 807, 745

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

TABLE III
Chemical Shifts of Protons in $^1\text{H-NMR}$ Spectra of Phenyl-1,3-diamine and Products of Reaction

Name of chemical compound	Chemical shifts (δ ppm)	Group
Phenyl-1,3-diamine	4.50	$-\text{NH}_2$
Benzene-1,3-diamine- <i>N,N,N',N'</i> -tetraethane-2,2',2'',2'''-tetraole (modifier A)	6.60–5.95 and 6.45–6.75	Aromatic protons
	3.20–3.70	$>\text{N}-\text{CH}_2-\text{CH}_2-\text{O}-$
	4.60–4.75	$-\text{OH}$
Benzene-1,3-diamine- <i>N,N,N',N'</i> -tetrapropane-2,2',2'',2'''-tetraole (modifier B)	5.80–6.00 and 6.80–7.00	Aromatic protons
	0.80–1.20	$-\text{CH}_3$ normal product
	1.20–1.35	$-\text{CH}_3$ anomol product
	2.80–3.60	$>\text{N}-\text{CH}_2-$
	3.60–4.15	$-\text{O}-\text{CH}<$
	4.60 and 4.95	$-\text{OH}$
	6.35–6.75 and 6.80–7.20	Aromatic protons

hydroxyl groups (Fig. 1). Similarly, in $^1\text{H-NMR}$ spectra (Fig. 2), the signal at 4.50 ppm from amine protons disappears and appears instead a signal from 4.60 to 4.75 ppm from hydroxyl protons in 2-hydroxyethyl groups (modifier A) or two signals at 4.60 and 5.00 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 3.20 to 3.70 ppm, whereas for modifier B three extra peaks from methyl protons are seen in the spectra in two ranges: the first one from 0.80 to 1.20 ppm for methyl protons in normal product and the second one from 1.20 to 1.35 ppm for methyl protons in anomol product, beside methylene protons signal at 2.90–3.60 ppm, as well as from methine proton at 3.60–4.10 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 oxygen in hydroxyl group, which is stronger than that from the nitrogen at aromatic ring. The signals from 5.80 to 7.00 ppm and from 6.40 to 7.20 ppm due to aromatic protons appear in spectra of modifier A and modifier B, respectively.

Gelation time for modified UP resins

The modifiers A and B prepared as described above. Modifier A, benzene-1,3-diamine-*N,N,N',N'*-tetraethane-2,2',2'',2'''-tetraole, and modifier B, benzene-

1,3-diamine-*N,N,N',N'*-tetrapropane-2,2',2'',2'''-tetraole, were built into the structure of UP resins and their effects on gelation time and stability of the resin was observed. The reference resin was prepared by condensation of phthalic and maleic anhydride with propane-1,2-diole (propylene glycol) and 3-oxapentane-1,5-diole (diethylene glycol).² This is a typical construction-type resin with 3-oxapentane-1,5-diole (diethylene glycol) used as a monomer 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 preliminary experiment not to exceed 2.0 mol %. This was sufficiently small quantity so that no gelation at polyesterification stage was observed in the presence of both multifunctional modifiers. In fact the highest amount of modifier used was 1.50 mol %, since any higher concentration did not result in significant changes of gelation time.

By using normalized procedures, the time of gelation at 25°C (time until air bubble was arrested in the test tube filled with resin containing initiator)²⁶ and the stability of resins at 70°C (time until air bubble was arrested in the test tube filled with resin containing no initiator)²⁷ were determined for all UP resins. The standard initiator for the cobalt-curing of UP resins was used. Namely, the system consisted of cobalt(II) octanate as accelerator and butanone peroxide initiator dispersed in dibutyl phthalate (Luperox K-1). The attempt of using benzoyl peroxide dispersed in dibutyl phthalate (Interox BP-50-P1)

TABLE IV
Elemental Analysis of Modifiers

Compound	%C		%H		%N	
	Calcd.	Found	Calcd.	Found	Calcd.	Found
Modifier A	59.14	58.91	8.51	8.49	9.85	9.51
Modifier B	63.50	63.81	9.47	9.38	8.23	8.11

TABLE V
Properties of UP Resins with Amine Modifiers Incorporated into Their Chemical Structure

Kind of modifier	Number of resin	Mole of amine accelerating groups/kg resin ($\times 10^{-3}$)	Wt % of modifier	AN (mg/KOH/g)	HN (mg/KOH/g)	Stability of resins at 70°C		Color
						Without ammonium salt (h)	With ammonium salt (h)	
1	2		3	4	5	6	7	8
None	1	0.000	0.00	45.23	55.18	825	2658	Colorless
Modifier A	2	0.113	0.01	43.75	54.39	447	1554	Yellowish
	3	0.226	0.02	46.63	55.96	444	1434	Yellowish
	4	0.565	0.05	43.02	51.66	441	1404	Yellow
	5	1.130	0.10	46.98	56.62	434	1389	Yellow
	6	2.825	0.25	48.51	58.28	381	1239	Dark yellow
	7	5.651	0.50	48.16	58.27	270	1059	Light brown
	8	8.477	0.75	43.62	52.21	162	969	Brown
	9	11.302	1.00	45.73	55.18	102	939	Brown
	10	14.128	1.25	42.46	51.57	90	879	Dark brown
	11	16.954	1.50	41.35	49.59	72	579	Brown black
Modifier B	14	0.094	0.01	48.78	58.65	669	1364	Yellowish
	15	0.189	0.02	46.86	48.39	645	1128	Yellowish
	16	0.472	0.05	42.48	51.07	612	1026	Yellow
	17	0.944	0.10	47.37	56.72	567	936	Yellow
	18	2.360	0.25	47.63	57.34	438	818	Dark yellow
	19	4.720	0.50	45.45	54.65	267	708	Light brown
	20	7.080	0.75	46.07	55.39	159	546	Brown
	21	9.440	1.00	44.68	53.26	111	456	Brown
	22	11.800	1.25	46.15	55.33	111	300	Dark brown
	23	14.160	1.50	46.52	55.98	114	192	Brown black

