

# N-Phenyl Piperazine-Polyester Derivative as Curing Activator of Unsaturated Resins

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## Synopsis

An oligomeric compound (Pol-2A) has been synthesized by a Michael-type addition of *N*-phenyl piperazine to double bonds of the maleic units of a polyester resin. This compound was used as activator (with benzoyl peroxide) in the curing of unsaturated polyester resins and compared in its efficiency with *N,N*-dimethylaniline (DMA). Pol-2A showed activator characteristics comparable to those of DMA, with a wider range of gel times, and similar mechanical properties of the end products, with the advantage of a severe lowering of diffusibility and related environmental toxicity.

## INTRODUCTION

The curing process of unsaturated polyester resins is currently carried out with "catalytic" systems consisting of an organic peroxide and an activator, which promotes by a redox mechanism the free radical formation at temperatures below those required for the peroxide alone.<sup>1-5</sup> Curing at lower temperatures assures a step of a larger workability of the resin blend, followed by the development of the cross-linking reaction in subsequent step, with a thermal effect, by which higher temperatures are reached.

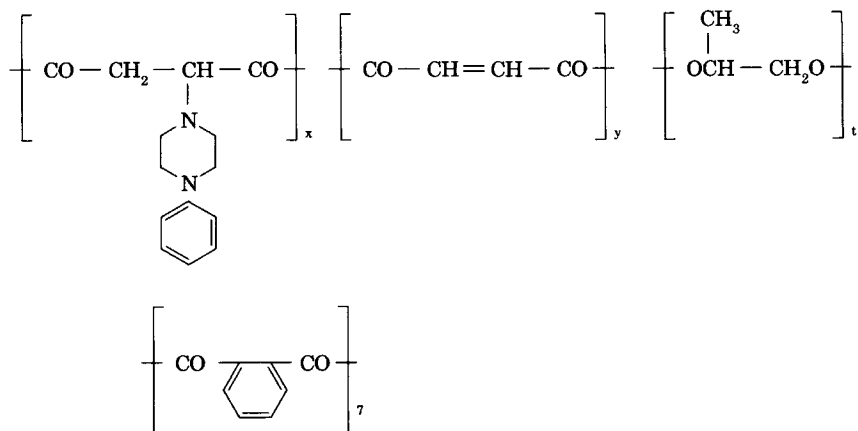
A number of activators have been proposed, but the best results are obtained with tertiary aryl amines.<sup>1-3</sup> A known disadvantage in using such amines is their toxicity and carcinogenicity, even at room temperature, due to their volatility and migrability, also from solid systems.<sup>9</sup> The aim of our present research is the use of activators having tertiary aryl amine functions chemically bound to heavier molecules in order to avoid their spreading out during the resin processing and from the solid end articles.<sup>10</sup>

In this work a new polymeric activator (Pol-2A) is synthesized by addition of an alkyl aryl amine to a polyester prepolymer and its efficiency evaluated from the curing reaction, by which the activator itself is eventually incorporated in the polymeric product, and from the properties of the cross-linked end materials.

## EXPERIMENTAL

### Synthesis of Pol-2A

The synthesized compounds Pol-2A has the following general formula:



where  $(x + y):t:z = 0.9:1:0.1$ . It was obtained by reacting *N*-phenyl piperazine (NPP) with a highly unsaturated polyester prepolymer prepared by polycondensation (by a usual procedure) of maleic and phthalic anhydrides with 1,2-propylene glycol. The addition is a Michael-type reaction between the aliphatic hydrogen of NPP and the activated double bond of the maleic units, in a methanol-toluene mixture at 30–40°C under nitrogen for 16–24 h (up to 90–95% of reacted double bonds).<sup>10</sup>

Product Pol-2A was separated by pouring the reaction mixture into petroleum ether and purified by dissolving the gummy precipitate in chloroform, washing the solution with diluted HCl and distilled water, then stirring over  $\text{K}_2\text{CO}_3$ , filtering, and reprecipitating into cold anhydrous *n*-heptane.

The product, dried under vacuum, was obtained in substantial yields. It is a pale yellow, hygroscopic powder, soluble in most organic solvents, including styrene, and insoluble in water, petroleum ether, and *n*-heptane.

All solvents were R.P.E. (from Farmitalia, Carlo Erba S.p.A., Milan, Italy); NPP (Fluka AG, Switzerland) was distilled under nitrogen and reduced pressure immediately before use; the polyester prepolymer was kindly supplied by Snial Polyester Resins S.p.A. (Colleferro, Italy).

