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## Liquid Crystals

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## The synthesis and characterization of a new class of liquid crystalline polymers based on s-triazine

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The synthesis and characterization of a new class of liquid crystalline alternating copolymers based on s-triazine rings, connected by flexible alkyldiamine spacers and other selected bridging groups is reported. The propensity of the system to demonstrate liquid crystallinity as a function of the bridging group is investigated. Unexpectedly, the homopolymer of the triazine ring connected by a flexible alkyldiamine spacer is also a liquid crystalline polymer. A new polymerization technique is reported in which the alkyldiamine serves the dual role of monomer and proton acceptor. These polymers form liquid crystalline glasses which are transparent and have good mechanical properties. This suggests that they could be interesting materials to be further studied in the context of non-linear optics.

### 1. Introduction

At present about 20 000 thermotropic liquid crystalline compounds are known. Most of them are closely related to a characteristic geometric molecular shape consisting of a rigid rod-like core or mesogenic unit [1]. In the past ten years several new substance classes have been synthesized which deviate somewhat from this classical model of rod-like molecules, but which nonetheless are effectively dominated by anisotropic geometrical considerations which enable them to form mesophases, i.e. twin compounds, polycatenar, discotic and pyramidal compounds and metal complexes [2]. The qualitative concept that mesophase formation, also for polymers, could be interpreted in terms of macroscopic molecular geometry independent of the nature of the individual bonds and atoms comprising the molecule was many years ago postulated by Vorländer in his classic paper of 1923 [3]. The lack of a generally accepted quantitative theory to predict mesomorphic behaviour does not however allow for rational molecular design.

Liquid crystalline polymers (LCP) also follow the above logic. When they do not have the intrinsic rigidity of aromatic polyesters or polyamides, they consist of sequences of rigid segments and more flexible segments or mesogenic units linked together. While borderline cases are to be anticipated, the rigid segments generally have sufficient rigidity and aspect ratio to be mesogenic in their own right.

The triazine ring is very similar, from a geometrical point of view, to the benzene ring except that substituents can only be placed at *meta*-positions. Nevertheless, it is possible to draw a molecule having the high aspect ratio suggested by de Gennes [4] to form a mesophase. This path was followed by Vora and Patel [5] who found liquid crystalline properties using triazine rings to form polyesters.

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In this work, we report the mode of preparation and systematic investigation of the liquid crystalline dependence on molecular structure, i.e. stiffness of linking groups, for triazine based homo- and co-polymers. A good general review on the synthesis and properties of regular polytriazines containing 250 references, has been given by Pankratov and Vinogradova [6].

Since a remaining chlorine atom in a disubstituted triazine ring is still quite reactive, thus imparting instability to the polymer obtained, it was decided to use the selective reactivity of three triazinic chlorine atoms first to block one of the reactive sites by reacting the first chlorine with a monofunctional compound. Subsequently using the selective reactivity of the other two chlorine atoms, we produced a sequenced polytriazine by reacting the blocked compound alternatively with a flexible and a rigid bifunctional molecule. By varying the blocking group, and the rigid and the flexible bridges between the triazine rings, a large variety of polymers can be obtained and evaluated with respect to their liquid crystalline properties (see figure 1). Flexible di-s-triazinic units derived from such reactions are described in table 1. Alkoxy blocking groups,  $R = -CH_3$  and  $-C_2H_5$ , were chosen, since the 2,4-dichloro-6-alkoxy triazines can be easily prepared, leaving the remaining two chlorine atoms quite reactive for subsequent nucleophilic substitution. As flexible spacers, aliphatic diamines were chosen since they are readily available with different chain lengths and are quite reactive in nucleophilic substitution of chlorine. The rigid comonomers are shown in table 2. These, in fact, are not totally rigid and were chosen to have a broad spectrum of relative flexibility.