Modifier A, benzene-1,3-diamine-*N,N,N',N'*-tetraethane-2,2',2'',2'''-tetraole; modifier B, benzene-1,3-diamine-*N,N,N',N'*-tetrapropene-2,2',2'',2'''-tetraole.

was unsuccessful for too long gelation times. The times of gelation were therefore measured for cobalt-curing system consisting of butanone peroxide (Luperox K-1) initiator and cobalt(II) octanoate accelerator. A series of curing experiments with cobalt curing system was performed with an addition of 0.3 wt % of benzyltriethylammonium chloride. As the amount of modifiers increased, the color of modified resins became darker and darker, from yellowish, yellow and dark yellow at the concentration of modifiers A and B equal about 0.01–0.25 wt % to light brown, brown, dark brown, and brown black at the concentration from 0.50 to 1.50 wt %. The UP resins were synthesized by carrying condensation of the components at 165–200°C under nitrogen until the AN of reaction mixture dropped down below 50-mg KOH per g of resin.²⁴ The results of stability tests are presented in Table V.

Stability of shelf life of UP resins reduced with increasing amount of modifiers A or B, which are added to a polycondensation. This was the result of the presence of tertiary amino groups at the aromatic ring built into polyester chain, the groups that are known for their significant reduction of threshold energy of double bond decomposition or cleavage. Even in absence of initiator the resin gelled

when heated to 70°C. In comparison, however, to the resins modified with 2-hydroxyalkyl derivatives of phenyl-1,4-diamine²⁰ the stability of these resins, as measured under identical conditions, was much improved. A significant decrease in stability was observed for the resins modified with 1.00–1.50 wt % of built-in modifiers A and B. The gelation was the more rapid the higher was the modifier contents. Generally, irrespective of the type of modifier A or B, the difference between the stability of resin with the lowest (0.01 wt %), and the largest (1.50 wt %) modifier content was about six times.

Gelation times for the modified resins are shown in Figures 3 and 4. In Figures 5 and 6, 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 reactivity and stability measurements were carried out by changing: the content of modifiers built into the structure of UP resins (Figs. 3 and 4), the amount of cobalt accelerator (Figs. 5 and 6).

The results lead to the conclusion that incorporation of modifier A into the structure of resin in the whole range of concentrations from 0.01 to 1.50 wt % results in faster gelation of resin compared with the resin without modifier. However, in the case of

