Amides from *N*-phenylpiperazine as low-toxicity activators in radical polymerizations

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N'-Acryloyl- (AcrNPP), *N'*-methacryloyl- (MetNPP) and *N'*-acetyl-*N*-phenylpiperazine (AcNPP) were synthesized and tested as activators in the benzoyl peroxide radical 'cold curing' of methyl methacrylate at 40°C. The three amides showed quite similar efficiencies as redox reducing agents, but different migrabilities from the final polymer. In amide release tests in methanol, the highest value was obtained with AcNPP; a notably lower release was observed with MetNPP and AcrNPP, the lowest being with the latter. This behaviour of the unsaturated amides is discussed in relation to their measured ability to copolymerize, as well as in relation to other factors affecting migrability.

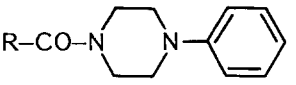
(Keywords: radical polymerization; redox initiation; *N'*-acryloyl-*N*-phenylpiperazine; *N'*-methacryloyl-*N*-phenylpiperazine; *N'*-acetyl-*N*-phenylpiperazine; methyl methacrylate)

INTRODUCTION

In a previous paper[1] it has been shown that an oligomeric unsaturated polyester *N'*-derivative of *N*-phenylpiperazine, purposely synthesized, is active as a reducing agent of benzoyl peroxide (BPO) in the curing of unsaturated polyester resins. In a subsequent work[2], the *N'*-acryloyl derivative of *N*-phenylpiperazine, i.e. an *N*-disubstituted acrylamide, was synthesized and examined as a functionalized monomer or comonomer in radical polymerization. This compound, with azobisisobutyronitrile (AIBN) as initiator, at 60–70°C gave homopolymers in substantial yields in 24–48 h, as well as copolymers with methyl methacrylate (MMA) or styrene. It also proved to copolymerize easily with MMA at 40°C in the presence of BPO, at a rate typical of a redox-initiated reaction, in which it also acts as reducing agent.

Interest in a compound of this kind may be due to the following reasons: (a) It bears an aromatic tertiary amine group known to be active in redox initiation, but with a toxicity that is expected to be lower than that of other commonly used tertiary arylamines (such as dimethylaniline or dimethyl-*p*-toluidine). (b) It should have a lower migrability in viscous blends or moulding compounds, as well as in final solid articles, due to its greater molecular size. (c) The unsaturated group should allow it to be incorporated chemically into the final material through copolymerization, thus completely avoiding any release into the environment.

In this paper the behaviour of the above-mentioned acrylicamide is tested in the redox 'cold curing' of MMA, and compared with that of two other similar saturated and unsaturated compounds, namely the corresponding acetamide and methacrylamide. The three compounds have been synthesized by condensation of *N*-phenylpiperazine (NPP) with the related acyl chloride, and have the general formula:



R =	$CH_2=CH-$	acrylamide	(AcrNPP)
R =	$CH_2=C(CH_3)-$	methacrylamide	(MetNPP)
R =	CH_3-	acetamide	(AcNPP)

EXPERIMENTAL

Materials

N-Phenylpiperazine (NPP; Fluka Reag. 95%), acryloyl chloride (Aldrich Reag. 98%), methacryloyl chloride (Fluka Reag. 97%), acetyl chloride (Aldrich Reag. 98%), triethylamine (TEA; Farmitalia-Carlo Erba, Pure Reag.) and methyl methacrylate (MMA; Aldrich Reag. 99%) were vacuum distilled before use. Azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO; Fluka, purum) were purified by dissolution in chloroform at room temperature and precipitation in petroleum ether or by adding twice the volume of methanol, respectively. All solvents were Merck Pure Reag.

Techniques

Elemental analyses were done by Redox snc, Cologno Monzese, Italy. Thin-layer chromatography (t.l.c.) was carried out on Stratocrom W 40 silica gel plates (Farmitalia-Carlo Erba), using I_2 as detecting agent. Differential scanning calorimetry (d.s.c.) was performed with a Mettler TA 3000 instrument, with samples of about 10 mg, at a heating rate 15°C min^{-1} from −150 to 200°C,