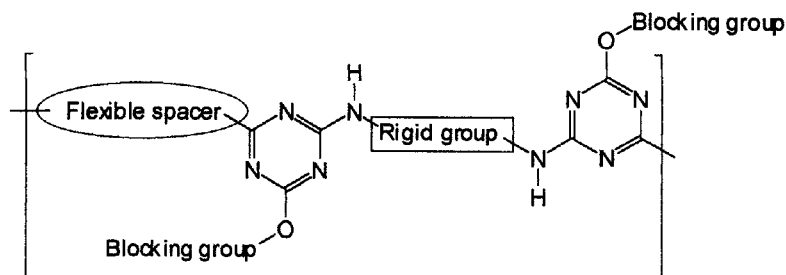
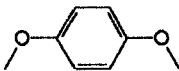
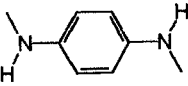
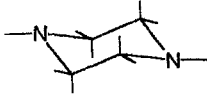


Figure 1. A schematic diagram of possible structures for liquid crystalline co-polymers based on triazine rings bridged alternately by flexible and rigid units, formula I.

Table 1. Di-s-triazinic monomers having flexible spacers.

Formula I	R	m	Symbol used
	$CH_3$	6	Me-6
	$CH_3$	12	Me-12
	$C_2H_5$	6	Et-6
	$C_2H_5$	12	Et-12

Table 2. Rigid chain extending linking groups.

Co-monomers	Symbol used
	HQ
	pPhDA
	PPZ
$\text{—HN—(CH}_2\text{)}_k\text{—NH—}$	<i>k</i> DA

## 2. Experimental

### 2.1. Purification of monomers

The synthesis, purification and characterization of the di-*s*-triazinic compounds are described in a previous paper [7]. The 'rigid comonomers' were of high purity and were further purified by classical techniques such as recrystallization or preparative chromatography.

### 2.2. Polymerization

Different methods of polymerization were evaluated—melt, solution and interfacial condensation. Melt polymerizations were not successful. Interfacial condensations were very difficult to perform, not totally reproducible and could be utilized only with short-chain aliphatic diamines.

The solution method, as described by Audebert [8] thus became the method of choice [5 mmols of each monomer were added to 50 ml of xylene containing 20 mmols of  $\text{Na}_2\text{CO}_3$  under a nitrogen sweep, with magnetic stirring at  $130^\circ\text{C}$  for 60 h]. As hydroquinone is less reactive than the corresponding diamine, more severe conditions were required to achieve reaction. Adequate conditions were found to be: 5 mmols of each monomer were added to 60 ml of trichlorobenzene under a nitrogen sweep with mechanical stirring at  $210^\circ\text{C}$  for 24 h. Under these conditions, the polymer stayed in solution and the HCl formed was removed by the nitrogen flow. All polymerizations were monitored by GC monitoring of the monomer concentration in the reaction solution. After polymerization, the polymers were washed and where possible, dissolved reprecipitated, and dried under vacuum (1 mm Hg) for 8–16 h at  $130^\circ\text{C}$ .

The polymers synthesized have been characterized by:

Elemental analysis for C, N, H and Cl content.

IR spectra.

Inherent viscosities for the determination of degree of polymerization were measured with a modified Desreux-Bischoff capillary viscometer using formic acid (0.25 g dl,  $30^\circ\text{C}$ ).

The determination of glass transition temperatures and crystalline melting ranges were carried out using a Perkin-Elmer DSC 7 with a Perkin-Elmer Professional computer 7700, at heating/cooling rates of  $10^{\circ}\text{C min}^{-1}$ .

Thermogravimetric analyses were performed with the same DSC apparatus (TGA 7 accessory) at a heating rate of  $20^{\circ}\text{C min}^{-1}$ . The thermal stability results reported here represent the temperature reached by the sample, under nitrogen flow, at 5 per cent weight loss.

X-ray analyses were performed for the determination of crystallinity. X-ray diffraction patterns of samples in the powdered form were collected with a Philips PW 1011/00 apparatus using  $\text{CuK}_{\alpha}$  radiation and a Ni filter. The diffraction patterns of thin films and plaques were collected with a Siemens Diffrac 500 apparatus.

Polarizing microscopic observations with a hot-stage (Mettler FP 80 and FP 82) allowed a determination of molecular order, as evidenced by the presence of birefringence, as a function of temperature.

### 2.3. Polymerization with a diamine proton acceptor

As an alternative to the solution method of Audebert, a method was developed in which two mols of diamine were reacted with one mol of the bis-triazine. One mol of diamine, evidently, enters into reaction to form the desired polymer, while the second mol reacts with the liberated HCl. As an example ET-6-12 can be prepared as follows.

