N-Acryloyl–*N'*-Phenylpiperazine as Curing Activator of Unsaturated Resins

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SYNOPSIS

N-acryloyl–*N'*-phenylpiperazine and three of its homopolymers of different molecular weight are tested as low toxicity redox activators in the BPO curing of unsaturated polyester resins. Gel times and other time and temperature parameters drawn from standard exothermal curves are determined with two kinds of resin, at different bath temperatures and amounts of activator. The reciprocal of gel time follows a kinetic equation with average order 0.85 with respect to the activator, and an activation energy of 19 kcal/mol. With polymeric activators it is a simple decreasing exponential function of intrinsic viscosity. Correlations are observed for other parameters relative to the second, faster step of the curing process, in general less sensitive to the mentioned variables. The crosslinked resins show mechanical properties similar to those obtainable with dimethylaniline as activator.

INTRODUCTION

The radical curing of unsaturated polyester resins at relatively low temperatures ("cold curing") is in general carried out by using a redox initiating system, frequently consisting of an organic peroxide and a tertiary arylamine, such as dimethylaniline (DMA) or dimethyl-*p*-toluidine (DMPT). These are known to be particularly active, but with the drawback of a fairly high toxicity towards the environment, due to their volatility and migrability, even from final solid materials.

In a previous paper,[1] we examined the possibility of using, as a reducing agent (activator), an arylamine of molecular size greater than that of compounds currently introduced in the practice (such as DMA or DMPT). The arylamine studied in that work was a compound of oligomeric size, obtained by reacting *N*-phenylpiperazine (NPP) with an unsaturated polyester prepolymer, so as to obtain a Michael-type addition of the NPP secondary amino hydrogens to activated double bonds of the maleic units of the prepolymer. In the curing process it showed a good efficiency as activator, with longer gel times but an equivalent fast progress of the second step of the reaction if compared to DMA, thus possibly allowing for longer working times of resin blends (as in the production of composite compounds) followed by a normally effective curing reaction.

In this work another solution is suggested and examined, namely, that of using a simpler monomeric *N'*-derivative of *N*-phenylpiperazine, which should be more mobile as activator, and at the same time able to be chemically incorporated by copolymerization in the end product. In a recent paper[2] it has been shown that *N*-acryloyl–*N'*-phenylpiperazine (AcrNPP) has a good ability to radically homopolymerize, and also copolymerize with methyl methacrylate or styrene, and this allowed such a compound to be thought of as a possible redox activator in the curing of unsaturated resins. In this work it was thus tested in this respect, and, in the interest of the whole research, its activator efficiency was also compared with that of some of its homopolymers of various molecular size.

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EXPERIMENTAL

N-Acryloyl-*N'*-Phenylpiperazine (AcrNPP)

AcrNPP was synthesized by reacting acryloylchloride with *N*-phenylpiperazine at low temperature, with the procedure already described in a preceding paper.[2] It is a white, crystalline powder, with mp 76.6°C.

AcrNPP Polymers (PAcr)

Three polymer samples were used as activators. They were prepared by polymerizing AcrNPP in a 10% (w/v) anhydrous benzene solution at 60°C for 16 h, under nitrogen atmosphere, in the presence respectively of 0.5% AIBN, 1% AIBN, and 0.5% AIBN + 1% dodecylmercaptane. The polymer products were separated by pouring the reaction mixture into *n*-heptane, and purified by dissolving them in chloroform and reprecipitating into anhydrous ethylether. The three samples, dried under vacuum, had the following intrinsic viscosity values in chloroform at 30°C (dL/g):

$$\text{PAcr-20: } [\eta] = 0.20;$$

$$\text{PAcr-16: } [\eta] = 0.16; \text{ PAcr-7: } [\eta] = 0.07$$

Polyester Resins (S20 and H35)

