

Novel Amine Preaccelerators for Polyester Resins

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ABSTRACT: The reactions between *N,N*-dimethyl-*p*-phenylenediamine and ethylene or propylene oxide were carried out to obtain 3-[*p*-(*N,N*-dimethylamino)phenyl]-3-azapentane-1,5-diol and 4-[*p*-(*N,N*-dimethylamino)phenyl]-4-azaheptane-2,6-diol, respectively. The structures of the products were determined using elemental analysis, ¹H-

NMR and IR spectroscopy techniques. The diols were incorporated into unsaturated polyester resins. The time of gelation and stability of the resins was observed. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2973–2976, 2003

Key words: polyesters; stabilization; resins; gelation

INTRODUCTION

Tertiary aromatic amines decompose peroxide compounds to yield radicals and therefore allow for a low-temperature copolymerization of polyester resins (solution of unsaturated polyester in a vinyl monomer). The mechanism of the process was described by Horner and Schlenk.¹

N,N-dimethylaniline, *N,N*-diethylaniline, and *N,N*-derivatives of *p*-toluidine are commonly used as accelerators in the low temperature curing of unsaturated polyesters.^{2–7} The amine accelerator and an initiator are added to the resin to initialize the curing process. To avoid the disadvantage of using three-component mixtures, the polyester resins can be preaccelerated at the manufacturing stage. Unfortunately, preaccelerated resins containing amines have poor stability. Resins with an accelerator chemically incorporated into the resin structure have better stability. Examples include 3-phenyl-3-azapentane-1,5-diol (*N,N*-bis(2-hydroxyethyl)aniline)⁸ that can be used as a glycol component of the polyester. The other glycol components are partially replaced by the mentioned compound in the polycondensation mixture. One can also find resins with the glycol component completely replaced by 3-phenyl-3-azapentane-1,5-diol.⁹ The resulting resins are particularly water-resistant.

Another method of incorporating a tertiary amine into the polyester chain involves using esters of aromatic dicarboxylic acids substituted in the meta-position by a tertiary amine group. These compounds can be transesterified by a glycol and then condensed with a mixture of maleic anhydride and phthalic anhydride,^{10,11}

The resins with an incorporated cure accelerator are relatively reactive at room temperature when benzoyl peroxide is added. They are applied in manufacturing glues, putties, fillers, laminates, etc.

It seems that an application of compounds containing two tertiary amine groups should significantly accelerate the decomposition of acyl peroxide and hence reduce the time of gelation of polyester resins at room temperature. Because of this, some efforts have been made to obtain *N,N*-bis(hydroxyalkyl) derivatives of *N,N*-dimethyl-*p*-phenylenediamine and incorporate them into polyester chains. Their influence on the time of curing and the stability of resins has also been studied.

EXPERIMENTAL

Synthesis of *N,N*-bis(hydroxyalkyl) derivatives of *N,N*-dimethyl-*p*-phenylenediamine

In a three-necked round-bottomed flask (250 cm³) equipped with a reflux condenser (when ethylene oxide was used, a salt-ice mixture was used as the cooling medium), a thermometer, and a stirrer, 13.6 g (0.1 mole) of *N,N*-dimethyl-*p*-phenylenediamine (pure, Aldrich, Germany) and 8.8 g (0.2 mole) of ethylene oxide (EO) (pure, Fluka, Switzerland) or 11.6 g (0.2 mole) of propylene oxide (PO) (pure, Fluka, Switzerland) were mixed. The content was heated to the boiling point (27°C for the reaction with EO or 37°C for PO). The temperature increased to 100°C as the reaction progressed. The mixture was heated until no more oxirane condensed on the condenser walls. The end of the reaction was established by determining the epoxy number of the mixture. Hydroxyethyl or hydroxypropyl derivatives of *N,N*-dimethyl-*p*-phenylenediamine were the products. The derivatives were then incorporated into polyester chains.

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Synthesis of polyester resins

In a round-bottomed flask (500 cm³) equipped with a stirrer, an inlet to inert gas, a thermometer, a Liebig condenser and a calibrated distillate collector, 76.1 g (0.5 mole) of phthalic anhydride (pure, Nitrogen Plants, Kędzierzyn, Poland), 49.0 g (0.5 mole) of maleic anhydride (pure, Nitrogen Plants, Kędzierzyn, Poland), 45.8 g (0.43 mole) of 3-oxapentane-1,5-diol (diethylene glycol, pure, Refinery Płock, Poland), 43.5–45.6 g (0.57–0.6 mole) of propane-1,2-diol (pure, Refinery Płock, Poland; the amount depended on the amount of accelerator added) and 3-[*p*-(*N,N*-dimethylamino)phenyl]-3-azapentane-1,5-diol (A) or 4-[*p*-(*N,N*-dimethylamino)phenyl]-4-azaheptane-2,6-diol (B) (amounts are presented in Table I) were added. The flask was purged with nitrogen for 30 min before heating was switched on. Then 0.18 cm³ of a 10% solution of hydroquinone (pa, POCh Gliwice, Poland) in acetone (pa, POCh Gliwice, Poland) was added and the content heated at 140–200°C under nitrogen for 6–9 h, while removing water (about 15 g), until the acid number of the mixture dropped down to below 50 mg KOH per gram of resin. The mixture was cooled to 100–110°C and diluted with 125 cm³ of styrene (pure, Chemical Plants, Oświęcim, Poland) stabilized with hydroquinone (2 cm³ of 10% solution of hydroquinone in acetone per 1 L of styrene).