In a thermostated 3 l reactor with external temperature regulation, a thermocouple for temperature measurement, mechanical stirring and access for nitrogen and refrigerant, 163 g (0.8 mols, purity 98 per cent) of 1,12-diaminododecane and 400 ml of *p*-xylene were introduced. As the diamine is only slightly soluble in *p*-xylene it was introduced in its melt state followed by the *p*-xylene.

The reactor was heated to  $40^{\circ}\text{C}$  and a solution of 155.2 g of 2,4-dichloro-6-ethoxytriazine (0.8 mols—purity 98 per cent) in 400 ml of *p*-xylene was added slowly, maintaining the temperature between  $40^{\circ}\text{C}$  and  $60^{\circ}\text{C}$ . A suspension of 1,12-diaminododecane dihydrochloride was obtained while the Et-12 compound formed stayed in solution. It was demonstrated that no polymerization occurs at the temperatures used for this reaction, i.e. the reactivities of the 2nd and 3rd triazinic chlorine atoms are sufficiently different to obtain quantitative selectivity. By GC analysis, a quantitative amount of the compound of general formula I was found. A quantitative amount of 1,12-diaminododecane dihydrochloride could also be extracted from the polymerization reaction by filtration and so recycled. For laboratory purposes, however, it may stay in the reaction flask and be eliminated at the end of polymerization.

Then a solution of 92.8 g of 1,6-hexanediamine (0.8 mols—purity 99 per cent) in 40 ml of *p*-xylene was added. The temperature was raised to  $140^{\circ}\text{C}$  and maintained there for 15 min. In this case, the diamine is fairly soluble in the solvent and must be added carefully to the polymerization reaction while the salt and the polymer precipitate. Apparently the polymer is sufficiently swollen by solvent to allow the polymerization to proceed even after precipitation. The two amine hydrochlorides were found in equal amounts confirming not only the copolymeric structure, but also the fact that the hydrochloride exchange from one to the other diamine did not occur on the time scale of the reaction.

The *p*-xylene was then decanted and, after slight cooling of the reactor, replaced by 400 ml of a 1 : 1 formic acid : methyl ethyl ketone mixture. After complete dissolution of the polymer and diamine hydrochlorides, the solution was removed from the reactor and poured into cold water. The diamine hydrochlorides are sufficiently water soluble to remain in solution while the pure polymer is obtained as a precipitate.

The polymer, a fine white powder, was filtered off, and washed twice with water, twice with acetone and once with ethyl ether. Finally the polymer was dried at 60°C for one day in an air circulating oven and under vacuum at 130°C for another day.

There were no observable differences between polymer Et-6-12 coming from the reaction of Et-6 monomer (table 1) with 1,12-diaminododecane and Et-12-6 polymer coming from the reaction of Et-12 with 1,6-diaminohexane. Moreover, by adding a mixture of the two diamines to the blocked triazine derivative, in which case a random distribution may occur, no noticeable differences on measured properties were observed.

#### 2.4. Film and plaque preparation

Thin films were prepared by solution casting. 1.5 g of polymer were dissolved in a 1 : 1 by weight mixture of formic acid and methyl ethyl ketone and 10 ml of the filtered solution were spread on an 8 × 8 cm glass plate. After spontaneous evaporation of the solvent (1 night), the film was dried under vacuum for 8 h.

Polymer plaques of 1 and 3 mm thickness were prepared by compression moulding at 180°C.

#### 2.5. Optimization of polymerization conditions

For the polymerizations of triazinic derivatives with diamines, the solution method as described by Audebert, seemed to be the most promising, but presented many disadvantages, such as long reaction times and large solvent volumes. An optimization of the conditions was therefore undertaken.

Polymerization conditions were optimized for the Et-6-12 polymer. The influences of many polycondensation parameters were evaluated and are here summarized.

##### 2.5.1. Monomers: purity and concentration

Starting from high purity monomers, freshly recrystallized from hexane (> 99.9 per cent GC analysis), we progressively passed to lower grade monomers, for example, 1,6-diaminohexane: 99 per cent, 1,12-diaminododecane: 98 per cent, as received from suppliers, without loss of polymer molecular weight, as evidenced from inherent viscosity and chlorine content determinations.