## Characterization of Pol-2A

### *Elemental Analysis*

C, H, and N% analyses of all samples of Pol-2A were in reasonable agreement with the expected formula, within the limits of normal accuracy. In the present work a sample was used at 95% addition (i.e.,  $x = 0.855$ ;  $y = 0.045$ ): found % C = 63.68; H = 6.90; N = 7.39; calculated % C = 63.88; H = 6.78; N = 7.98.

### *Thin-layer Chromatography*

Chromatography on Silica gel plates Stratocrom W<sub>40</sub> (Farmitalia Carlo Erba S.p.A.), using a  $\text{CHCl}_3$ -acetone mixture (1:1) + 1% glacial acetic acid, gave the following  $R_f$  values: 0.62 (Pol-2A) and 0.08 (NPP).

*Infrared Spectroscopy*

The spectra, with a Perkin-Elmer 457 spectrophotometer in  $\text{CHCl}_3$  solution, were in reasonable agreement with the expected structure. In particular, they clearly show the typical absorption bands of the polyester backbone; the bands of aliphatic  $\text{CH}_2$  and  $\text{N-CH}_2$  stretching ( $2800\text{--}2920\text{ cm}^{-1}$ ) of the NPP; those of NPP aromatic ring ( $1450\text{--}1600\text{ cm}^{-1}$ ;  $690\text{--}750\text{ cm}^{-1}$ ); and those of the aromatic and aliphatic C-N stretching ( $1000\text{--}1350\text{ cm}^{-1}$ ).

*Wide-Angle X-ray Diffraction*

The patterns of powdered samples were recorded with a Philips PW 1050 counter diffractometer, using  $\text{CuK}\alpha$ , radiation. All samples of Pol-2A proved to be completely amorphous.

*Differential Scanning Calorimetry*

DSC thermograms were recorded by a Mettler TA 3000 instrument with samples of about 10 mg, a heating rate of  $10^\circ\text{C}/\text{min}$  from  $-100^\circ$  to  $200^\circ\text{C}$ . The trace of Pol-2A (as obtained from the synthesis) shows a glass transition near  $7^\circ\text{C}$  and an endothermic effect beginning at about  $100^\circ\text{C}$ , which may be attributed to a water loss, in agreement with a weight loss in the thermogravimetric analysis. In a subsequent run the same sample showed only a glass transition at about  $28^\circ\text{C}$ . No decomposition of the samples was observed below  $200^\circ\text{C}$ .

*NMR Spectrometry*

NMR spectra of Pol-2A and of the starting polyester were recorded with a Varian 360/A spectrometer in  $\text{CDCl}_3$  solution. Considering the complex structure of the starting polyester, it is difficult to give specific assignments for every absorption peak. If compared with that of the starting polyester, the NMR spectrum of Pol-2A shows the piperazine methylene absorptions ( $\delta = 3.7$  and  $3.15$ ) and the aromatic protons peaks of the phenyl group bound to the piperazine (from  $\delta = 6.7$  to  $\delta = 7.4$ ). Clearly, the peak at  $\delta = 6.85$  of the olefinic protons of maleic anhydride is no longer detectable.

**Polyester Resins**

Two commercial types were used, as received: H35 (SNIATRON 3559, SNIAL S.p.A., Roma), and S20 (NEOXIL 235, SAVID S.p.A., Como), whose basic composition is given in Table I.

TABLE I  
Basic Composition of the Polyester Resins

Resin	Monomeric components				
	Maleic anhydr. (mol)	Phtalic anhydr. (mol)	1,2-Propylene glycol (mol)	Styrene (% by weight)	Hydroquinone (ppm)
H35	0.7	0.3	1.0	27	90
S20	1.0	1.0	2.1	34	90

### Gel Time Tests

The efficiency of Pol-2A as activator was evaluated first by gel time tests, according to the standard SPI Procedures for Running Exotherm Curves—Polyester Resins (September 1960) by adding different amounts of Pol-2A and 1% benzoyl peroxide (Fluka AG, Switzerland) to either of the two polyester resins. Due to the higher content of maleic anhydride, the resin H35 was more reactive than S20.

Exotherms were determined at three different bath temperatures (35, 45, and 60°C); the corresponding curves were automatically plotted by a Speed-omax (Leeds and Northrup) recorder.

For comparison, corresponding tests with *N,N*-dimethylaniline (DMA) as activator were carried out, using the weight percentage of amine equal to those of the *N*-phenylpiperazine units in the corresponding tests with Pol-2A.

