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Novel poly(etheraroyl-co-terephthal) hydrazides with liquid crystalline behaviour

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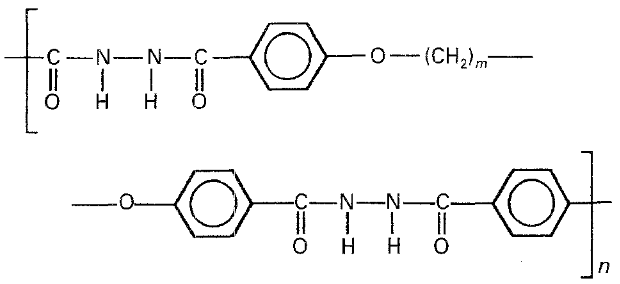
Novel poly(etheraroyl-co-terephthal)hydrazides with liquid crystalline (LC) behaviour, synthesized by solution polycondensation followed by non-solvent coagulation in water, have been characterized by means of Fourier Transform infrared (FT–i.r.), differential scanning calorimetry (DSC) and wide angle X-ray scattering (WAXS) techniques. DSC thermograms and WAXS intensity profiles of "as polymerized" and coagulated homo- and copolymers are strongly dependent upon the molecular structure and constitution of the polymers: the poly(etheraroyl-hydrazide) homopolymer shows an LC behaviour and such a characteristic is maintained in copolymers with low content of terephthaloyldichloride comonomer, while a further increase in comonomer content attenuates this LC attitude. Annealing treatments on "as polymerized" and coagulated copolymers are able to transform the LC phase "metastable at room temperature" into crystalline and/or amorphous phases.

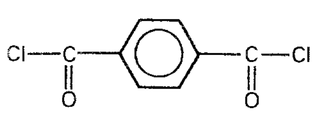
1. Introduction

In a previous paper [1] the synthesis of novel aromatic poly(etheraroyl-hydrazides) incorporating 4-oxybenzoyl units, whose general formula is (with methylene units, *m*, ranging from 2 to 12) was reported. The increasing number of methylene units in the backbone gives rise to polymers which melt before the hydrazidic linkage undergoes thermal intracyclodehydration to oxadiazole [2]; the influence of the *m* value upon properties has been investigated [3].

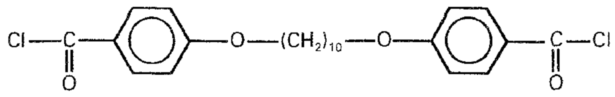


Preliminary results concerning the synthesis procedure, the thermal behaviour, the molecular and superreticular structure of a wide series of copolymers are reported in the present paper. Polymers are obtained through a copolymerization reaction starting from the following monomers

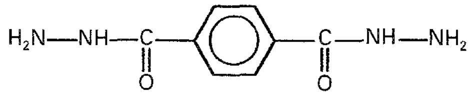
Monomer 1



Monomer 2

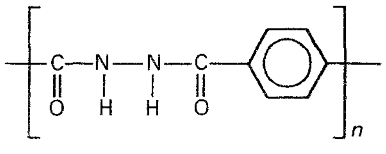


Monomer 3



The properties of these copolymers have been studied as a function of composition and have been compared with those of the two homopolymers, whose molecular structure is hereafter reported

Homopolymer A (PHZ)



Homopolymer B (PEHZ)

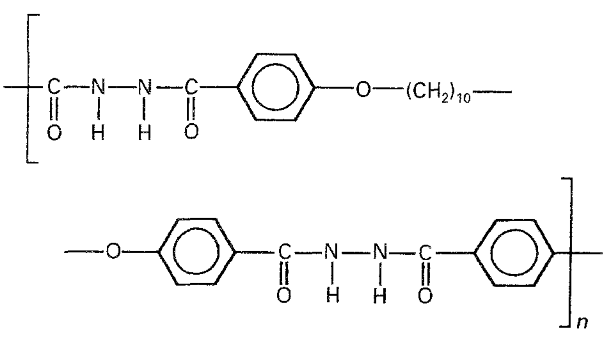


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TABLE I Codes and composition of the investigated homo- and copolymers

Homo- or copolymer	x (%)[a]	y (%)[a]	$R = x/y$
PEHZ (homopolymer B)	–	100	–
PEHZ 85	15	85	0.18
PEHZ 75	25	75	0.33
PEHZ 50	50	50	1.00
PEHZ 25	75	25	3.00
PEHZ 15	85	15	5.67
PHZ (homopolymer A)	100	–	–

[a] Where x and y are the mole per cent of the comonomers 1 and 2, respectively.