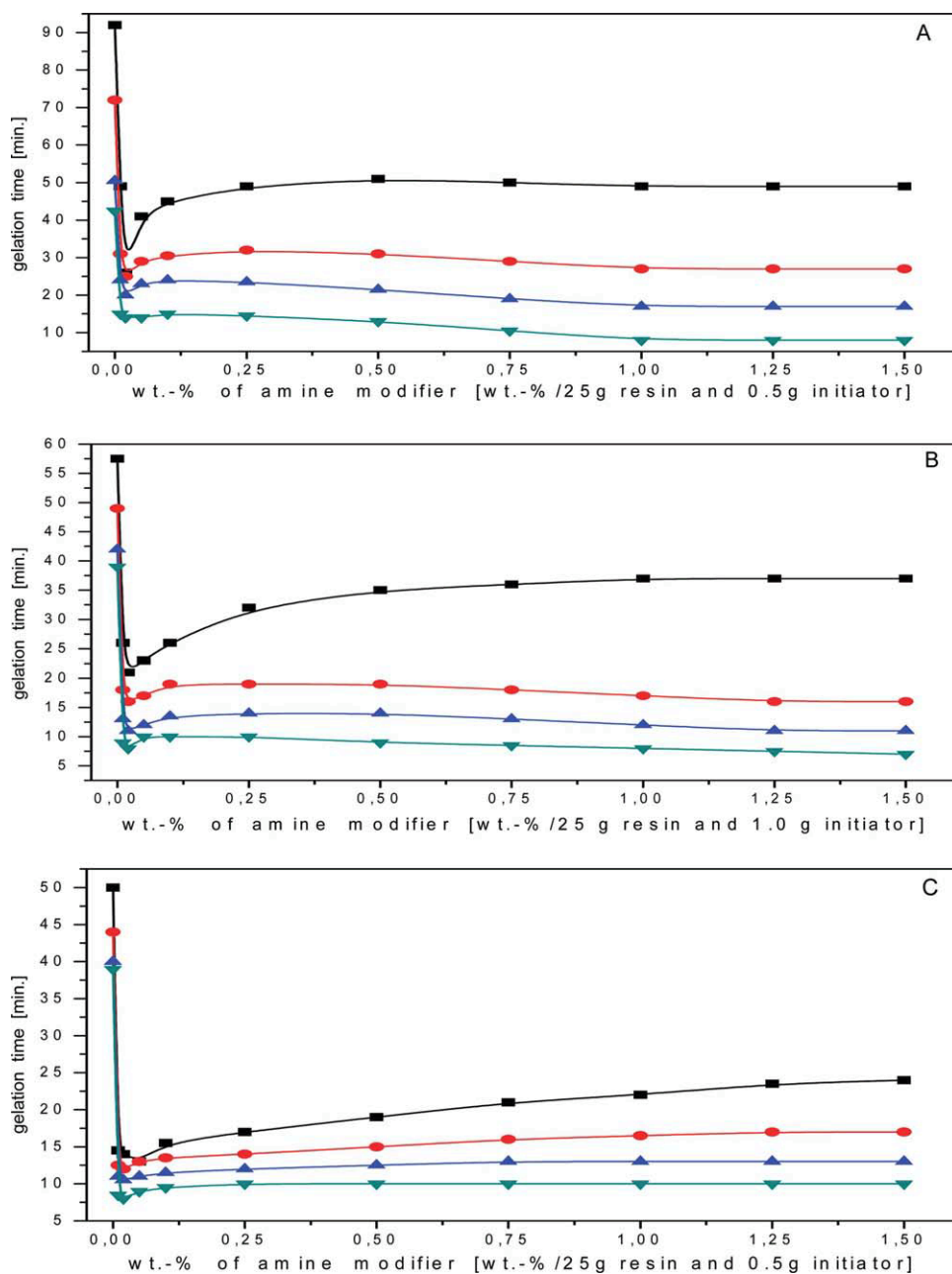
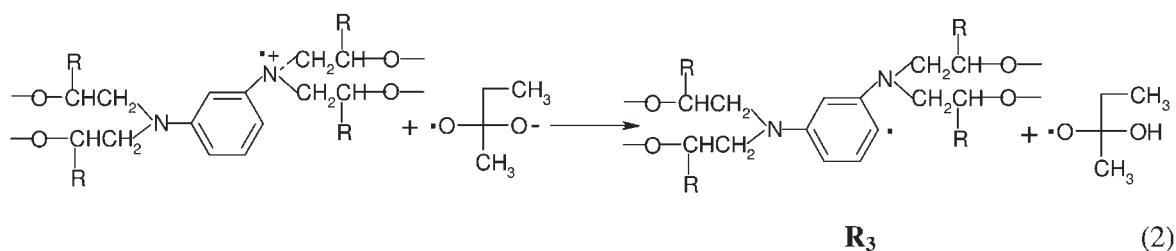
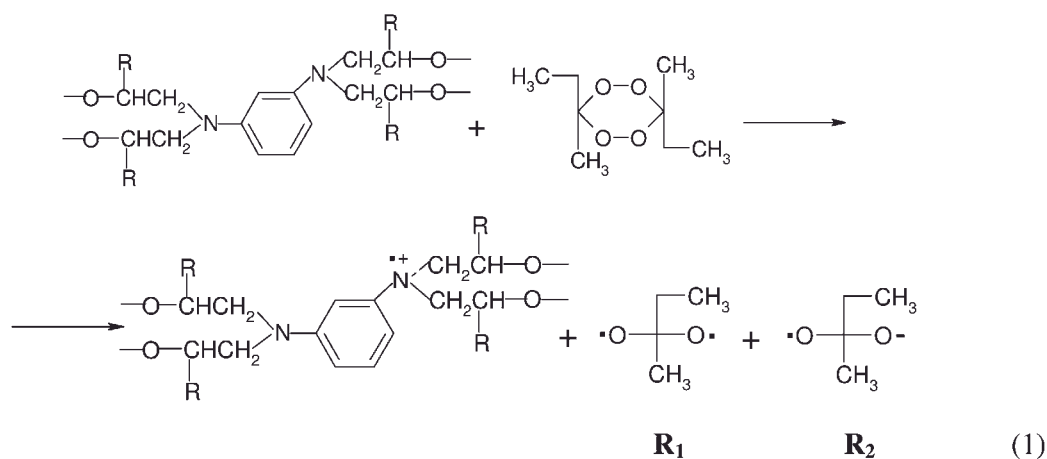


Figure 3 Gelation times of UP resins with various amount of chemically incorporated modifier A. To 25 g of resin, 0.5 g (plot A), 1.0 g (plot B), and 1.5 g (plot C) of butanone peroxide initiator was added; the amounts of cobalt accelerator solution: (■), 0.10 cm³; (●), 0.15 cm³; (▲), 0.25 cm³; (▼), 0.50 cm³. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

modifier B, a significant influence on the changes in gelation time had addition of cobalt accelerator (1.0% solution of cobalt(II) octanoate in styrene). An extension of gelation time for the resins with modifier B can be observed, especially for a system, which contains a small amount of cobalt accelerator (0.10 cm³/25 g of modified resins).

The reason might be the high concentration of amine. The modifier acts as a scavenger of radicals

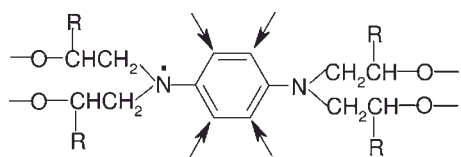
formed from initiator. As follows from literature data,^{19,28–31} amines may act not only as promoters of initiator decomposition but also as stabilizers preventing radicals formed naturally to propagate into a chain reaction in organic systems. Also the amines built into resin may react with macroradicals, thus reducing the rate of polymerization. The process may proceed according to the following scheme [eqs. (1) and (2)]:



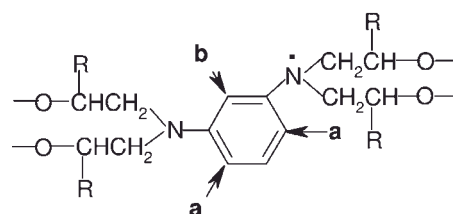
where: R = -H or -CH₃

As a result of these reactions diradicals (**R₁**), anion radicals (**R₂**), and also mesomerically stabilized radicals formed from the built-in polyester chain aminomodifier (**R₃**) are formed from peroxide molecules. These radicals initiate the process of polymerization.