Benzoyl peroxide was purified by dissolving it in  $\text{CHCl}_3$  and adding twice the volume of MeOH; DMA was distilled under nitrogen at reduced pressure before use.

### Cross-linked Resin Characterization

The curing efficiency with Pol-2A as activator, compared with that with DMA, was also evaluated from properties of the resulting cross-linked resins.

#### *Materials*

Curing was carried out with 1% by weight of benzoyl peroxide, and 0.5% by weight of DMA or a corresponding aminic amount of Pol-2A at room temperature by casting the resin between two glass plates separated by rubber strips.

Three different conditioning or postcuring treatments were indicated as:  $A = 24$  h at 23°C;  $B = A + 18$  h at 50°C;  $C = B + 24$  h at 60°C;  $D = C + 24$  h at 60°C.

#### *Flexural Properties*

Flexural modulus and strength were determined with an INSTRON Dynamometer (Mod. 1121) by three-point bending tests, according to ATM-D-790-71. Every experimental point is an average of at least nine specimens.

#### *Hardness*

Rockwell hardness tests were performed with a CEAST Durometer, Scale E, according to ASTM-D2240-68 (100 kg;  $\frac{1}{8}$  in.). Every experimental point is an average of eight specimens.

## RESULTS AND DISCUSSION

Figures 1 and 2 show the results of gel time with resins H35 and S20 as a function of the concentration of activator Pol-2A (1% benzoyl peroxide), at different temperatures, compared with corresponding results with DMA instead of Pol-2A.

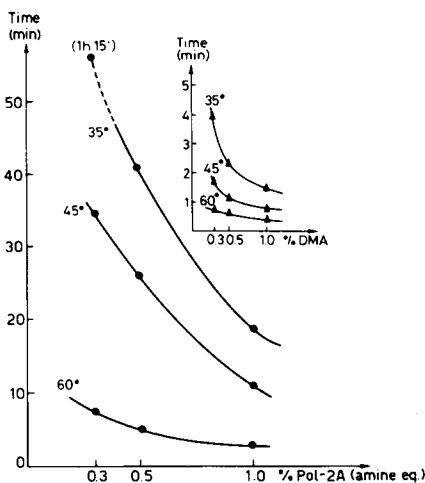


Fig. 1. Gel times of H35 resin in the presence of Pol-2A or DMA as activator (with 1% of benzoyl peroxide).

Table II reports the values of the main parameters of the exothermal curves recorded in every test: temperature of the exothermal peak; time interval  $\Delta t$  from gel formation to exothermal peak; ratio  $R$  between  $\Delta t$  and gel time.

Clearly, gel times are longer with the polymeric activator than with *N,N*-dimethylaniline but qualitatively follow a same pattern, with a somewhat wider regulation domain of gel times with Pol-2A. The values of  $\Delta t$  are also longer with Pol-2A, whereas the ratios  $R$  are much shorter, so that the cross-linking time is relatively shorter when referred to the gel time, without noticeable differences in the peak temperatures.

In Figure 3 the logarithm of gel time is plotted against the reciprocal of the absolute temperature for various experiments, using resins H35 and S20 and Pol-2A and DMA as activator, at four temperatures (some additional tests were made at 25°C). An overall energy of activation  $E = 14.0 \div 15.5$

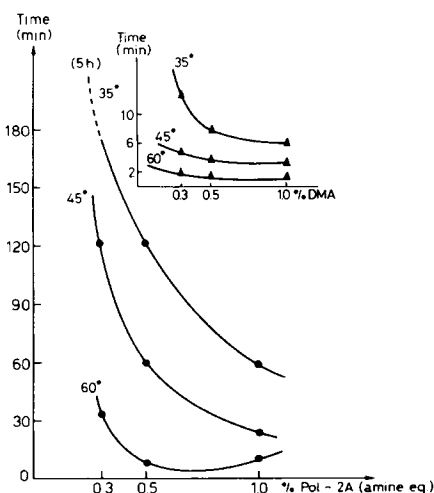


Fig. 2. Gel times of S20 resin in the presence of Pol-2A or DMA as activator (with 1% of benzoyl peroxide).