Codes and molecular compositions of homopolymers and P(HZ–EHZ) copolymers are listed in Table I. The copolymers have a ratio, $R = x/y$, ranging from 0.18 to 5.67, where x and y represent the mole per cent of the two comonomers.

The homopolymer A, PHZ, is a polyterephthalhydrazide, whose synthesis is well known in the literature [4].

The homopolymers and copolymers have been synthetized by polycondensation in solution of dimethylacetamide (5% LiCl); the procedure is reported in detail in [5].

FTIR, DSC and WAXS techniques have been used to characterize the "as polymerized" as well as the annealed homo- and copolymers. The present note specifically refers to interesting relationships found between the molecular composition and phase structure development in the condensed state, as well as above melting and before the intracyclodehydration reaction temperature.

2. Experimental procedure

The inherent viscosities, η_{inh}, $= \ln(t/t_0)/c$ were measured by a Ubbelhode viscosimeter in hexamethylphosphoramide (HMPA) at 30 °C.

FT–i.r. spectra were obtained on a Nicolet 5 DX-B spectrometer with a resolution of $4\,cm^{-1}$ (60 scans collected). Samples were prepared by compressing the powders into KBr discs.

DSC analysis was performed on a Mettler TA-3000 apparatus, equipped with a control and programming unit (microprocessor Tc 10 A) for elaboration of the stored data, and a calorimetric cell DSC-30, which allowed scans from − 170 to 600 °C. All the experiments were run under N_2 at a scan rate of $20\,°C\,min^{-1}$.

WAXS measurements were carried out at a temperature of 20.0 ± 0.5 °C on a PW 1050/71 Philips powder diffractometer (nickel filtered CuK_α radiation) in the reflection mode, scanning 2θ angle in continuous. To obtain smooth WAXS intensity profiles with good reproducibility and resolving power (without point–point intensity collection) the scan and chart speed were 0.25° 2θ min^{-1} and 0.5 cm min^{-1}, respectively. In the figures the experimental WAXS powder diffractograms are shown directly. All the spectra were performed in the 2θ range 1–60°.

3. Results and discussion

The synthesis of novel copolymers prepared and investigated by the authors is carried out by solution polycondensation [5]. The polymers are collected by non-solvent coagulation in water: this process leads to so-called "as polymerized" samples.