By comparing the effects of the modifiers derived from phenylene-1,3-diamine with those derived from phenylene-1,4-diamine (cf. Ref. ²²), it should be noted that in the case of hydroxyalkyl derivatives of phenylene-1,4-diamine, there are more active sites available at the aromatic ring, capable of initiating polymerization and all of these active sites are equally probable:



Radicals generated in each of these places may attack double bonds in the chain of unsaturated resin or in styrene with equal probability, thus beginning the process of gelation of UP resin. In the case of hydroxyalkyl derivatives of phenylene-1,3-diamine, there are limited chances for radicals to react because of unfavorable location of two bulky substituents at nitrogen atoms creating a steric hindrance. Only three accessible places exist:



Strictly speaking, from stereochemical point of view, only two sites are available (denoted with letter **a**). Any activity of a radical in position **b** seems much limited because of the hindrance by hydroxyalkyl groups. The extra hindrance exerts also methyl groups in the 2-hydroxypropyl substituents of modifier B. This seems to be the reason for much longer gelation times of resins modified with this compound, particularly when small amount of cobalt accelerator is applied (Fig. 3). The rate of radical generation is then reduced hence leading to slower gelation of polyester resins. Somewhat higher concentration of cobalt salts is needed to accelerate radical generation and reduce the gelation time (Fig. 4).

The resins modified with benzene-1,3-diamine-*N,N,N',N'*-tetraethane-2,2',2'',2'''-tetraole (modifier A) do not show this effect. The lack of bulky methyl group in the substituent of modifier A provides an easier access to both reactive sites: **a** and **b** (Fig. 3). An increase in cobalt(II) content substantially

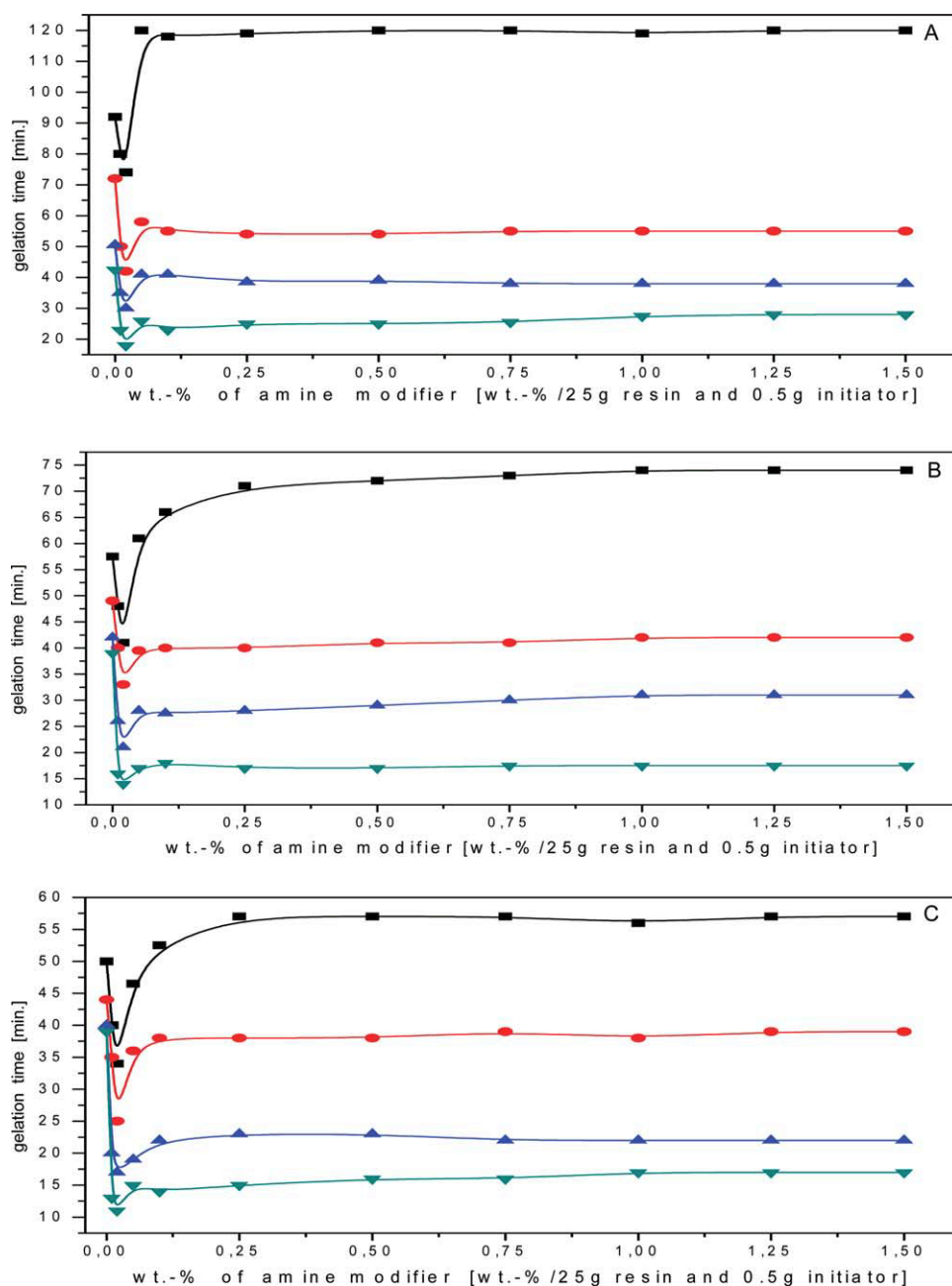
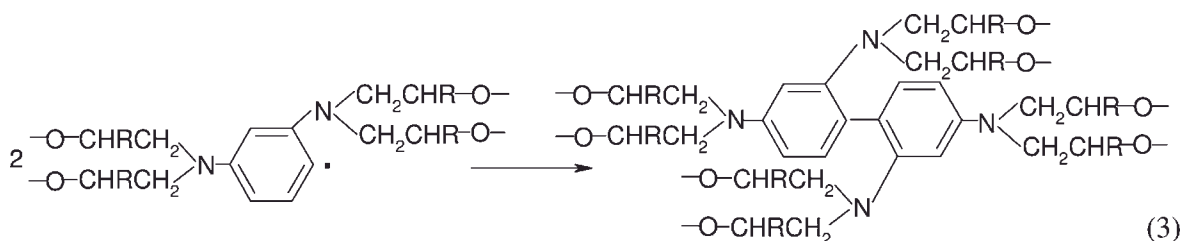


