

Polymers and copolymers of *N*-acryloyl-*N'*-phenyl-piperazine

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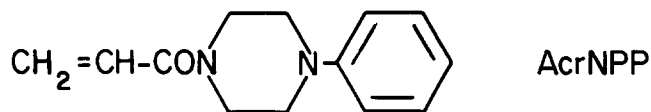
N-acryloyl-*N'*-phenyl-piperazine (AcrNPP) has been synthesized by condensation of acryloylchloride with *N*-phenylpiperazine. In the presence of 0.5–1% AIBN, in 1:1 toluene solution, at 60–70°C in 24–48 h it gave homopolymers in substantial yields, with $[\eta] = 0.16\text{--}0.24 \text{ dl g}^{-1}$ (chloroform). With methylmethacrylate (MMA) or styrene as comonomer, at 60°C in 24 h copolymers were also obtained in good yields. With benzoyl peroxide, fast copolymerizations could be performed at 40°C, since AcrNPP also acted as redox initiation promoter. Reactivity ratios with methylmethacrylate were estimated: $r_1 = 0.25$ (AcrNPP); $r_2 = 2.5$ (MMA). Linear correlations between composition and absorbance ratios of infrared bands of the copolymers were also established.

(Keywords: *N*-acryloyl-*N'*-phenyl-piperazine; polymers; copolymers; i.r.-characterization; radical polymerization; redox initiation)

INTRODUCTION

The synthesis of functional polymers and/or copolymers is of increasing interest in macromolecular chemistry. In particular, polymers bearing specific chemical functions on side groups of a substantially inert macromolecular main chain may solve a variety of problems in technical as well as in biomedical or pharmacological applications.

In this work, a functional vinyl monomer, namely a disubstituted acrylamide, was synthesized, in which the amidic group is associated with an aromatic tertiary amine function in a piperazinic cycle:



The ability of this monomer to homopolymerize in the presence of radical initiators and to copolymerize with methylmethacrylate or styrene has been studied.

EXPERIMENTAL

Materials

Acryloyl chloride (Aldrich Reagent, 98%), *N*-phenylpiperazine (Fluka Reagent, 95%), and triethylamine (Farmitalia-Carlo Erba, pure reagent) were distilled under reduced pressure before use. Methylmethacrylate (MMA) and styrene (STY) (Aldrich Reagent, 99%) were purified by distillation. Azo-bis-isobutyronitrile (AIBN) and benzoyl peroxide (BPO; Fluka, purum), were purified by dissolving the commercial product in chloroform and reprecipitating it in petroleum ether. All solvents were pure reagents (Farmitalia-Carlo Erba or Merk).

Techniques

Thin layer chromatography (t.l.c.) was performed on

silica gel plates (Stratocrom W40; Farmitalia-Carlo Erba), using a chloroform:isopropanol mixture (9:1) + 2% TEA as eluent mixture and I_2 as detecting agent.

Elemental analyses were done by redox s.n.c. (Cologno Monzese, Italy).

Fourier transform infrared spectroscopy (FTi.r.) was performed on thin films obtained by evaporating chloroform solutions of the samples and recording the spectra on a Perkin-Elmer 1710 infrared Fourier transform spectrophotometer.

^1H n.m.r. spectroscopy was carried out with a Varian 360/A spectrometer, using CDCl_3 as solvent and TMS as internal reference.

Differential scanning calorimetry (d.s.c.) thermograms were recorded with a Mettler TA 3000 instrument, with samples of $\approx 10 \text{ mg}$ and a heating rate of $15^\circ\text{C min}^{-1}$ from -150 to 200°C . Indium was used as the calibrant for temperature measurements.

Wide-angle X-ray diffraction spectra were obtained from a Philips PW 1050 counter diffractometer using $\text{CuK}\alpha$ radiation on powdered samples.

Intrinsic viscosities $[\eta]$ were measured in chloroform, at 30°C , using a FICA viscomatic viscosimeter.

Synthesis of AcrNPP

A solution of acryloyl chloride (10.33 ml; 0.127 mol) in anhydrous (CaH_2) toluene (80 ml) was added dropwise under vigorous stirring to a solution of *N*-phenylpiperazine (NPP; 20.6 g; 0.127 mol) and anhydrous (CaH_2) triethylamine (17.7 ml; 0.127 mol) in anhydrous (CaH_2) toluene (20 ml). The reacting mixture was initially kept at $0 \pm 5^\circ\text{C}$ in an ice/acetone bath and, after addition of the acryloyl chloride, was stirred for 2 h, leaving the temperature slowly to rise to room temperature. The precipitated triethylamine hydrochloride was then eliminated by filtration and the solution evaporated to dryness under vacuum at 40°C .