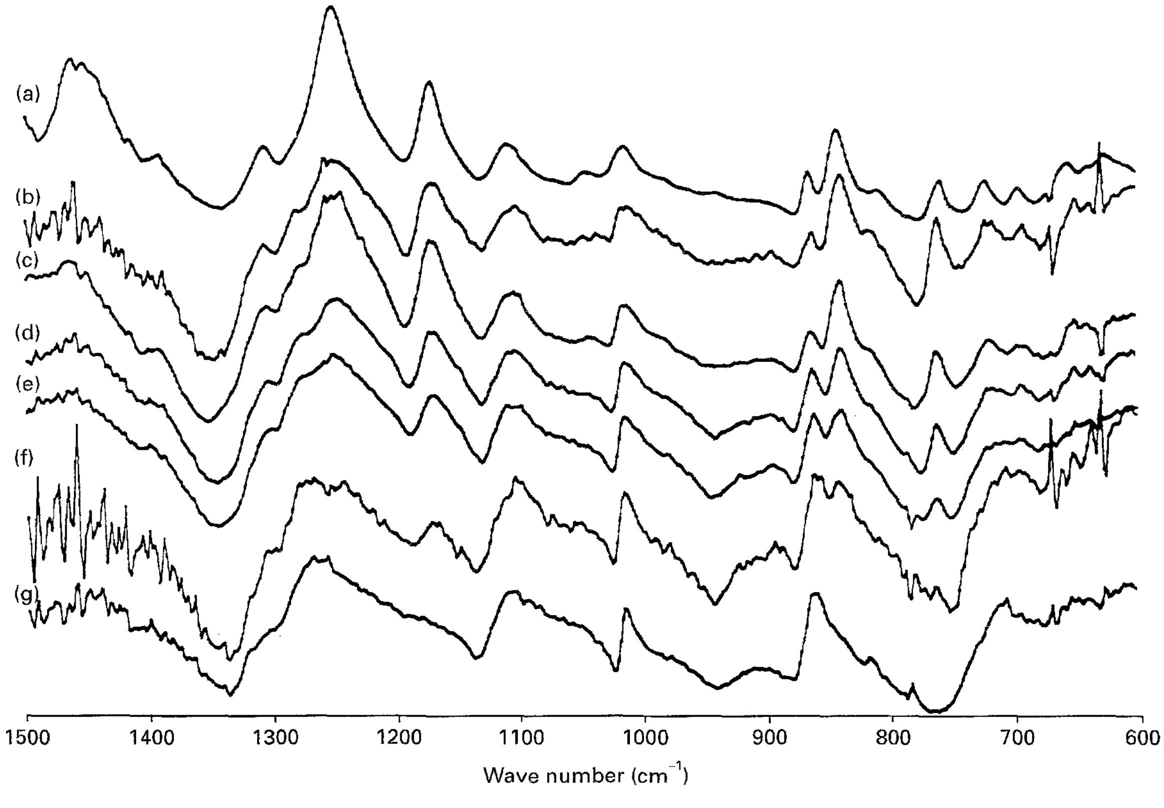


Figure 1 FT–i.r. spectra of the "as polymerized" homo- and copolymers: (a) PEHZ, (b) $R = 0.18$, (c) $R = 0.33$, (d) $R = 1.00$, (e) $R = 3.00$, (f) $R = 5.67$, and (g) PHZ.

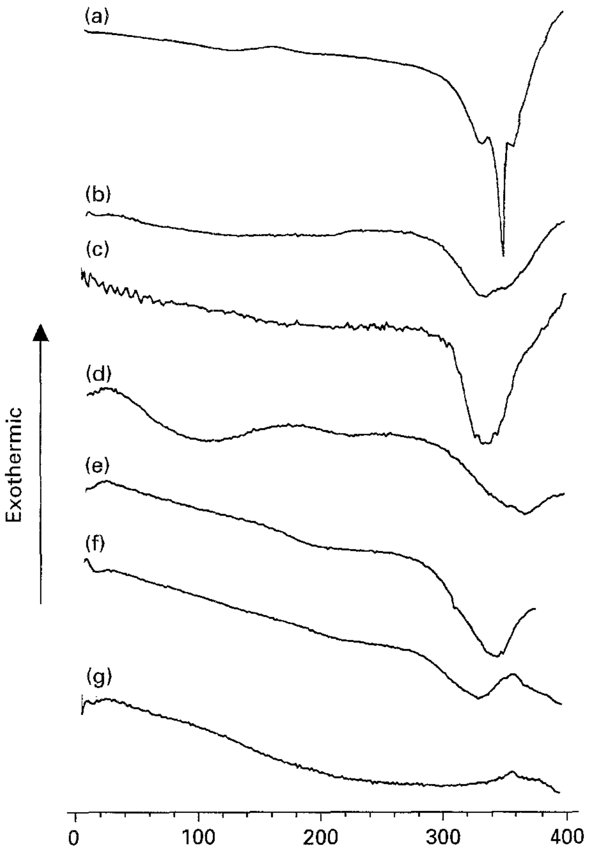


Figure 2 DSC traces of the "as polymerized" homo- and copolymers (scan rate 20 °C min^{-1}): (a) PEHZ, (b) $R = 0.18$, (c) $R = 0.33$, (d) $R = 1.00$, (e) $R = 3.00$, (f) $R = 5.67$, and (g) PHZ.

It is important normally to know the polyhydrazides structure as obtained through coagulation from the polymerization medium, because the processing of classical polyhydrazides is effected by "non-solvent spinning" from such a solution [4].

It was impossible to correlate η_{inh} with the viscosity–average molecular weight as no report in the literature was found for κ and α polyhydrazides values similar, at least, to the authors. Nevertheless the $\eta_{inh} = 0.5$–1.2 of polymers fell well inside the range of those normally reported for aromatic polyesters [6] containing *p*-oxybenzoic units.