Figure 4 Gelation times of UP resins with various amount of chemically incorporated modifier B. To 25 g of resin, 0.5 g (plot A), 1.0 g (plot B), and 1.5 g (plot C) of butanone peroxide initiator was added; the amounts of cobalt accelerator solution: (■), 0.10 cm³; (●), 0.15 cm³; (▲), 0.25 cm³; (▼), 0.50 cm³. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reduces gelation time, since more reactive aromatic radicals can be formed. On the other hand, at the smallest amount of cobalt accelerator (0.10 cm³/25 g

of resin), the presence of aromatic radicals becomes large and the reaction of curing becomes hindered because of inhibition due to the process:



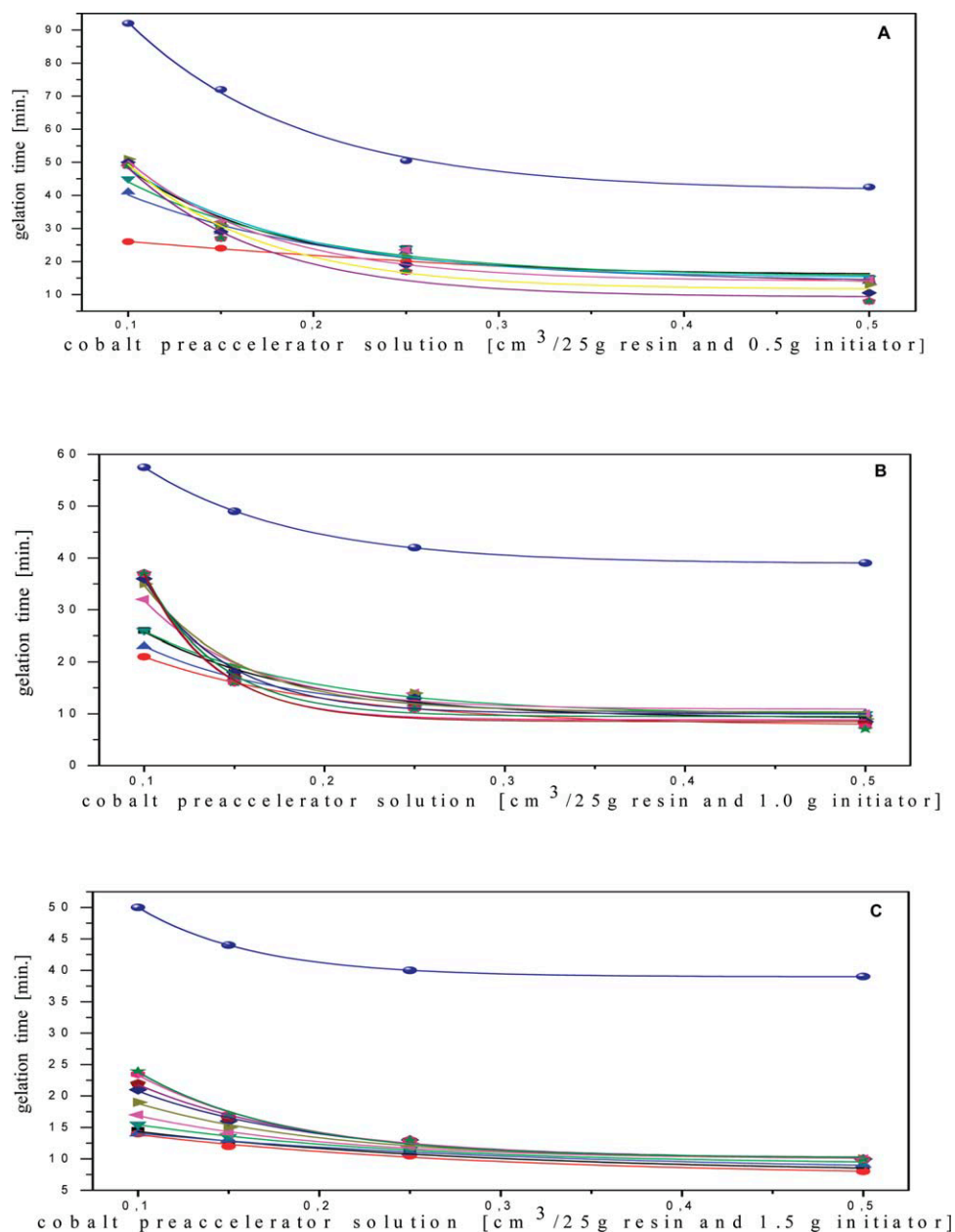


Figure 5 Gelation times of UP resins with various amount of cobalt accelerator solution and various amounts of chemically incorporated modifier A. To 25 g of resin, 0.5 g (plot A), 1.0 g (plot B), and 1.5 g (plot C) of butanone peroxide initiator was added; the amounts of chemically incorporated modifier 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 %; (●), 0.0 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Four series of experiments were performed with 0.10, 0.15, 0.25, and 0.50 cm³ of cobalt accelerator. The times of gelation for unmodified resin were 92, 72, 50.5, and 42.5 min, respectively, in the presence of the normative amount of initiator (i.e., 0.5 g of initiator per 25 g of resin).²⁶ The results for preaccelerated resins are plotted against the percentage of the modifier added are shown in Figures 3 and 4. It can be seen from the plots that the shortest gelation times are when the amount of modifiers A or B changes from 0.01 to 0.25 wt % with the minimum at 0.02 wt %.

Above ca. 0.25 wt % of the modifiers the gelation time remains on a more or less constant level.

When the amount of initiator was doubled (i.e. increased to 4 wt % of the resin),²⁶ in the presence of the same concentration of cobalt(II), the gelation time of modified resins reduced by ca. 30–45% (cf. curves A and B in Figs. 3 and 4). With an increase of cobalt concentration, however, gelation times became less and less reduced, both for the systems cured with the normative (0.5 g) and above normative amount of peroxide initiator; the plots became