By double crystallization from solution of the product

in anhydrous n-heptane in the presence of a small amount of 2,6-di-*t*-butyl-*p*-cresol and then drying under vacuum, a white crystalline powder was obtained with a 60% yield.

Homo and copolymerization procedure

In a typical procedure, 1 g AcrNPP and an appropriate amount (0.5–1%) of AIBN were dissolved in 1 g anhydrous (CaH₂) toluene in a test tube, under nitrogen atmosphere. After standing in a thermostatic bath for a fixed time, the homogeneous reaction mixture was diluted with 5 ml toluene and poured into 75 ml methanol under stirring. The precipitated polymer was recovered, washed with fresh methanol and dried under vacuum. The same procedure was followed for copolymerization, starting with 1 g of comonomer mixture.

Non-isothermal low conversion copolymerizations of AcrNPP with methylmethacrylate were also performed, in the presence of benzoyl peroxide, at 40°C. In this case the test tube, with 10 g of monomer mixture, was equipped with a centred thermocouple branched to a temperature recorder. At the first rise of temperature, the test tube was taken off the thermostatic bath and the copolymer immediately precipitated and recovered as described.

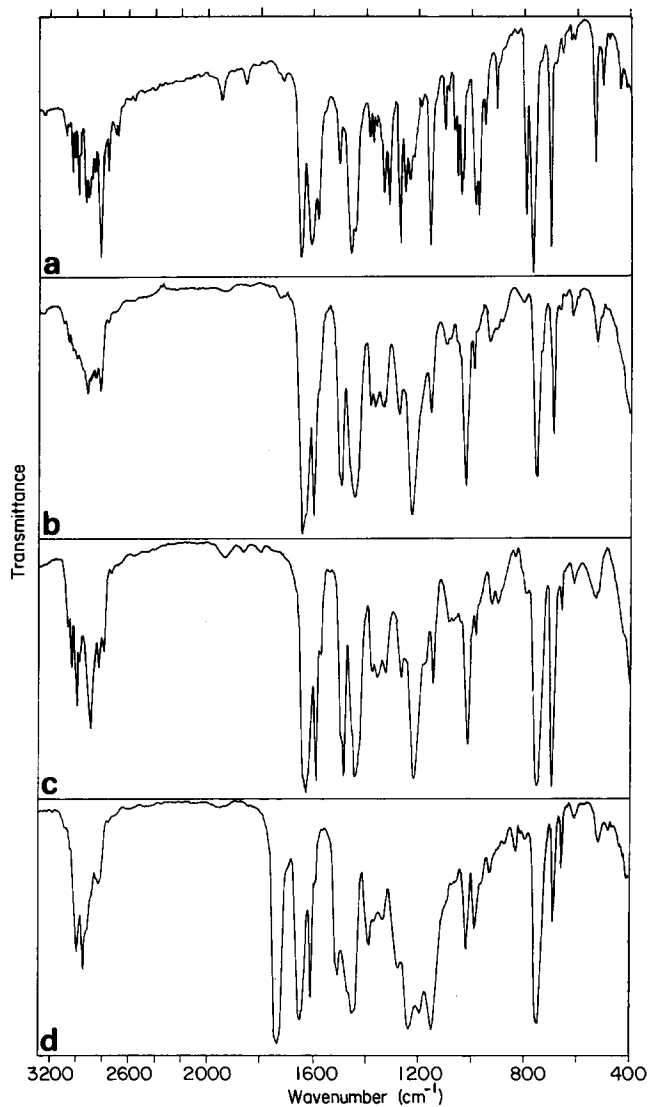


Figure 1 FTi.r. spectra of: (a) AcrNPP; (b) AcrNPP homopolymer; (c) AcrNPP/Sty=50/50 copolymer; (d) AcrNPP/MMA=50/50 copolymer

RESULTS AND DISCUSSION

Monomer characterization

As far as we know, AcrNPP has previously been mentioned in a pharmacological work¹, but has not been described in detail. As obtained in our synthesis, as a white crystalline powder, it is insoluble in water, petroleum ether and n-heptane and soluble in acetone, chloroform, benzene, toluene, ethylether, methanol, isopropanol and dimethylsulphoxide. By appropriate tests, it proved to be non-hygroscopic.

T.l.c. gave a single spot, with $R_f = 0.6$ (NPP: $R_f = 0.07$). C, H and N analyses of all tested samples were in good agreement with the expected formula (e.g. found: C = 72.37, H = 7.32, N = 12.81%; calculated: C = 72.19, H = 7.45, N = 12.95%).