Two commercial resins were used for the curing tests as received: Neoxil 235, SAVID S.p.A., Como (S20), and Sniatron 3559, SNIAL S.p.A., Roma (H35). They consisted of the polyester prepolymer from maleic and phthalic anhydrides, and 1,2-propylene glycol, dissolved in styrene (66 and 73% by weight, respectively). The H35 resin contained a higher ratio of maleic to phthalic anhydride (0.7 : 0.3 instead of 0.5 : 0.5 mol/mol). Both were also used in the preceding work.[1]

Curing Tests

The activator efficiencies of the described monomeric and polymeric compounds have been evaluated according to the standard SPI Procedure for Running Exotherm Curves—Polyester Resins (Sep. 1960), by adding in the beaker 1% benzoylperoxide (BPO) and different amounts of activator to either of the two polyester resins, with bath temperature T_b = 35, 45, and 60°C.

For a part of the tests only the gel time t_g was measured; in the remainder the whole exotherm curve was automatically recorded by a Speedomax (Leeds and Northrup), from which further parameters were evaluated: (a) the maximal temperature T_{max} at the exothermal peak and the rise of temperature $\Delta T = T_{max} - T_b$; (b) the time interval Δt from gel formation to exothermal peak, and the ratio R of Δt to t_g.

Benzoyl peroxide (Fluka A. G., Switzerland) was purified by dissolving the commercial product in $CHCl_3$, by adding twice the volume of methanol, and by vacuum-drying the precipitated product.

Mechanical Characterization

Flexural properties of crosslinked S20 and H35 samples, cured at room temperature in glass plates molds, combined with 0.5 wt % activator and 1 wt % BPO, were determined after different post-curing treatment of the specimens. These were indicated as: A = 24 h at room temperature; $B = A$ + 18 h at 50°C; $C = B$ + 24 h at 60°C; and $D = C$ + 24 h at 60°C.

Flexural modulus and strength were measured according to ASTM D-790-71 (three point bending),

Table I Gel Times with Monomeric and Polymeric Activators (Resin: S20; BPO 1 % w)

Bath Temperature (°C)	% Weight Activator	Gel Time (min)			
		PAcr-20	PAcr-16	PAcr-7	AcrNPP
45	0.3	365	230		81
	0.5	186	132	66	38
	1.0	102	70		23
	2.0	54			
60	0.3	68	54		21
	0.5	40	27	19	13
	1.0	27	21		7.2
	2.0	21			

with an Instron Dynamometer 1121-10KN. Every experimental point is given as a value average of six specimens.

RESULTS AND DISCUSSION

All the experimental results of the curing tests are reported in Table I and II. Table I collects the values of gel time measured in the same conditions with the four activators used in this work. Table II presents instead all the data relating to the runs in which the whole thermal curve was recorded, i.e., all the numerical values of gel time and of the parameters singled out from the experimental curves.

The activator efficiency of AcrNPP is in general higher than that of its oligomeric polyester derivative (Pol-2A) tested in the same conditions in the preceding work,[1] being the gel times with the former about 2/3–3/4 those with the latter. This may be attributed to a greater average mobility of AcrNPP in the system.

A clear influence of the molecular size on the activator efficiency can now be seen in Table I, by comparing the gel times with AcrNPP to those with its homopolymers PAcr of different molecular weight.