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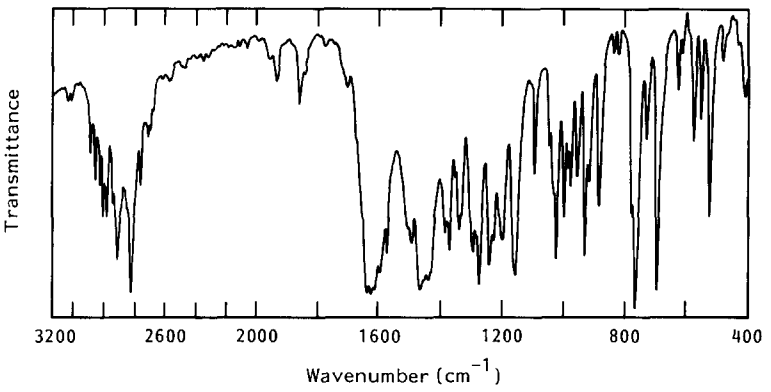

Figure 1 *FT*i.r. spectrum of *N'*-methacryloyl-*N*-phenylpiperazine

with indium as calibrant. ^{1}H n.m.r. spectra were obtained with a Varian 360/A instrument, using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. A Perkin–Elmer 1710–Infrared Fourier Transform spectrophotometer was used to record *FT*i.r. spectra on thin films prepared from chloroform solutions. High-performance liquid chromatography (h.p.l.c.) analyses were done with a Bio-Rad Protein Chromatography System, equipped with a 250 × 4 mm Bio-Sil ODS-10 column (Bio-Rad, C-18 bonded silica).

Amide synthesis

The three amides were synthesized by reacting *N*-phenylpiperazine with acryloyl, methacryloyl and acetyl chloride, respectively, in the presence of TEA in anhydrous (CaH_2) toluene solution at low temperature, following the procedure already described in a preceding paper[2].

'Cold curing' test

In order to test the efficiency of the amides as redox activators, redox-initiated MMA polymerizations were carried out in a test-tube of 18 mm diameter, equipped with a thermocouple connected to a temperature recorder and centred, through a cork guide, in the core of the reaction chamber. The test-tube was placed in a thermostatted bath at 40°C, and 5 g of freshly distilled MMA containing a pre-fixed amount of amide were poured into it. Another 5 g of MMA, in which 0.4 g of BPO were just dissolved, were then added and mixed in the test-tube, and from that moment the core temperature was recorded, so that the test was characterized by a temperature–time curve.

Amide release test

The release of the amides from three typical final polymers was evaluated by extraction tests in methanol. For each polymer sample, 2.5 g MMA were polymerized in an 18 mm diameter test-tube at 40°C for 24 h, in the presence of 100 mg BPO and 0.22 mmol of the amidic activator. Immediately afterwards, each whole sample, obtained in a cylindrical piece, was dipped in 20 ml of methanol in a closed vessel and left up to 7 days in a thermostatted chamber at 24°C. At different times, the amide content of the methanol solution was evaluated by analysing 20 μl samples of this solution with reversed-phase h.p.l.c.

H.p.l.c. analyses were performed at a flow rate of 1 ml min^{-1}, using H_2O/MeOH as eluant (40/60 in the case of AcrNPP and MetNPP; 50/50 in the case of AcNPP) and u.v. detection of 240 nm. The amide content was obtained by comparison with the peak area of known standard samples, the elution time being 8.5 min for AcrNPP, 11 min for MetNPP and 14.5 min for AcNPP.

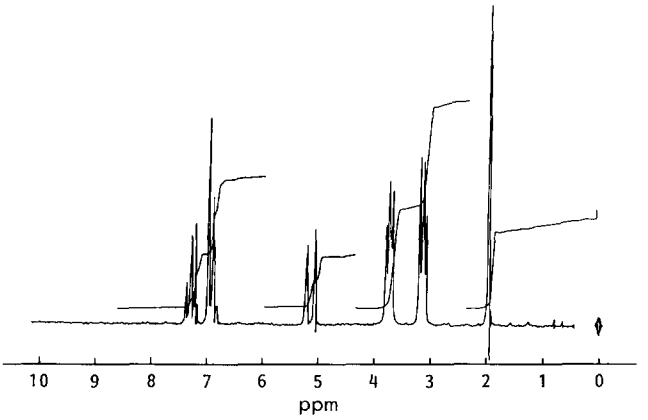

Figure 2 ^{1}H n.m.r. spectrum of *N'*-methacryloyl-*N*-phenylpiperazine

RESULTS AND DISCUSSION

Amide characterization

The main characteristics of the acrylamide (AcrNPP) used in this work have already been reported in a preceding paper[2].

The acetamide (AcNPP) prepared by us showed the essential characteristics already described in the literature[3]. Our method of synthesis, through acetyl chloride, gave a typical product yield of 85%, instead of 45% as in ref. 3 through acetylation. Our product shows a single spot by t.l.c. in acetone/chloroform 1:1 (+1% acetic acid) and R_f = 0.41 (NPP, R_f = 0.12). It is a white crystalline powder, with melting 'peak temperature' 92°C via d.s.c.