##### 2.5.2. Polymerization temperature and time.

If diamines are used as the proton acceptors, reaction times can be lowered to less than one hour. Otherwise, with Na<sub>2</sub>CO<sub>3</sub> as the proton acceptor, more than 10 h are required.

##### 2.5.3 Molar ratio between different monomers

The molar ratio of diamine as proton acceptor must be maintained within 2 per cent of the stoichiometric value, in order to achieve high molecular weight polymer.

##### 2.5.4. Necessity of anhydrous conditions

Anhydrous conditions are not necessary. Polymerizations still ran satisfactorily with a water content of up to 10 per cent by weight.

### 2.5.5. *Stirring conditions*

Stirring is not an essential parameter. Slow, fast and irregular stirring did not affect the molecular weight of the polymer obtained as evaluated from the inherent viscosities and chlorine content measurements.

### 2.5.6. *Polymer purification conditions*

The final purification of polymer is essential to eliminate the presence of diamine salts (or sodium salt in the case of  $\text{Na}_2\text{CO}_3$ ) which lead to a dramatic deterioration of polymer properties with respect to thermal stability. After various attempts, best conditions were found by dissolving the polymer in formic acid (or a mixture of formic acid with 50 per cent of a polar solvent as methyl ethyl ketone, dioxane DMSO or DMF) and precipitating in water (or a dilute soda solution). The solvent must dissolve the polymer and the salts, while the latter must stay in solution when the mixture is added to the polymer non-solvent.

## 3. Results and discussion

### 3.1. *Polycondensation of di-triazinic compounds of formula I with hydroquinone*

The polymers containing hydroquinone were obtained using a special procedure as noted above, but nevertheless their relatively high chlorine content suggested a low degree of polymerization. Table 3 shows some characteristic features of these polymers. The chlorine content gives an indication of the number average molecular weight of the polymer, i.e. an end group analysis on the presumption of stoichiometric balance between the monomers. With reference to the results shown below in table 3, Me-12-HQ, with a Cl content of 7 per cent and Et-12-HQ with a Cl content of 0.75 per cent give molecular weights of 500 and 5000, respectively, i.e. degrees of polymerization of c. 0.9 and 9. Being condensation polymers, the weight average molecular weights should be at least a factor of 2–3 higher. Hence, molecular weights can be estimated even in the absence of solubility. Elemental analyses, as well as IR spectra, confirmed the expected polymer structures.

Table 3. Polymers based on formula I and hydroquinone.

Polymer	Yield/ per cent	Cl content/ per cent	X-ray spacing/Å	Phase present	TGA degradation/°C
Me-6-HQ	30	4.5	4, 11	Amorphous	230
Et-6-HQ	76	4.5	4, 11	Amorphous	230
Me-12-HQ	72	7	4.3, 7	Amorphous	230
Et-12-HQ	31	0.75	4.3, 7	Amorphous	230

These polymers are amorphous and intractable, having a TGA degradation temperature of 230°C. There is no evidence of any transitions from polarizing microscopy or DSC at temperatures up to 300°C. The amorphous nature is evidenced by two broad X-ray reflections, as exemplified in figure 2. There is ample evidence in the literature for amorphous polymers having two diffuse reflections [9].

### 3.2. *Polycondensation of di-triazinic compounds of formula I with p-phenylenediamine*

Polymerizations were performed under the conditions described by Audebert. For all polymers, the chlorine content was less than 0.2 per cent. Considering the relatively

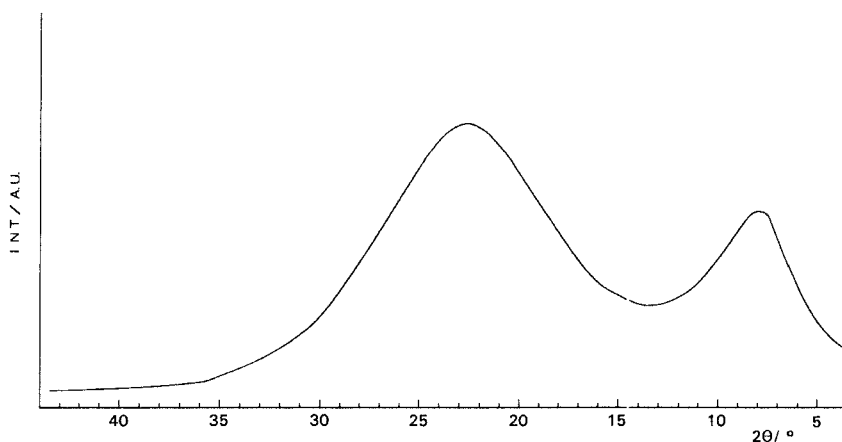


Figure 2. A room temperature X-ray powder diffractometer trace of the Me-6-HQ copolymer demonstrating its amorphous nature by the presence of two diffuse reflections.