Table II Parameters Determined in Selected Curing Tests

Bath Temperature T_b (°C)	% Weight Activator	Gel Time t_g (min)	Exoth. Peak Temperature T_{max} (°C)	ΔT ($T_{max} - T_b$) (°C)	Δt (min)	R ($\Delta t/t_g$)
		Resin: S20; Activator: AcrNPP; BPO 1% w				
35	0.3	177	118	83	33.5	0.19
	0.5	124	107	72	42.5	0.34
	1.0	65	112	77	31.0	0.48
45	0.3	81	129	84	17.5	0.22
	0.5	38	143	98	15.5	0.41
	1.0	23	116	71	17.0	0.74
60	0.3	21	146	86	7.5	0.36
	0.5	13	145	85	10.0	0.77
	1.0	7.2	141	81	7.5	1.05
		Resin: H35; Activator: AcrNPP; BPO 1% w				
35	0.3	36.5	142	107	13.5	0.37
	0.5	30.0	126	91	12.5	0.42
	1.0	16.5	107	72	7.2	0.44
45	0.3	22.5	140	95	9.5	0.42
	0.5	11.5	120	75	7.5	0.65
	1.0	5.3	132	87	5.0	0.94
60	0.3	4.5	144	84	5.0	1.1
	0.5	3.7	134	74	6.0	1.6
	1.0	2.2	138	78	5.5	2.5
		Resin: S20; Activator: PAcr-20; BPO 1% w				
45	0.3	365				
	0.5	186	55	10	56	0.30
	1.0	102	72	27	47	0.46
	2.0	54	116	71	28.5	0.53
60	0.3	68	138	78	20.5	0.30
	0.5	40	148	88	18	0.45
	1.0	27	129	69	20	0.74
	2.0	21	124	64	22	1.05

Within the limits of the considered intrinsic viscosity values, the results of Table I can be quantitatively well described by the following equation:

$$t_g = t_{gm}\exp(\beta[\eta]) \quad \text{or}$$
$$1/t_g = 1/t_{gm}\exp(-\beta[\eta]) \qquad (1)$$

where t_g is the gel time with a polymeric activator of intrinsic viscosity $[\eta]$, t_{gm} that with the monomeric activator (with $[\eta]$ near zero), and β a constant.

The validity of this relation is shown in Figure 1 on a semilogarithmic plot, from which the slope β appears to be independent of the activator concentration, but dependent on temperature, with the approximate values:

β = 7.0 at 45°C and 6.0 at 60°C

($[\eta]$ in dL/g; t_g in min)

which would indicate a greater increase of mobility of the polymeric activators when the temperature is increased.

As for the relation between gel time and activator concentration, in Figure 2 an example of graphical dependence is given with the data at 45°C. As usual for redox initiated systems, by increasing the concentration of the reducing agent (at a constant amount of peroxide) the gel times gradually decrease towards a minimum value.

Now, the gel time may be considered as a kinetic

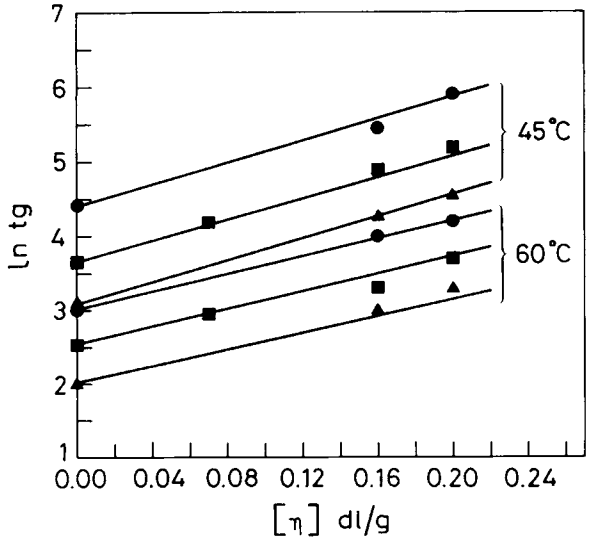

Figure 1 Logarithm of gel time vs. activator intrinsic viscosity at different temperatures and activator amounts (wt %): (●) 0.3; (■) 0.5; (▲) 1.