TABLE II  
 Gel Time Parameters

T experiences (°C)	% Activity	H35 Resin			S20 Resin		
		Ex. peak T (°C)	$\Delta t^a$	R <sup>b</sup>	Ex. peak T (°C)	$\Delta t^a$	R <sup>b</sup>
▲ % DMA							
35	0.3	119	6' 30"	1.70	132	6' 00"	0.48
	0.5	113	4' 30"	2.00	123	5' 40"	0.68
	1.0	106	5' 10"	3.40	116	3' 20"	0.92
45	0.3	128	2' 20"	1.30	115	4' 30"	0.96
	0.5	123	2' 40"	2.50	128	6' 00"	1.57
	1.0	100	3' 35"	4.30	122	5' 20"	1.46
60	0.3	133	2' 30"	3.40	137	3' 50"	2.29
	0.5	142	3' 45"	6.50	120	5' 30"	4.11
	1.0	117	3' 30"	8.60	108	5' 00"	5.00
● % Pol-2A							
35	0.3	100	20' 40"	0.29	n.d.	n.d.	n.d.
	0.5	112	16' 30"	0.40	115	32' 50"	0.27
	1.0	100	12' 50"	0.68	121	26' 10"	0.44
45	0.3	148	10' 40"	0.31	122	21' 40"	0.18
	0.5	142	9' 40"	0.37	117	20' 10"	0.34
	1.0	126	6' 40"	0.60	109	17' 50"	0.76
60	0.3	143	6' 15"	0.83	150	9' 50"	0.40
	0.5	150	8' 05"	1.56	138	9' 40"	0.91
	1.0	127	8' 30"	3.10	124	8' 10"	0.93

<sup>a</sup>  $\Delta t$  = time interval from gel formation to exothermal peak.

<sup>b</sup> R =  $\Delta t$  over gel time.

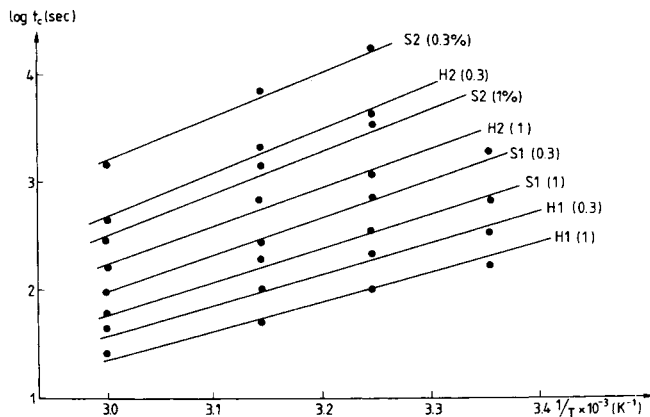


Fig. 3. Arrhenius plot of gel time for H35 resin (H) and S20 resin (S) with DMA (1) or Pol-2A (2) as activator in the amount indicated in brackets (with 1% of benzoyl peroxide).

kcal/mol can be calculated. This result may be interpreted by the theoretical model of Gordon et al,<sup>11</sup> according to which

$$E = 2E_{cp} - E_t$$

where  $E_{cp}$  and  $E_t$  are the activation energies of the cross-propagation step and of the termination between two monomeric radical respectively. By putting  $E_t$  at about 2-3, a value of 8-9 kcal/mol can be estimated for  $E_{cp}$ .

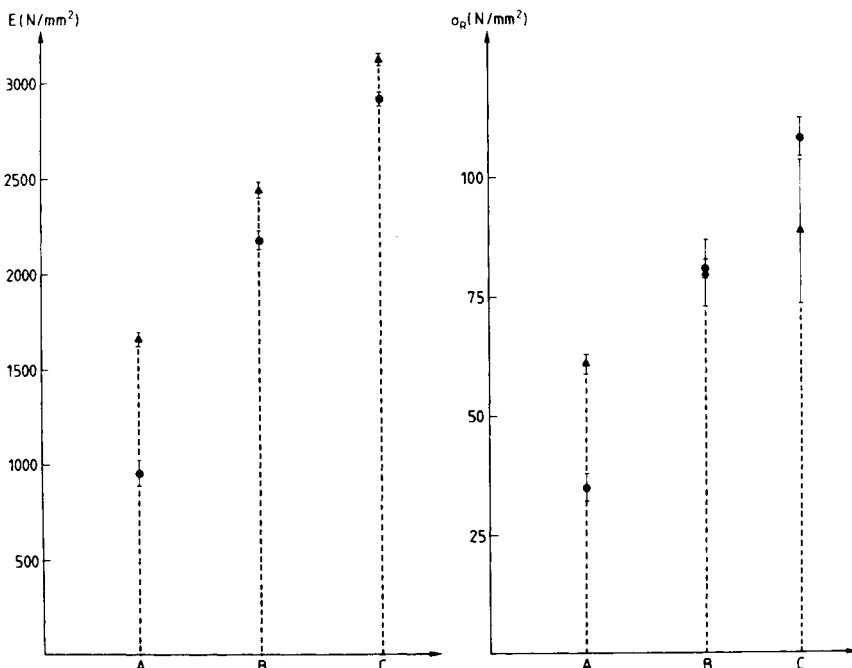


Fig. 4. Flexural elastic modulus  $E$  and strength  $\sigma_R$  of H35 resin, cross-linked with 1% by weight of benzoyl peroxide, and 0.5% by weight of DMA (▲) or a corresponding aminic amount of Pol-2A (●), after A, B, C, and D postcuring treatments (see text).