The methacrylamide (MetNPP) to our knowledge has not been described previously. By our synthesis through methacryloyl chloride it was obtained with a typical yield of 77%. Elemental analysis: C 72.37%, H 7.32%, N 12.81% (theor. C 72.19%, H 7.45%, N 12.95%). It gives a single spot by t.l.c. in acetone/chloroform 1:1 (+1% acetic acid) and R_f = 0.47 (NPP, R_f = 0.12). It is a white crystalline powder, which shows a sharp endotherm via d.s.c., with 'peak temperature' 75°C. Its i.r. and n.m.r. spectra are reported in *Figures 1* and *2*.

Table 1 Copolymerizations of AcrNPP and MetNPP with MMA at 60°C, 24 h, 0.5% AIBN (1:1 toluene)

Comonomer mixture		AcrNPP		MetNPP	
MMA (wt%)	Amide (wt%)	Copolymer yield (%)	AcrNPP (wt%) in copolymer	Copolymer yield (%)	MetNPP (wt%) in copolymer
100	0	81	0	81	0
75	25	86	13	55	1.3
50	50	73	24	31	2.0
25	75	66	39	21	3.1
0	100	72	100	–	–

Amide polymerizability

The good ability of AcrNPP to homo- and copolymerize by a radical mechanism has been demonstrated in a preceding paper[2].

Corresponding polymerizability tests have been performed in this work with the new amide, MetNPP. A 1:1 toluene solution of MetNPP, with 0.5–1% AIBN added, was kept in a nitrogen atmosphere at 60°C for 24–48 h. It was then poured into an excess of methanol. To our surprise, no precipitate was obtained. Corresponding copolymerization tests with MMA plus 0.5% AIBN, after 24 h at 60°C, gave the results reported in *Table 1*, where they are compared with the corresponding ones[2] obtained with AcrNPP.

A marked difference of behaviour may thus be observed for the two amides. MetNPP, in contrast to AcrNPP, has an apparently negligible ability to homopolymerize and only a weak reactivity in the copolymerization with MMA, with evident retardation effects.

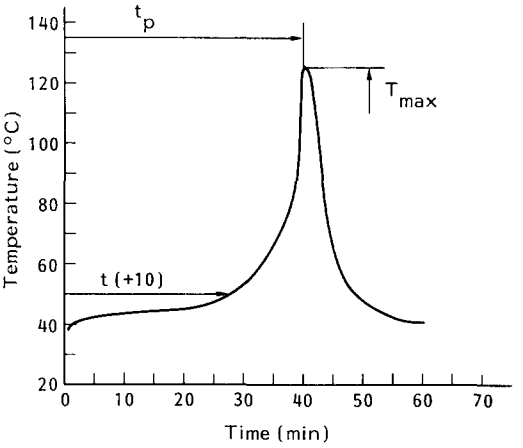

Figure 3 Example of temperature–time curve of an MMA polymerization at 40°C, with 4% BPO, 5% AcrNPP, with related parameters indicated (see text)

Redox activation efficiency

The efficiencies of the three amides as activators in redox initiation were evaluated and compared by using each of them at different concentrations in MMA polymerizations performed in a similar way to that followed for curing monomer–polymer mixtures in their application as methacrylic bone cements or dental biomaterials. The reference condition chosen was a fast, non-isothermal polymerization, in the presence of 4% by weight BPO, without avoiding contact with atmospheric oxygen and humidity, in a thermostatted bath at 40°C.

In *Figure 3* is reported an example of a typical polymerization run observed through the temperature–time curve recorded in the course of the experiment. In the chosen conditions the inhibition period is negligible or very short, and not detectable practically through the thermal curve. Polymerization proceeds with a gradual increase of temperature for a certain time and then undergoes a marked acceleration due to the well known gel effect, so that a sharp peak of temperature is observed, immediately followed by the end of the reaction and the related thermal effect.

The essential information of every thermal curve has been quantitatively summarized through three main parameters: (a) the time $t(+10)$ at which the increase in temperature reaches 10°C (in our case the absolute value of 50°C); (b) the time t_p at which the temperature peak takes place; and (c) the maximal temperature T_{max} at the peak.

The experimental values of these three parameters are reported in *Figure 4* as a function of the molar amount of amide in the system. All the data are presented for each parameter in a common plot, from which it is apparent that the three amides have practically the same efficiency as activators, any deviation from an average relation being within the experimental accuracy. This would mean that the acylic group, saturated or not, of the different amides does not play a noticeable role in the mechanism of redox initiation, which remains typical of the common structure of the three molecules.