In Figures 1a and 2, the i.r. and nuclear magnetic resonance (n.m.r.) spectra of AcrNPP are reported, in which specific bands can be recognized. The wide-angle X-ray diffraction spectrum, reported in Figure 3, reveals typical peaks of very high crystallinity. With d.s.c. AcrNPP shows a sharp melting endotherm, with 'peak temperature' 76.6°C, $\Delta H = 110 \text{ J g}^{-1}$, and no decomposition or thermal polymerization effects up to 200°C.

Homopolymers

Polymerizations were performed by putting a toluene solution 1:1 w/w of AcrNPP, containing 0.5–1% AIBN (on the monomer), in a thermostatic bath at 60 and 70°C for 24–48 h. Polymers were obtained as a white powder in substantial yields: 72–88% with $[\eta] = 0.16\text{--}0.24 \text{ dl g}^{-1}$. At 70°C with 1% AIBN, the yield was 86% at 24 h and 88% at 48 h, with $[\eta] = 0.16 \text{ dl g}^{-1}$.

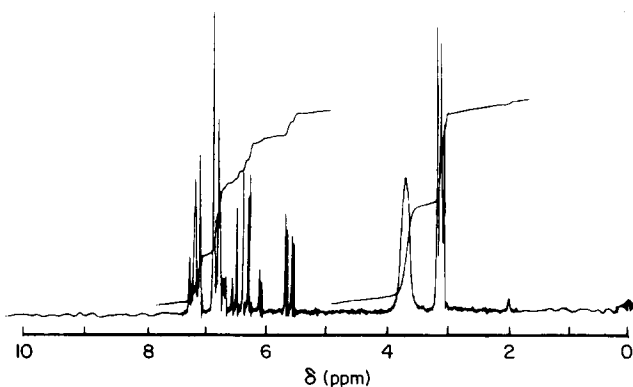


Figure 2 N.m.r. spectrum of AcrNPP

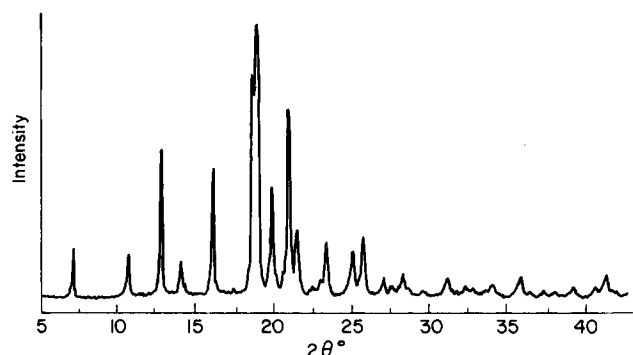


Figure 3 Wide-angle X-ray powder diffraction spectrum of AcrNPP

The polymers were soluble in chloroform, benzene and toluene and insoluble in water, methanol and acetone.

A typical sample of homopolymer gave elemental C, H and N analysis in good agreement with the expected structure and the i.r. spectrum of *Figure 1b*. With t.l.c. it showed a single normally dispersed band and with X-ray proved to be completely amorphous. D.s.c. thermograms showed only a glass transition at about 105°C and no other thermal effects up to 200°C.

Copolymers

The ability of AcrNPP to copolymerize was tested with methylmethacrylate and styrene. The results of a series of copolymerizations with methylmethacrylate at 60°C for 24 h with 0.5% AIBN are summarized in *Table 1*. Copolymer composition was calculated from the data of elemental analysis. Under the chosen reaction conditions, the AcrNPP content of the copolymers is about one half that of the initial monomer mixture. Similar results were obtained with styrene as comonomer.

A series of non-isothermal copolymerizations with methylmethacrylate were also performed at 40°C in the presence of benzoyl peroxide. In this case AcrNPP acted simultaneously as comonomer and redox promoter, so that the reactions proceeded quickly. Detailed results will be given in a future paper; for this work, some of these copolymerizations were performed at low conversion in order to evaluate reactivity ratios approximately. The results are reported in the composition diagram of *Figure 4* (AcrNPP as monomer 1), in which the theoretical Mayo-Lewis curve is also drawn with the selected values $r_1=0.25$ and $r_2=2.5$. This copolymerization is therefore non-azeotropic, with a prevailing tendency to alternation of the unit disposition along the

Table 1 Results of copolymerizations AcrNPP with MMA at 60°C for 24 h with 0.5% AIBN (1:1 in toluene)

Monomers	AcrNPP in monomer mixture (wt%)	Yield (%)	AcrNPP in copolymer (wt%)
AcrNPP	100	72	100
AcrNPP/MMA	75	66	39
AcrNPP/MMA	50	73	24
AcrNPP/MMA	25	86	13
MMA	0	81	0

chain, governed by the cross-reactivity of the AcrNPP end radical toward molecular methylmethacrylate

I.r. spectra of all copolymers and corresponding homopolymers have been recorded. As an example, in *Figure 1c* and *d* the spectra of two copolymers from 50:50 monomer mixtures of AcrNPP/Sty and AcrNPP/MMA are reported.