high values of the inherent viscosities obtained, reasonably high molecular weights can be expected. Elemental analysis and IR spectra confirm the expected structures. Table 4 shows the main characteristics of these polymers. The polymers having the ethoxy blocking group seem to be more stable than those having the methoxy group.

X-ray diffraction patterns for these polymers are similar to those for the HQ-derivatives discussed above. The polymers having the longer  $C_{12}$  flexible chain show birefringence at room temperature which is stable and maintained till more than  $100^{\circ}\text{C}$  above the glass transition temperatures. More careful observation shows greater birefringence and fluidity of the ethoxy compound, Et-12-*p*PhDA, which is totally liquid above  $200^{\circ}\text{C}$  and first loses its birefringence above  $230^{\circ}\text{C}$  at a heating rate of  $2^{\circ}\text{C min}^{-1}$ . If one were dealing with an amorphous glass that was birefringent due to stress-optical effects, surely the birefringence would be lost when heating at  $2^{\circ}\text{C min}^{-1}$  to  $100^{\circ}\text{C}$  above  $T_g$ . The DSC trace for this compound is shown in figure 3 where one can observe the  $T_g$  at  $124^{\circ}\text{C}$  and a broad endotherm centred around  $220^{\circ}\text{C}$ , corresponding to isotropization. These compounds are thus liquid crystalline glasses having an isotropization temperature in excess of the glass transition. The polymers having the shorter  $C_6$  chain as flexible spacer do not show birefringence under the polarizing microscope.

### 3.3. Polycondensation of di-triazinic compounds of formula I with piperazine

Polymerizations were performed under the same conditions as with *p*-phenylenediamine. The chlorine content is also lower than 0.2 per cent, and as previously, the inherent viscosities are high, giving rise to the expectation of high molecular weight products. IR spectra and elemental analysis confirm the expected structure. The polymer having the shortest flexible chain,  $C_6$ , and the methoxy blocking group is unstable on heating. Table 5 shows the main characteristics for these polymers.

With the exception of the Me-6-PPZ polymer, which does not melt and decomposes rapidly, all other polymers are birefringent under the polarizing microscope. The Et-6-PPZ polymer showed an endothermic transition at  $161^{\circ}\text{C}$  by DSC analysis, but no evidence of melting was observed by microscopy.



Table 4. Polymers based on formula I and p-phenylene diamine

Polymer	Yield/per cent	Inherent viscosity/dl g <sup>-1</sup>	X-ray spacing/Å	Phase present at ambient temperature	T <sub>g</sub> /°C	Phase present T > T <sub>g</sub>	DSC peak/°C [isotropization]	TGA degradation/°C
Me-6-pPhDA	77	3	10, 4	Amorphous	—	—	—	Unstable
Et-6-pPhDA	58	4.6	10, 4	Amorphous	146	Amorphous	—	330
Me-12-pPhDA	80	4.2	18, 4.3	LC glass	130	LC	220	300
Et-12-pPhDA	76	2	4.3	LC glass	124	LC	230	330