Analytic methods

The epoxy number of the reaction mixture was determined by titrating a sample with a dioxane solution of hydrochloric acid.¹²

The acid number was determined by titrating a sample dissolved in a toluene/ethanol mixture (2 : 1, v/v) with a 0.1 M alcoholic solution of KOH.

The elemental analysis (C, H, N) of the products A and B was performed using an EA-1108 analyzer (FISONS, Italy). The infrared (IR) spectra were recorded on a Fourier transform IR PARAGON 1000

TABLE I
Properties of Polyester Resins with Chemically Incorporated Accelerators

Type of accelerator	Amount of Accelerator (wt %)	Time of Gelation (min)	Stability at 70°C (h)
A	0.50	9.5	12.0
	1.00	5.5	12.0
	1.50	4.0	12.0
	2.00	7.5	24.0
	0.50	18.5	10.0
B	1.00	6.5	15.0
	1.50	7.5	33.0
	2.00	12.0	39.0
C	2.00	48.0	42.0

TABLE II
Elemental Analysis of Products of Reaction of *N,N*-dimethyl-*p*-phenylenediamine with Oxiranes

Oxirane	Elemental Analysis					
	C (wt. %)		H (wt. %)		N (wt. %)	
	calc.	found	calc.	found	calc.	found
EO	64.17	64.29	8.92	8.93	11.80	12.50
PO	64.57	66.63	10.77	9.59	10.86	11.10

spectrometer (Perkin-Elmer Corp, Norwalk, CT). The samples for IR analysis were prepared in the form of capillary films. The ¹H-NMR spectra of products A and B were recorded on an 80 MHz BS-586A spectrometer (TESLA, Czech Republic). The solvent was *d*₆-dimethylsulfoxide (DMSO) with hexamethyldisiloxane (HMDSO) internal standard.

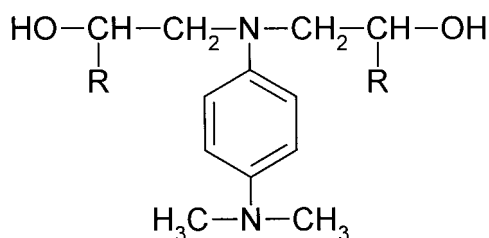
The time of gelation at 25°C (time until air bubble was arrested in test tube with resin and initiator) was determined following a normalized procedure¹³ by mixing 25 g of the resin with 0.5 g Interlox BP-50-P1 (50% solution of benzoyl peroxide in dibutyl phtalate, Peroxid-Chemie GmbH, Germany).

The stability of the resins at 70°C (time until air bubble was arrested in test tube with the resin and no initiator) was determined for 25 g of the resin.¹⁴

RESULTS AND DISCUSSION

The reactions between *N,N*-dimethyl-*p*-phenylenediamine and EO (PO) were carried out to obtain *N,N*-bis(hydroxyalkyl) derivatives of *N,N*-dimethyl-*p*-phenylenediamine. The molar ratio of *N,N*-dimethyl-*p*-phenylenediamine to EO (PO) was 1 : 2. Amines were mixed directly with the appropriate amount of oxirane and the mixture was heated. In the beginning, the process was conducted in a heterogeneous system. When the temperature exceeded 30°C, the amine melted and the reaction mixture became homogeneous. The reaction was conducted for more than 10 h. Resinous dark brown products were obtained.

The structure of resulting diols was confirmed using elemental analysis (Table II), IR spectra (Table III) and ¹H-NMR spectra (Table IV). It can be described by:

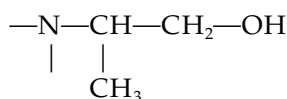


where R is H or CH₃

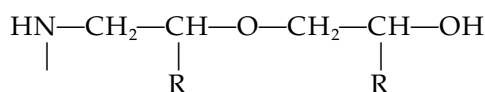
It seems worth pointing out that in the reactions with PO, the abnormal product

TABLE III
Absorption Bands of IR Spectra of Products of Reaction of *N,N*-dimethyl-*p*-phenylenediamine with Oxiranes