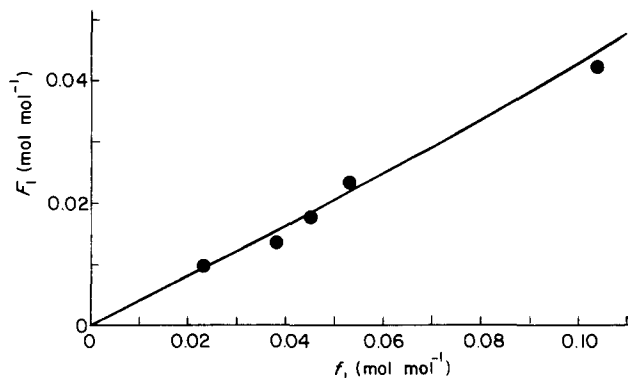


Figure 4 Composition diagram of AcrNPP copolymerization with MMA, 40°C, BPO 2% (AcrNPP = monomer 1). f_1 , F_1 , Mole fractions of AcrNPP in monomer mixture and copolymer, respectively. —, Theoretical Mayo-Lewis equation with $r_1=0.25$, $r_2=2.5$.

Table 2 I.r. bands selection and assignment for STY, MMA and AcrNPP homopolymers

Wavenumber (cm ⁻¹)	Assignment ^a	PS	PMMA	PANP
3000–3100	$\nu(\text{C-H})_{\text{BE}}$	—	—	—
2820–2920	$\nu(\text{C-H})_{\text{AL}}$	—	—	—
2850–2930	$\nu(\text{C-H})_{\text{AL}}$	—	—	—
2950	$\nu_{\text{as}}(\text{CH}_3)$	—	—	—
2840–3000	$\nu(\text{C-H})_{\text{AL}}$	—	—	—
1735	$\nu(\text{C=})_{\text{ES}}$	—	—	—
1645	$\nu(\text{C=O})_{\text{AM}}$	—	—	—
1495	$\nu(\text{C=C})_{\text{BE}}$	—	—	—
1600	$\nu(\text{C=C})_{\text{BE}}$	—	—	—
1450	$\delta(\text{CH}_2)$	—	—	—
1150–1245	$\nu(\text{C-O})_{\text{ES}}$	—	—	—
1230	$\nu(\text{C-N})_{\text{AR}}$	—	—	—
1025	$\nu(\text{C-N})_{\text{AL}}$	—	—	—
760	$\gamma(\text{C-H})_{\text{AR}}$	—	—	—
700	$\gamma(\text{O})$	—	—	—

^a BE, benzene ring; AL, aliphatic; ES, ester; AM, amide

Table 3 Composition and i.r. absorbance ratios of homo and copolymers of AcrNPP, MMA and STY

Initial monomer mixture (w/w)	AcrNPP in copolymers (wt%)	Absorbance ratios (cm ⁻¹ /cm ⁻¹)		
		A(1735)/A(1645)	A(1735)/A(1450)	A(1645)/A(1450)
AcrNPP	100	—	—	2.01
AcrNPP/MMA (75/25)	39	1.05	1.49	1.42
AcrNPP/MMA (50/50)	24	1.72	1.88	1.10
AcrNPP/MMA (25/75)	13	3.85	3.00	0.78
MMA	0	—	3.75	—
		A(2820)/A(2850)	A(1645)/A(1760)	A(1600)/A(760)
AcrNPP	100	—	2.46	1.61
AcrNPP/Sty (75/25)	44	1.07	1.28	0.96
AcrNPP/Sty (50/50)	29	0.79	1.15	0.83
AcrNPP/Sty (25/75)	12	0.50	0.81	0.71
Sty	0	—	—	0.33

The correspondence of the copolymer compositions found by elemental analyses with absorbance ratios between appropriate bands present in each copolymer and in either or both the corresponding homopolymer spectra has been checked. In *Table 2* a selection of the main bands of the homopolymers involved is shown, with their structural assignments. In *Table 3* calculated absorbance ratios relating to different bands are presented.

For MMA copolymers, as expected, the 1735/1645 and 1735/1450 cm^{-1} ratios decrease, whereas the 1645/1450 cm^{-1} ratio increases with AcrNPP content in the samples. For styrene copolymers, the values of the absorbance ratios considered increase with AcrNPP content. In all cases a good linear correlation has been

found between the values of absorbance ratio considered and the percentage N found by elemental analyses.

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REFERENCE

- 1 Prasad, R. N., Hawkins, L. R. and Tietje, K. *J. Med. Chem.* 1968, **6**, 1144