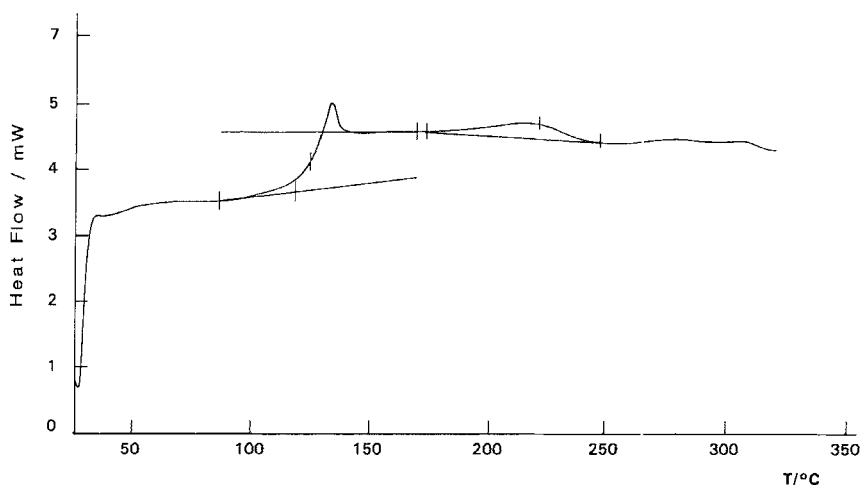


Figure 3. A DSC trace for the Et-12-pPDA copolymer showing its glass transition and isotropization endotherm.

Polymers having the  $C_{12}$  flexible chain showed melting transitions by DSC analysis near  $250^{\circ}\text{C}$  (table 5), but under the microscope, real fluidity was seen only at higher temperatures  $20\text{--}40^{\circ}\text{C}$ . In the presence of air, they become brown before any loss of birefringence could be seen. The Me-12-PPZ polymer showed a melting transition on the first DSC scan and a  $T_g$  on the second one. On the other hand, Et-12-PPZ showed a melting transition during the first scan at  $10^{\circ}\text{C min}^{-1}$  and crystallization on cooling.

Figure 4 shows the X-ray diffractogram of Et-6-PPZ as a representative example of the family in which multiple sharp crystalline reflections can be seen.

### 3.4. Polycondensation of di-triazinic compounds of formula I with linear aliphatic diamines

This polymer family is a peculiar one inasmuch as the 'rigid group' is quite flexible for the longer homologues. Ethylenediamine would be considered as fairly rigid and, in fact, more than one type of liquid crystal is based on this group as the link between two aromatic rings [10]. On the other hand, 1,6-diaminohexane is undoubtedly flexible.

Polymerizations were performed under the same conditions as with *p*-phenylenediamine. Chlorine content is lower than 0.2 per cent and inherent viscosities are very high, polymer solubility permitting, ranging from  $5.5$  to  $12\text{ dl g}^{-1}$ , giving the expectation of high molecular weight polymers. IR spectra and elemental analysis confirm the expected structure.

For the two polymers having the shortest aliphatic chains  $C_2$  and  $C_6$ , i.e. Me-6-2 and Et-6-2, no solvent was found. With exception of the Et-6-2 polymer, which moreover showed no thermal transitions on DSC analysis until degradation occurred at  $280^{\circ}\text{C}$  and Me-6-2 which showed a simple  $T_g$  behaviour at  $137^{\circ}\text{C}$ , these polymers showed birefringence under the polarizing microscope at room temperature and maintained this during heating at  $2^{\circ}\text{C min}^{-1}$  until  $250\text{--}300^{\circ}\text{C}$ . They also had  $T_g$ s at quite low temperatures and gave amorphous X-ray scattering patterns as in figure 5, with two broad peaks at room temperature. Table 6 gives the main characteristics for these polymers, and also reports softening temperatures observed during microscopic observations.

Table 5. Polymers based on formula I and piperazine.

Polymer	Yield/per cent	Inherent viscosity/dl g <sup>-1</sup>	Phase present at ambient temperature	DSC melting endotherm/°C	Microscope observation melting/°C	Phase present $T > T_m$	TGA degradation/°C
Me-6-PPZ	63	2.6	—	—	—	—	Unstable
Et-6-PPZ	87	1.7	Crystalline	161	—	LC	320
Me-12-PPZ	73	6.3	Crystalline	250 (1st scan) $T_g = 182$ (2nd scan)	290	LC	320
Et-12-PPZ	75	5.5	Crystalline	243	280	LC	320