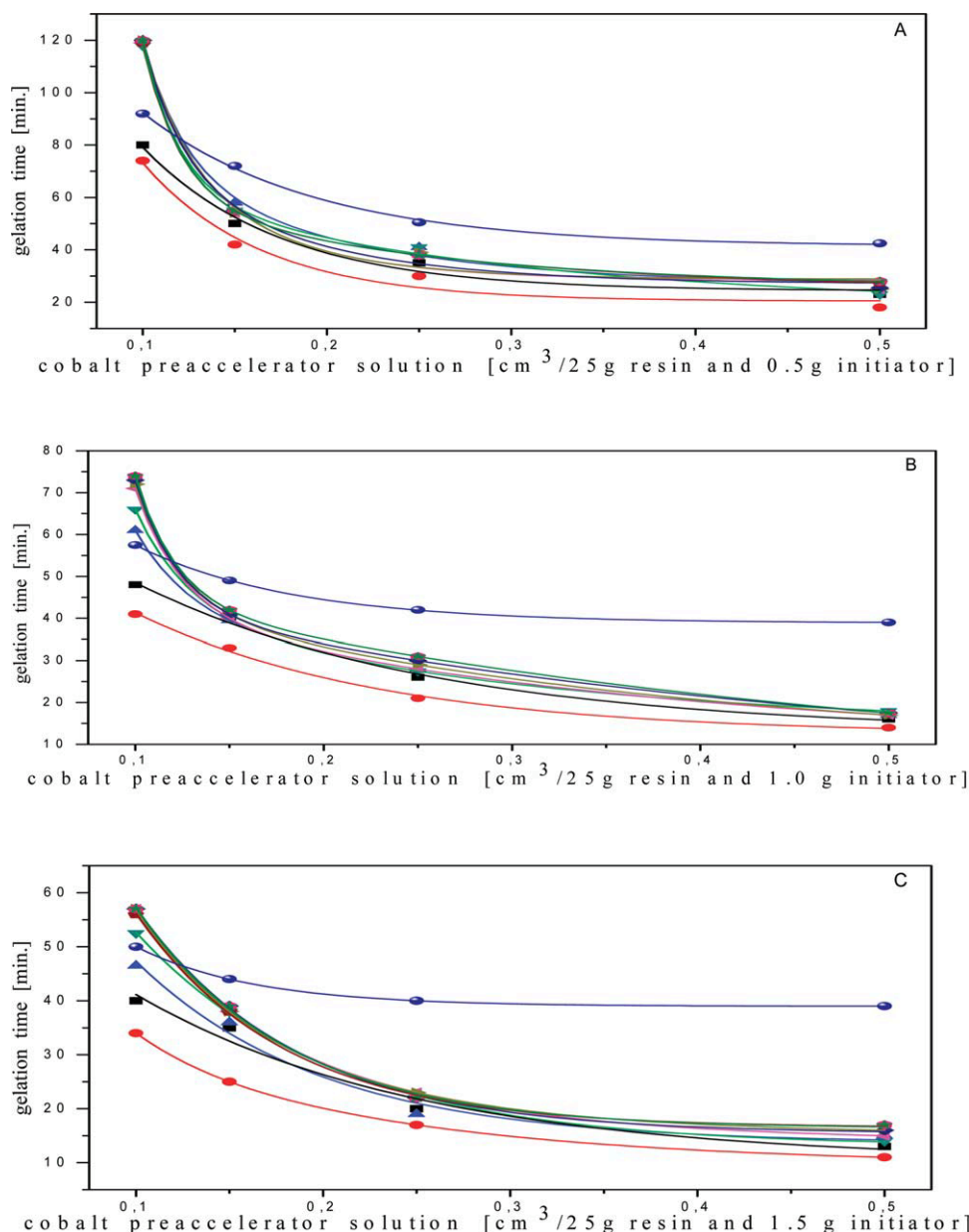


Figure 6 Gelation times of UP resins with various amounts of cobalt accelerator solution and various amounts of chemically incorporated modifier B. To 25 g of resin, 0.5 g (plot A), 1.0 g (plot B), and 1.5 g (plot C) of butanone peroxide initiator was added; the amounts of chemically incorporated modifier 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 wt %; (○), 0.0 wt %. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

flat. This was the reason why the difference between the shortest and longest gelation times in Figures 5 and 6 diminished with increasing cobalt(II) content.

The quickest in gelation were the resins with incorporated ca. 0.02 wt % of each modifier. An increase in the amount of initiator to 1.5 g (6% of resin) did not change gelation time of the resin; the reduction was only about ca. 10% (with respect to the system with 1.0 g of initiator per 25 g of resin) (cf. plot C in Figs. 3 and 4). Thus, by doubling the amount of initiator from 2 to 4% the reduction of gelation time was ca. 50%, whereas further increase of

initiator to 6% resulted in only a small reduction of the time of curing.

The reduction of resin shelf stability, as measured according to standard procedures²⁷ (cf. Table V, column 6), is a serious disadvantage of resins modified with various additives. The same applies to the resins modified with modifiers A or B, particularly those containing 1.00–1.50 wt % of the modifiers. Tertiary aromatic amines built in the polyester chains generally reduce both gelation time and shelf stability. By following the changes in the normative stability, one can classify the resins into those of

TABLE VI
Comparison of Gelation Times for UP 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	24.0	50.0	35.0	48.0
0.02	20.0	57.0	30.0	55.0
0.05	23.0	52.0	41.0	49.0
0.10	24.0	47.0	41.0	47.0
0.25	23.5	35.0	38.5	42.0
0.50	21.5	28.0	39.0	40.0
0.75	19.0	21.0	38.0	39.0
1.00	17.0	20.0	38.0	39.0
1.25	17.0	19.0	38.0	39.0
1.50	17.0	19.0	38.0	39.0

good stability, i.e., those containing 0.01–0.50 wt % of modifiers A or B with the stability time at 70°C from 447 to 270 h or 669 to 267 h, respectively, and those of small stability with time from 162 to 72 h (modifier A) and from 159 to 111 h (modifier B) (cf. Table V, column 6).

Figures 5 and 6 contain also the plots illustrating the dependence of gelation time on cobalt concentration for unmodified resins. Clearly, for all resins with a built-modifier A (Fig. 5) gelation times are significantly shorter as compared with those for the unmodified ones. As can be seen in Figure 6, the effect of built-in modifier B is weaker and the differences between gelation times for resins modified and unmodified are smaller than in the case of modifier A. This seems to be a result of significantly slower gelation process due to the size of 2-hydroxypropyl substituent in modifier B.