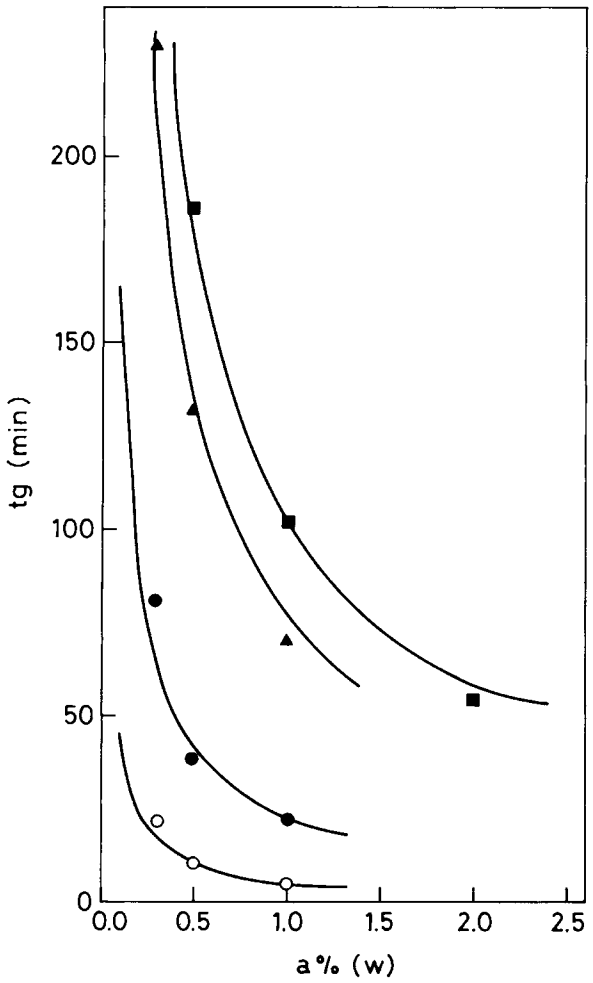

Figure 2 Relation between gel time and amount of activator, 45°C, BPO 1% [Resin S20: (■) PAcr 20; (▲) PAcr 16; (●) AcrNPP. Resin H35: (○) AcrNPP]. The curves were drawn according to eq. (2) with α = 0.85.

quantity, empirically useful, but, as normally determined, certainly affected by inaccuracy of its value. Nonetheless, its reciprocal may be seen as an "image" of the average overall rate of the moderate first step of the curing reaction, from the beginning to gel formation, which then is critically followed by a fast second step with a more complex mechanism and considerable thermal effect ("gel effect").

On this ground, in the presence of a constant amount of peroxide, the following approximate kinetic equation, relative to the first step, may be postulated:

$$1/t_g = ka^{\alpha} \qquad (2)$$

(neglecting any correction due to an independent BPO thermal decomposition) where a is the acti-

vator concentration, α the order with respect to the activator, and k an overall constant in the chosen conditions.

By checking this equation with the gel time data of Table I and II, a fairly good agreement is found. The value of α, although scattered between 0.6 and 1 for a single or different series of data, apparently does not manifest any noticeable trend relative to the varying type of activator, temperature, or type of resin. Thus, if an overall average is made on the 10 series of data, the mean value $\alpha = 0.85$ may be estimated. With this value were drawn the solid curves on Figure 2.

By putting $\alpha = 0.85$ in eq. (2), and calculating by the best fitting the value of k at each bath temperature, an overall activation energy may be evaluated through the Arrhenius equation. From all the data, an average of 19 kcal/mol may thus be found, apparently displaced towards 18 with the monomeric AcrNPP and towards 20 with the higher molecular weight polymeric (PAcr)s. These values are substantially of the order of those of common radical polymerizations and copolymerizations.

The second, faster step of the curing reaction, from the thermal point of view, appears to be poorly sensitive to a change of type and amount of activators, type of resin, and bath temperature. In fact, the value of the thermal excursion ΔT (difference between peak and bath temperature), though somewhat scattered, is almost constant in all the experiments of Table II (save for some data relative to the polymeric PAcr-20). This should be due to comparable limiting conditions of very fast reaction, that lead, in a short time, to a comparatively high heat evolution and cumulation in the system, with relatively small changes in the heat dissipation conditions.

The time interval Δt from the gel formation to the exothermal peak is instead sensitive to changes of temperature and type of resin or activator, but not much of amount of activator (save again for some data relative to PAcr-20). The consequent relation between Δt and gel time may be examined through their ratio R, which is instead sensitive to all the mentioned variables, including the activator concentration, being the first step of the reaction involved in the calculation of its value, very sensitive to this last variable.