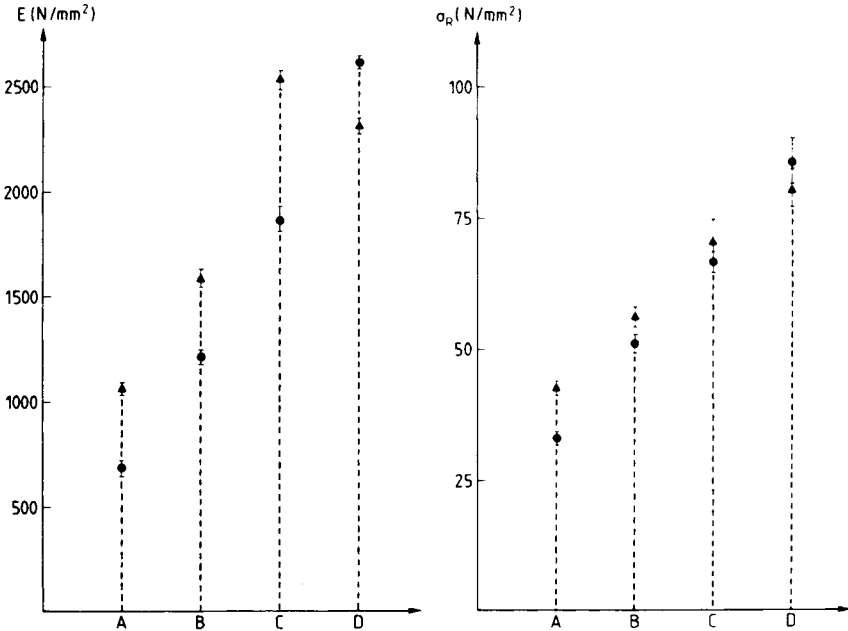


Fig. 5. Flexural elastic modulus  $E$  and strength  $\sigma_R$  of S20 resin, cross-linked with 1% by weight of benzoyl peroxide, and 0.5% by weight of DMA (▲) or a corresponding aminic amount of Pol-2A (●), after A, B, and C postcuring treatments (see text).

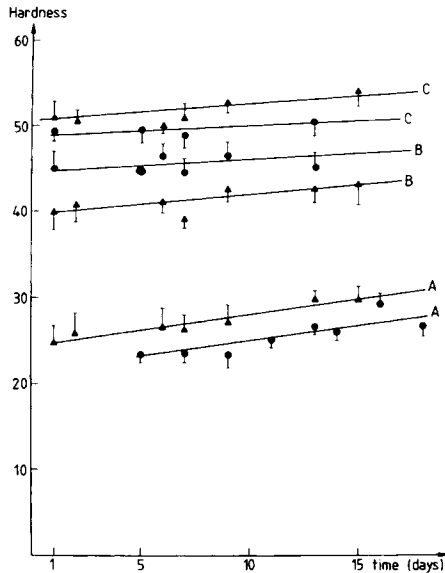


Fig. 6. Rockwell hardness values (scale E) of S20 resin, cross-linked with 0.5% by weight of DMA (▲) or a corresponding aminic amount of Pol-2A (●) after A, B, and C postcuring treatments.



These results are very similar to those of Gordon et al.<sup>11</sup> with polyester fumarate resins and methyl methacrylate as monomer and to the calorimetric determinations of Horie et al.<sup>12</sup> with polyester fumarate resins and styrene with different catalytic systems.

The results of the mechanical characterization of the corresponding cross-linked materials are summarized in Figures 4 through 6. In general, the postcuring treatments appear to have a rather large influence on the properties of the end materials, irrespective of the activator used. Some slight differences seem to be observed, for example in the moduli with the less reactive resin S20 in favor of DMA, but in the flexural strength with the resin H35 in favor of Pol-2A, whereas the hardness tends to conform when longer thermal postcuring is applied. As a matter of fact, no definite conclusions of actual differences in the mechanical behavior with the use of the two activators can be drawn by the present investigation.

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