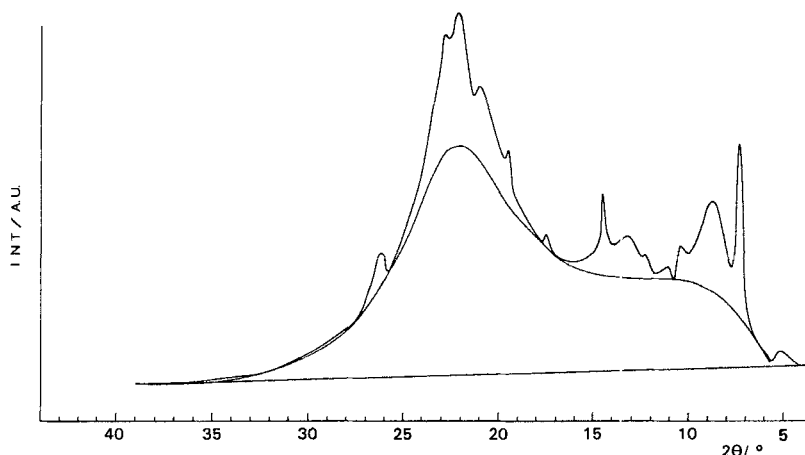


Figure 4. A room temperature X-ray powder diffractometer trace of the Et-6-PPZ copolymer demonstrating its crystalline nature by the presence of multiple sharp reflections.

Curiously, the polymers of this series, with the greatest propensity to form mesophases, are those having the most flexibility, the extreme being Me-12-12 and Et-12-12. Reconsidering table 1, one realizes that in this latter case there is a  $-(\text{CH}_2)_{12}-$  flexible spacer separating single 6-membered rings with an  $-\text{NH}-$  linking group. By conventional wisdom, a single ring does not have sufficient geometrical anisotropy or aspect ratio to behave as a mesogenic unit and one should therefore not expect liquid crystallinity in this case at all.

Similar phenomena were observed and discussed in previous work [7] on the analogous low molar mass compounds. In that case, as in this one, it was argued that some type of intermolecular interaction, perhaps through hydrogen bonds, is required in order to achieve some supramolecular structure which spontaneously stiffens the molecules in such a way as to give rise to anisotropic aggregates which are capable of liquid crystal formation.

This family of polymers is thus interpreted as forming liquid crystalline glasses, maintaining their birefringence until more than  $200^\circ\text{C}$  above  $T_g$  for extended periods. Optical birefringence of an amorphous polymer is excluded.

### 3.5. Considerations of the proton acceptor

Different proton acceptors were tested with the following results: Tertiary amines reacted with the chlorine atoms of the triazine, giving stable complexes and so making them unusable. Inorganic bases, except sodium hydroxide which is too strong and hydrolyses the triazinic derivatives, are efficient but make polymerization very slow due to their insolubility in the organic solvent. Furthermore  $\text{Na}_2\text{CO}_3$  generates  $\text{CO}_2$  during polymerization.

### 3.6. Polymer characterization

The physical-chemical properties of the Et-6-12 polymer were characterized in more detail. The values reported here refer to the polymer obtained using conditions described in the experimental part under Polymerization:

Inherent viscosity	2.32 dl g <sup>-1</sup> (30°C; formic acid)
	0.30 dl g <sup>-1</sup> (30°C; TCE)

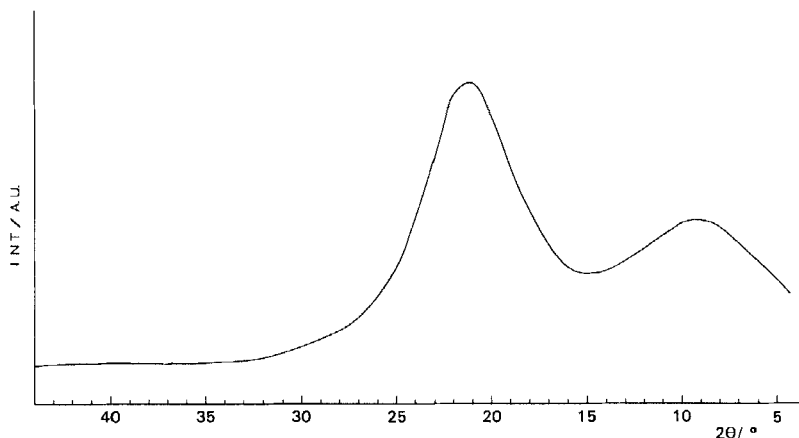


Figure 5. As in figure 2 but for a compression moulded plaque of the Et-6-12 copolymer showing its lack of crystallinity.