The stability of UP resin can be improved by using quaternary ammonium salt stabilizers.^{31,32} The stability of resins at 70°C (Table V, columns 6 and 7) improved in the presence of the ammonium 0.3 wt % benzyltrimethylammonium chloride stabilizer, but to the extent again depending on the amount of aromatic amine modifier built into resin. Again, the stability of resins containing modifier built into polyester chain and the stabilizer differed depending on the amount of the modifier. Generally, the improvement of stability caused by the ammonium stabilizer was better for modifier A than for modifier B. The stability time increased by 2–9 times, the highest increase being observed for resins with 0.75–1.50 wt % of either modifier. The character of stability dependence on the amount of amine built into resin did not change in the presence of quaternary ammonium salt.

Gelation times were measured for the resins stabilized with benzyltrimethylammonium chloride and initiated with a selected curing system consisting of 0.25 cm³ of cobalt accelerator and 0.5 g of peroxide per 25 g of resin. The results are shown in Table VI. The gelation times were increased for resins containing from 0.01 to 0.50 wt % of built-in modifiers A or B. With more modifiers, the resulting differences in gelation times for resins containing, or not, the ammonium stabilizer were rather small.

To summarize, for UP resins containing built-in modifier A, much narrower range of gelation times is observed, as compared with those containing modifier B. The gelation times for the former changed from 17 to 51 min for the normative content of initiator (2 wt %) and depend on the amount of cobalt(II) accelerator (0.10–0.50 cm³ per 25 g of resin). In the case of modifier B, the respective gelation times were 18–120 min. The use of an overnormative amount of initiator (4.0 or 6.0 wt %) reduced gelation times, as expected.

The three parameters have a major effect on the gelation time for UP resins. These are 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 least important seems to be 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. In Table VI are listed the gelation times of the compositions containing ammonium salt stabilizer with 2.0 wt % of

initiator and 0.25 cm³ of cobalt accelerator per 25 g of resin. The gelation time are twice as long for the resin containing from 0.01 to 0.1 wt % as a modifier A and B, while above this concentration the rate of gelation of modified resin remains almost identical. Gelation times are twice as long for the resins containing from 0.01 to 0.1 wt % of either A or B modifier, as compared with unmodified resins, whereas above these amounts, gelation times are almost identical.