The FT–i.r. spectra of all examined samples, "as polymerized", are shown by Fig. 1 in the range 1500–600 cm^{-1}. In the case of homopolymer A, poly(etheraroyl-hydrazide), peaks at 1305, 1170, 841 and 758 cm^{-1} are present, while they are absent in homopolymer B. The peaks present at 1170 (bending) and 758 cm^{-1} (rocking) are typical of ether absorption, while the other peaks are typical of -CH_2- sequences.

The DSC thermograms and WAXS intensity profiles of "as polymerized" PEHZ, PHZ and copolymers are shown in Figs 2 and 3, respectively: it can be seen that both DSC traces and WAXS profiles are strongly dependent upon the molecular structure of the polymer. A careful cross analysis of DSC and WAXS data was performed: the results for homopolymers A and B and for the complete series of copolymers are hereafter reported.

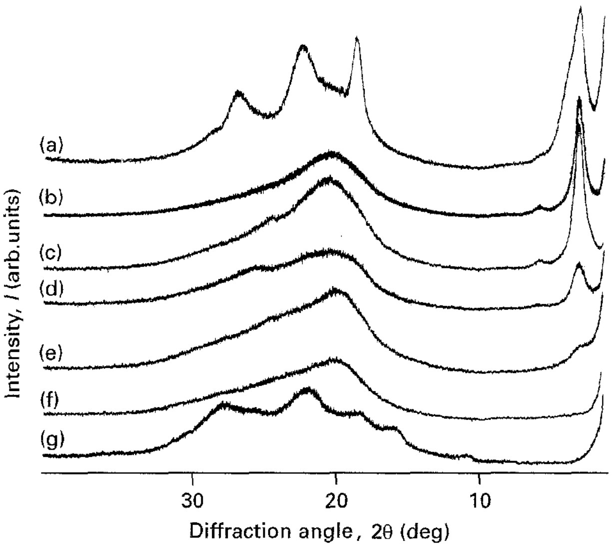


Figure 3 WAXS intensity profiles of the "as polymerized" homo- and copolymers: (a) PEHZ, (b) $R = 0.18$, (c) $R = 0.33$, (d) $R = 1.00$, (e) $R = 3.00$, (f) $R = 5.67$, and (g) PHZ.

3.1. PEHZ homopolymer

From DSC thermograms it emerges that this polymer is characterized by the following thermal transitions

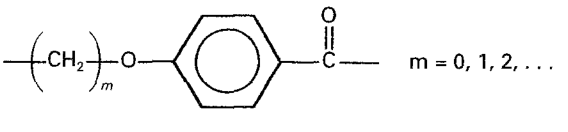
1. A glass transition at 167 °C.
2. Three well distinct (though partially overlapped) endothermic peaks in the range 320–360 °C. The corresponding peak temperatures are $T_1 = 327$ °C, $T_2 = 343$ °C, and $T_3 = 354$ °C.
3. Above T_3 the samples start to degrade.

The cross analysis of the WAXS intensity profile allows one to understand the phase structure of polymerized PEHZ at room temperature (r.t.) and to interpretate the kind of transitions occurring during heating up. The diffractogram of PEHZ at r.t. (see Fig. 3) shows

1. Three intense and well resolved crystalline peaks in the 2θ range of 15–35°, the peak maxima being centred at $2\theta_1 = 18.5°$, $2\theta_2 = 22.2°$ and $2\theta_3 = 26.7°$.
2. An amorphous halo centred at $2\theta = 20.3°$.
3. A very sharp and very intense peak in the low angle region centred at $2\theta = 2.9°$, to which corresponds a periodicity of 3.05 nm.

The cross interpretation of DSC and WAXS suggests that, after coagulation and precipitation, the "as polymerized" samples of PEHZ are characterized at r.t. in the condensed state by a complex phase structure, while in solution the polymer molecules are probably aggregated in LC domains [6–8]. The very sharp and intense peak at small angles in the WAXS profiles, as reported in the literature [7–10], could indicate the existence of layered LC structure.