Oxirane	Band Location (cm ⁻¹)	Type of Vibrations and Functional Group	
EO	3300	ν_{OH}	
	3010-3000	$\nu_{C_{ar-H}}$ (weak)	
	3000-2790	ν_{CH_3} , ν_{CH_2}	
	1630, 1510, 1470	ring vibrations	
	1450, 1350, 1330	δ_{CH_3} , δ_{CH_2} , δ_{OH}	
	1260, 1210, 1130, 1100	ν_{C-OH} , ν_{C-N} , $\nu_{C_{ar-N}}$	
	945	skeleton vibrations	
		$\delta_{C_{ar-H}}$ in 1,4 substituted derivatives of benzene	
		820	ν_{OH}
		3300	$\nu_{C_{ar-H}}$ (weak)
PO	3010	ν_{CH_3} , ν_{CH_2} , ν_{CH}	
	2950-2780	ring vibrations	
	1610, 1510, 1480	δ_{CH_3} , δ_{CH_2} , δ_{CH} , δ_{OH}	
	1450, 1370, 1320	ν_{C-OH} , ν_{C-N} , $\nu_{C_{ar-N}}$	
	1260, 1240, 1140, 1080	skeleton vibrations	
	950	$\delta_{C_{ar-H}}$ in 1,4 substituted derivatives of benzene	
		820	ν_{OH}
		3300	$\nu_{C_{ar-H}}$ (weak)



was also obtained. The ¹H-NMR spectra (Table IV) confirmed this fact. On the other hand, no product of subsequent substitution Artwork required in below equation



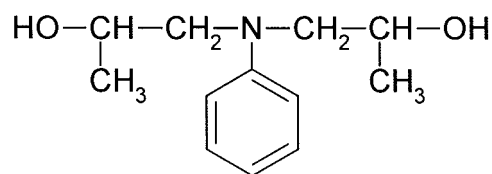
was found to be formed (lack of secondary amine N—H deformation vibrations at 750–700 cm⁻¹ in IR spectrum).

The derivatives of *N,N*-dimethyl-*p*-phenylenediamine can be incorporated into polyester chains because of the presence of two hydroxy groups capable of reacting with acid anhydrides, and the presence of two tertiary nitrogen atoms is expected to improve the reactivity of the resins.

To confirm the usefulness of the compounds, they were added in appropriate amounts (Table I) to polyester resins. The syntheses were carried out under the same conditions used for producing the most common polyester resins in Poland. A range from 0.5 to 2 wt % of compound A (B) was added to the reaction mixture. The amount of propane-1,2-diol was reduced accordingly. The condensation was carried out until the acid number of the reaction mixture dropped below 50 mg KOH per gram of resin. In the next step, the modified

polyester was dissolved in styrene to determine the time of gelation and the stability of the resin (Table I).

The results were compared with those obtained for a reference resin containing 2 wt % of 4-phenyl-4-azaheptane-2,6-diol [Compound (C)]



that was prepared for comparison.

As can be seen from Table I, the incorporation of compounds including two tertiary amine groups into a polyester chain substantially reduces the time of gelation. It can be reduced to as little as 4 min (in the case of the resin with 1.5 wt % of incorporated A). Such a strong effect is not observed for 4-phenyl-4-azaheptane-2,6-diol (time of gelation: 48 min). Unfortunately, the stability of resins modified in the proposed way is relatively poor (10–39 h). To improve this property, 0.1–0.5 wt. % of quaternary ammonium salts were added to a hot styrene solution of the polyester.^{5,15–17}

Resins with the smallest gelation times were modified by adding 0.3 wt % of benzyltriethylammonium

TABLE IV
Chemical Shift of Protons in ¹H-NMR Spectra of Products of Reaction of *N,N*-dimethyl-*p*-phenylenediamine with Oxiranes

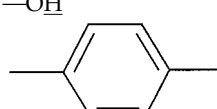
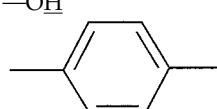
Oxirane	Chemical shift(δ ppm)	Group
EO	2.6	—N(CH ₃) ₂
	3.3-3.5	$\text{---N---CH}_2\text{---CH}_2\text{---O}$
	4.3	—OH
	6.5	
	1.0-1.1, split due to presence of products of normal addition along with products of abnormal one	$\text{---CH}_2\text{---CH---CH}_3$ OH $\text{---CH---CH}_2\text{---CH}_3$ OH
PO	2.6	—N(CH ₃) ₂
	3.3-3.6	$\text{---N---CH}_2\text{---CH}_2\text{---O}$
	4.2	—OH
	6.5	

TABLE V
Properties of Polyester Resins with Chemically Incorporated Accelerator A and with 0.3 wt. % of Stabilizer

Amount of Accelerator, wt. %	Time of Gelation at 25°C (min)		Stability at 70°C (hours)	
	Without Stabilizer	With Stabilizer (TEBA)	Without Stabilizer	With Stabilizer (TEBA)
1	5.5	7.0	12	54
1.5	4.0	5.0	12	96

chloride (easily obtained in a reaction of triethyloamine with benzyl chloride) at 70–80°C. The salt substantially improved the stability of the resins (even by a factor of eight), while the gelation time rose only very slightly (by 1–3 min; Table V).

Because of the very short gelation time, the resins with chemically incorporated accelerator A (B) can be applied in manufacturing, for example as blasting cartridges to provide strong joints between walls and foundations.

CONCLUSIONS

N,N-dimethyl-*p*-phenylenediamine reacts with EO (PO), yielding diols containing two tertiary amine groups. When the compounds are chemically incorporated into unsaturated polyester chains, it significantly reduces the gelation time of their styrene solutions. Because of the relatively poor stability of the modified resins, they should be extra stabilized, for example by adding benzyltriethylammonium chloride.

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