In order to check whether the use of the activators studied in this work practically implies differences in the properties of the final products, a comparison was made between some mechanical properties of the two resins crosslinked using AcrNPP and PAcr-16, and those of corresponding products obtained with dimethylaniline DMA (data taken from the preceding work[1]).

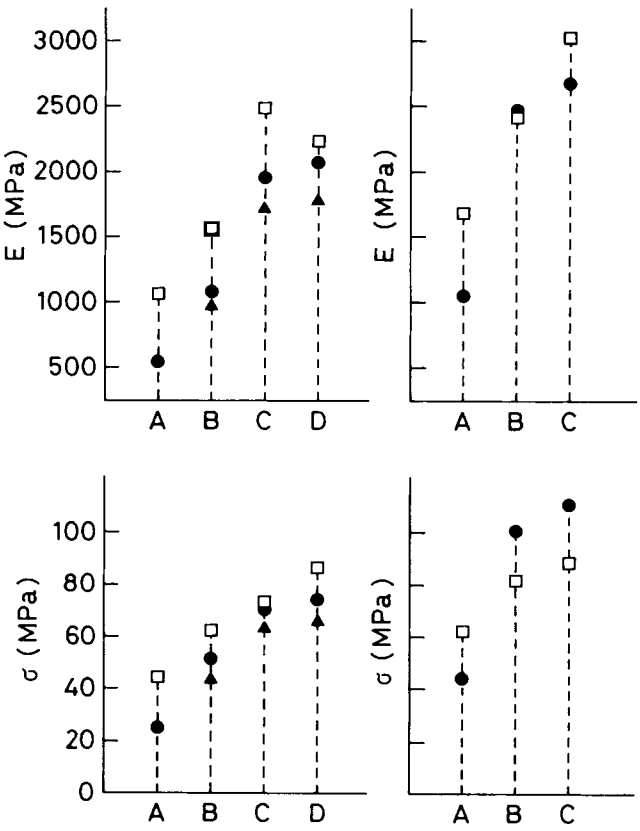

Figure 3 Flexural modulus-E and strength or of resins crosslinked with AcrNPP, PAcr16, and DMA as activator, at room temperature, with 1 wt % BPO and 0.5 wt % activator [Resin S20 (left) and Resins H35 (right)]: (●) AcrNPP; (▲) PAcr 16; (□) DMA.

Figure 3 reports and compares the values of flexural modulus and strength of the final products after various post-curing treatments. On the whole, taking into account the relative accuracy of such determinations, no substantial differences are observed. It may be said that the properties are slightly better using DMA for any treatment, especially those after milder post-curing conditions, which would indicate a little more advanced reaction conversions in the curing with DMA. However, with more severe post-curings the properties of the different products tend to conform. It might be also observed that the values of the properties with the polymeric PAcr-16 are invariably slightly lower than those with the monomeric AcrNPP, which would be in agreement with the slightly lower efficiency of the polymeric activators evaluated on the ground of the gel times.

In conclusion, the use of AcrNPP and its polymers as activators in the curing of unsaturated poly-

ester resins leads to results qualitatively similar to those obtained with the corresponding polyester NPP derivative (Pol-2A) of the preceding work,[1] and quantitatively more effective with monomeric AcrNPP.

The use of all these NPP activators results in gel times longer than those obtainable with the more conventional, though more toxic, dimethylaniline, and in a completely equivalent development of the subsequent faster step of the curing reaction. Furthermore, the chemical incorporation of the AcrNPP activator in the cured material, and the negligible migrability of the corresponding polymeric or oligomeric counterparts, warrant a reduced amine toxicity towards the environment to the final products.

Thus, when longer working times are requested or accepted in technological applications, a favorable compromise between costs, lower toxicity, and desired gel times should be easily found in practice, possibly designing activators mixtures.

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