The mesogenic groups



responsible for such kinds of high intense and sharp WAXS diffraction peaks in the low angle 2θ region, have been found to impart LC behaviour to polyesters or polyesterimide polymers. For the first time, to the authors' knowledge, the same mesogenic groups have been found to impart LC behaviour to polyhydrazides copolymers.

The observation of the LC peak in the WAXS profile at r.t. is accounted for by the coagulation procedure followed by the authors. As a matter of fact the low temperature of the non-solvent bath (r.t.) and consequently the high rate of precipitation of the polymers hinder the total transformation of the LC domains, probably preexisting in solution, to the crystalline phase [9].

Consequently at room temperature, below the temperature at which the glassy phase forms, i.e. T_g, the following phases coexist: (glassy amorphous + crystalline + LC). At this temperature of course the LC phase is metastable and accounts for the low angle peak [7–9] observed in the diffractogram of the "as polymerized" sample.

Following this interpretation, T_1, T_2 and T_3 endothermic DSC peaks are easily associated with the transition of PEHZ crystals to LC (T_1), to the isotropization of LC superreticular structures (T_2) and to the intracyclodehydration reaction (T_3).

3.2. PHZ homopolymer

The DSC trace of the "as polymerized" sample shows neither endothermic peaks nor detectable T_g in the investigated range. This behaviour is already reported for all aromatic polyhydrazides [4, 6] which undergo thermal cyclodehydration to polyoxadiazoles before the melting temperature.

From the corresponding WAXS intensity profile four crystalline peaks with middle intensity are detected. A noticeable amorphous halo centred at 21.7° 2θ is superimposed on these crystalline peaks. Not one peak in the small angle region ($2\theta < 5°$) is present. From the above it can be concluded that, at r.t. glassy (or rubbery) amorphous and crystalline phases are the only two phases present in "as polymerized" PHZ samples.

3.3. P(HZ–EHZ) copolymers

The DSC thermograms of copolymers show a very broad endothermic peak in the range 280–360 °C. T_g is evident only in the case of the copolymers with $R = 1.00$ ($T_g = 137$ °C), $R = 3.00$ ($T_g = 191$ °C) and $R = 5.67$ ($T_g = 170$ °C), see Fig. 2.

From the WAXS intensity profiles one observes that

1. All the "as polymerized" copolymers at room temperature are amorphous, no crystalline peak being detectable (see Fig. 3).

2. The low angle peak is clearly observed in copolymers PEHZ 85 ($R = 0.18$), PEHZ 75 ($R = 0.33$), PEHZ 50 ($R = 1.00$); in the case of PEHZ 25 ($R = 3.00$) only a shoulder is visible.

3. The intensity of the low angle peak, starting from $R = 0.33$, sharply decreases with increasing HZ comonomer content (see Fig. 3).

Comparison of DSC and WAXS of copolymer samples seems to indicate that these polymers are unable to crystallize following the coagulation process. Such behaviour could be ascribed to the precipitation procedure and/or to the fact that copolymerization introduces constitutional defects along the backbone. The ability to form LC domains is still preserved at least in samples with a higher content of PEHZ comonomer. For such copolymers, as in the case of PEHZ homopolymer, transformation of the LC phase to the amorphous state probably seems to be, at least partially, hindered [8].

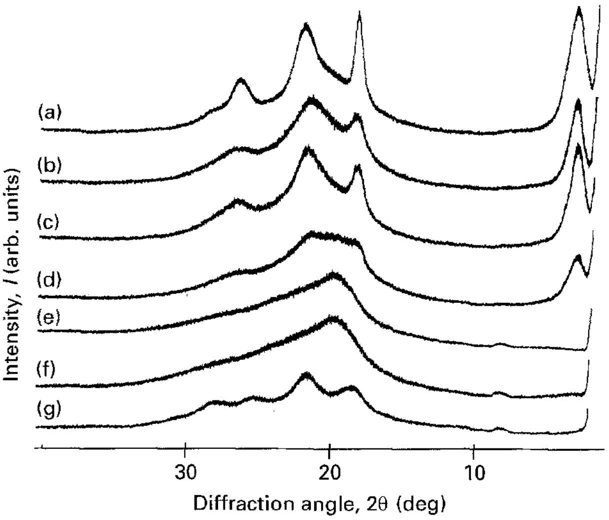


Figure 4 WAXS intensity profiles of the homo- and copolymers annealed at 200 °C: (a) PEHZ, (b) $R = 0.18$, (c) $R = 0.33$, (d) $R = 1.00$, (e) $R = 3.00$, (f) $R = 5.67$, and (g) PHZ.