CONCLUSIONS

1. Aromatic ring containing amine modifiers for UP resins were obtained by reacting *m*-phenylenediamine with oxiranes: ethylene or propylene oxide (modifier A or B, respectively).
2. The modifier A introduced into resins structure at the stage of polycondensation effectively reduced gelation time of the resin in the cobalt curing system.
3. The modifier B reduced the gelation time in the cobalt curing system into a much smaller extent.
4. The reduction of gelation time was observed in the presence of, at most, 0.02 wt % of the modifiers. For resins modified with 0.05–1.50 wt % of modifier B 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 0.02 wt % of either modifier was used.
5. By using more than ca. 0.25 cm³ of cobalt accelerator per 25 g of resin did not improve the resin reactivity (i.e. reduction of gelation time), irrespectively of the amount of initiator.
6. By introducing ammonium salt stabilizer (benzyltriethylammonium chloride) to the modified UP 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 for resins containing from 0.01 to 0.1 wt % modifiers A and B. Again the reactivity depended on the amount of the built-in amine modifier.

References

1. Kłosowska-Wońkiewicz, Z.; Jedliński, Z. *Polimery* 1970, 15, 1.
2. Conrad, W. Ger. Pat. (East) DD-227711 (1986); CA 104, 208379d (1986).
3. Konishi, A.; Irie, T.; Ariga, N.; Sekiguchi, H. Jpn. Pat. JP-2250025 (1987). Available at: www.derwent.com.
4. Konishi, A.; Irie, T.; Ariga, N.; Sekiguchi, H. Jpn. Pat. JP-1026653 (1989). Available at: www.derwent.com.
5. Zbanatskaya, N.; Veselovskij, R. A.; Ryzhevskij, M. E.; Tsedrik, Y. N.; Kochkov, Y. P.; Laznaya, N. I. Ukrain. Pat. SU-1467137 (1990). Available at: www.derwent.com.
6. Meier, H. M.; Dhein, R.; Wikel, J.; Klein, G.; Kloeker, W. Ger. Pat. DE-3345102 (1985); CA 1985, 103, 196858y.
7. Akimoto, H.; Narasaki, S.; Miyamoto, R. Jpn. Pat. JP-3149256 (1981). Available at: www.derwent.com.
8. Sato, S. Jpn. Pat. JP-3188033 (1981). Available at: www.derwent.com.
9. Kłosowska-Wońkiewicz, Z.; Królikowski, W.; Penczek, P. *Polyester Resins and Laminates* (in Polish); WNT: Warsaw, 1986.
10. Beck, M.; Hombach, R.; Meckel, W. Ger. Pat. DE-3643788 (1988); CA 1989, 110, 39557b.
11. Birkmeyer, W. J.; Saunders, J. B., Jr.; Schilliger, W. J. U.S. Pat. 4,775,597 (1988); CA 1989, 110, 40630b.
12. Denis, J.; Garapon, J.; Damin, B.; Leger, R. Eur. Pat. EP-271385 (1988); CA 1989, 110, 98628y.
13. Nishikawa, Y.; Kihara, S. Jpn. Pat. JP-9207925 (1985). Available at: www.derwent.com.
14. Duliban, J. *Macromol Mater Eng* 2001, 286, 624.
15. Duliban, J. *Polimery* (Warsaw) 2004, 49, 774.
16. Duliban, J. *Macromol Mater Eng* 2006, 291, 137.
17. Duliban, J. *Macromol Mater Eng* 2007, 292, 1126.
18. Jada, S. S. *Makromol Chem* 1982, 183, 1763.
19. Horner, L.; Schloenk, E. *Angew Chem* 1949, 61, 711.
20. Kłosowska-Wońkiewicz, Z.; Penczek, P.; Gąsior, R. *Plaste Kautschuk* 1976, 23, 251.
21. Tsuchida, E.; Tomoto, T. *J Chem Soc Jpn Ind Chem Sect* 1970, 73, 2040.
22. Duliban, J. *J Appl Polym Sci* 2011, 120, 311.
23. Brojer, Z.; Hertz, Z.; Penczek, P. *Epoxy Resins* (in Polish); PWN: Warszawa, 1972; p 462.
24. Gajewska, T.; Truszkowska, Z. Polish Standard PN-87/C-89082/11 (Polish version of ISO 2114–1974), Institute of Industrial Chemistry, Warsaw.
25. Gajewska, T. Polish Standard PN-87/C-89082/12, Institute of Industrial Chemistry, Warsaw.
26. Gajewska, T.; Truszkowska, Z. Polish Standard PN-87/C-89082/15 (Polish version of ISO 2535–1974), Institute of Industrial Chemistry, Warsaw.
27. Truszkowska, Z. Polish Standard PN-86/C-89082/09, Institute of Industrial Chemistry, Warsaw.
28. Carleton, E. U.S. Pat. 2,195,362 (1936).
29. CIBA Aktiengesellschaft. U.S. Pat. 2,255,313 (1941).
30. Noller, D.; Stengel, S.; Mageli, O. *Mod Plast* 1962, 39, 147.
31. Siedow, L. N. *Plast Massy* 1962, 12, 16.
32. Oleksy, M.; Galina, H. *Polimery* (Warsaw) 2000, 45, 541.