The average relation for $t(+10)$ seems not to be completely monotonic, but increases somewhat on the right, which could reveal some changes in the first part of the process when the amide concentration reaches relatively high values.

The time t_p at which the thermal peak occurs follows a similar trend, but the difference $t_p - t(+10)$ appears to increase slightly with increasing amide concentration. A corresponding, more evident, decrease is observed in T_{max}, so that the accelerated part of the process (gel effect) seems to undergo some attenuation when the amide concentration exceeds relatively low values (0.05–0.1 mmol g^{-1}).

Amide release tests

Figure 5 shows the results of a test of release of amides from the final solid polymers immersed in a standard geometrical specimen in methanol, chosen as a conventional good extracting solvent.

A marked difference is immediately apparent between the behaviours of the unsaturated amides and the saturated one. The least release takes place with AcrNPP, which is the amide with the greatest ability to copolymerize and to be incorporated into the product during the curing of the system. Nevertheless, the release of MetNPP is only about 30% higher (compared with

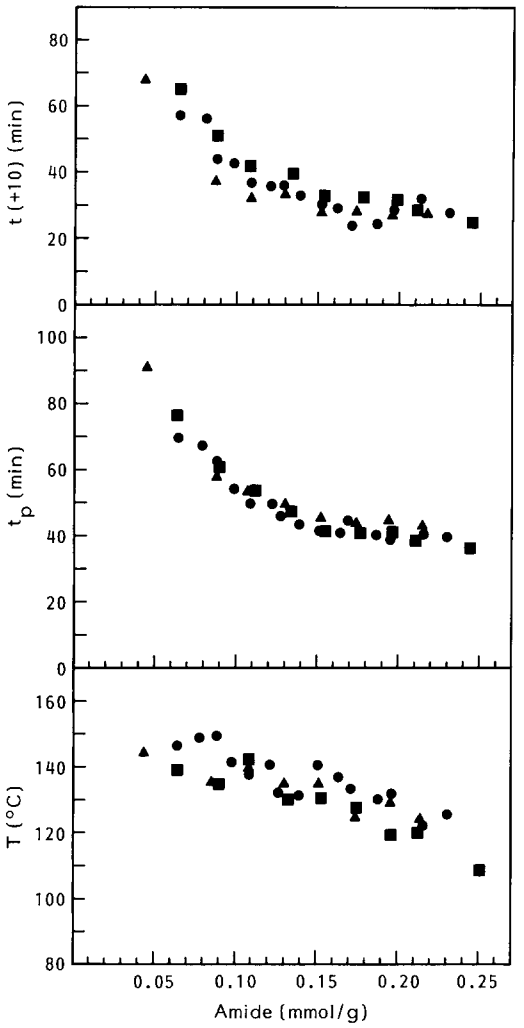

Figure 4 Time for an increase in temperature of 10°C, time at the exothermal peak and maximal peak temperature of MMA polymerizations at 40°C, in the presence of 4% BPO and different amounts of the three amide activators: (●) AcrNPP; (▲) MetNPP; (■) AcNPP

over 200% for AcNPP), and this seems to correspond only partially to the tendency of MetNPP to copolymerize, which was found to be markedly lower than that of AcrNPP.

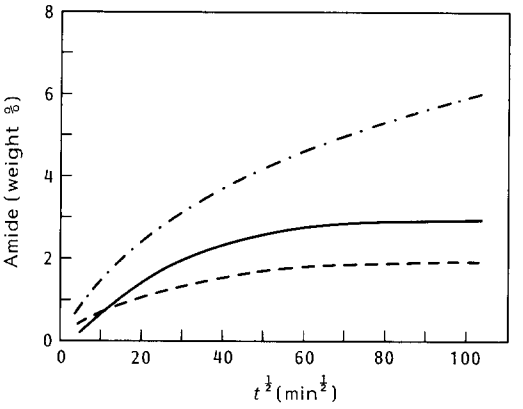

Figure 5 Release of the three amides in methanol from typical samples of final MMA polymers: (---) AcrNPP; (——) MetNPP; (-·-·-) AcNPP

This might indicate that other factors should be taken into account. The difference in molecular size can justify a difference in migrability of the two unsaturated compounds as such, but the relevant difference with AcNPP can hardly be explained in this way. On the other hand, it cannot be forgotten that, in the complex whole mechanism, some side-reaction of the unsaturated groups could yield derivatives having either lower migrability or a different sensitivity to the h.p.l.c. analysis as performed in this work.

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