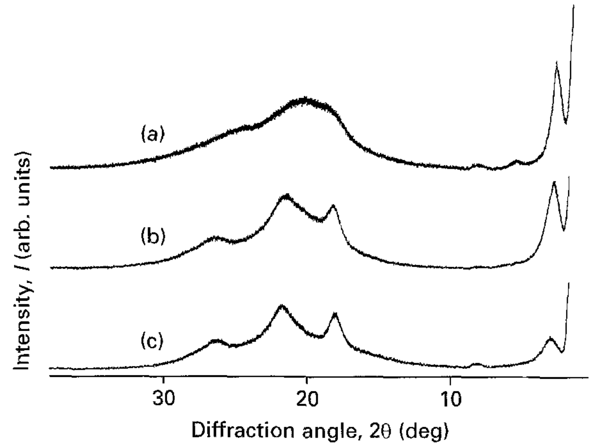


Figure 5 WAXS intensity profiles of the PEHZ 75 copolymer ($R = 0.33$): (a) "as polymerized", (b) annealed at 200 °C, and (c) further annealed at 250 °C (see also Table II).

Furthermore, the influence of aliphatic spacer content on the amount of LC phase clearly indicates the mesogenic nature of the small angle peak in the X-ray diffraction patterns.

3.4. Annealed samples

For a better understanding of the above results and to give an appropriate interpretation to them, the "as polymerized" homo- and copolymers samples were annealed at a temperature (200 °C) well above T_g, for 6 h under nitrogen, and then cooled to r.t. WAXS intensity profiles were then collected (see Fig. 4).

TABLE II Superreticular parameters as a function of the thermal treatment of the PEHZ 75 copolymer ($R = 0.33$)

Copolymer	WAXS profile[a]	LC paracrystalline reflection			
		Diffraction angle 2θ (°)	Spacing, d (nm)	Intensity, I (a.u.)	Peak half-width, $L_{1/2}$ (°2θ)
"As polymerized"	a	2.88 ± 0.05	3.07 ± 0.04	104 ± 1	0.55 ± 0.05
Annealed at 200 °C for 6 h	b	3.00 ± 0.05	2.95 ± 0.04	82 ± 1	0.83 ± 0.03
Further annealed at 250 °C for 4 h	c	3.15 ± 0.05	2.81 ± 0.04	28 ± 1	1.00 ± 0.03

[a] See also a, b and c spectrum, respectively, (Fig. 5).

Only in the case of the copolymer with $R = 0.33$ the sample, after thermal treatment, was further annealed at a higher temperature (250 °C) for 4 h, cooled at r.t., and then examined again by WAXS (see Fig. 5).

From WAXS profiles one observes that, following annealing, crystalline peaks develop in samples with $R = 0.18$, $R = 0.33$ and $R = 1.00$, while the intensity and sharpness of the low angle peak decreases more and more as annealing proceeds (cf. Figs 4 and 5 with Fig. 3 and see Table II). The annealing seems to influence the maximum position of the low angle peak (Table II).

Such a result can be accounted for by assuming that annealing at $T > T_g$ is able to transform the metastable LC phase into a crystalline and/or amorphous phase.

4. Conclusions

Preliminary results indicate that PEHZ homopolymer is likely to be characterized by LC behaviour. Such a characteristic is maintained in copolymers with a relatively low HZ content. The LC attitude is attenuated by increasing the content of HZ in the copolymerization. The conditions (rate and temperature) of coagulation and precipitation using a non-solvent seem to determine, together with the concentration of PEHZ in the reacting solution and at least for some copolymers, the phase structure development in the condensed state. This behaviour is observable in the case of PEHZ-rich copolymers.

Work is under progress to understand better how the conditions of the synthesis process, together with the molecular constitution of macromolecules, may influence the phase structure of homopolymers and copolymers in the condensed state and its evolution following thermal treatment. Furthermore the authors are investigating the structure and phase behaviour of the polyoxadiazoles, obtained after corresponding intracyclodehydration reaction.

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