$T_g$	80–85°C (see figure 6)
Polarizing microscopy	Birefringent from room temperature up to 200–230°C
Chlorine content	<0.2 per cent
Thermogravimetric analysis	Stable until 300–320°C (see figure 7)
Moisture absorption	0.5 per cent
X-ray analysis	Two broad peaks at 4.2 Å and 10.6 Å.

Bulk properties of the polymer were analysed using 1 mm plaques. These plaques were completely transparent and pliable, but giving rise to brittle fracture; in some ways they qualitatively resemble polymethyl methacrylate. Polarizing microscope observations showed the plaque to be birefringent when viewed along the  $X$  and  $Y$  axes (see figure 8) at room temperature. After heating to 180°C, a slight birefringence also appears along the  $Z$  axis. The lack of birefringence when viewed along the  $Z$  direction would be a logical consequence of the random planar, pseudo-isotropic orientation obtained by squeeze flow during compression moulding. X-ray diffraction measurements did not indicate a preferred molecular organization in any one direction. Film thicknesses were measured by interference fringes in the IR spectra [11] and were all around 30  $\mu\text{m}$ . These films are highly transparent and have good mechanical properties. IR and UV spectra are reported (see figures 9–10). While it is difficult to prepare stress free mouldings or film castings, it was noted previously that the birefringence for this polymer is maintained in excess of 200°C above  $T_g$ . The measured birefringence is thus ascribed to liquid crystallinity.

It is generally accepted that a liquid crystalline glass is a non-mobile, glassy, frozen, liquid crystalline phase with an unchanged liquid crystalline structure from that above the glass transition temperature. The liquid crystal should therefore have the same optical properties above and below the glass transition. The transparency noted in liquid crystalline polymers [12] derives from the increased persistence length of the

Table 6. Polymer based on formula I and aliphatic diamines.

Polymer	Yield/per cent	X-ray spacing/Å	Phase present at ambient temperature	$T_g/^\circ\text{C}$	Phase present $T > T_g$	TGA degradation/ $^\circ\text{C}$
Me-6-12	88	8.8, 4.2	LC glass	55	LC	320
Et-6-12	88	8.8, 4.2	LC glass	73	LC	320
Me-12-12	83	18, 4.3	LC glass	56	LC	320
Et-12-12	88	18, 4.3	LC glass	93	LC	320
Me-6-2	66	9.8, 4	Amorphous	137	Amorphous	280
Et-6-2	42	8.5, 4	Amorphous	—	—	280
Me-12-2	59	18, 4.3	LC glass	95	LC	280
Et-12-2	85	4.3	LC glass	90	LC	310

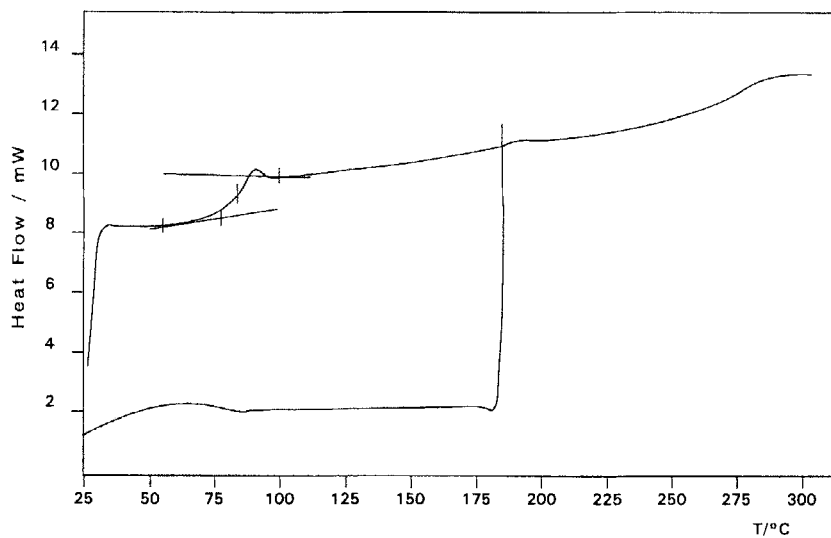


Figure 6. A DSC trace (2nd heating) for the Et-6-12 copolymer showing its glass transition and the lack of melting endotherms.

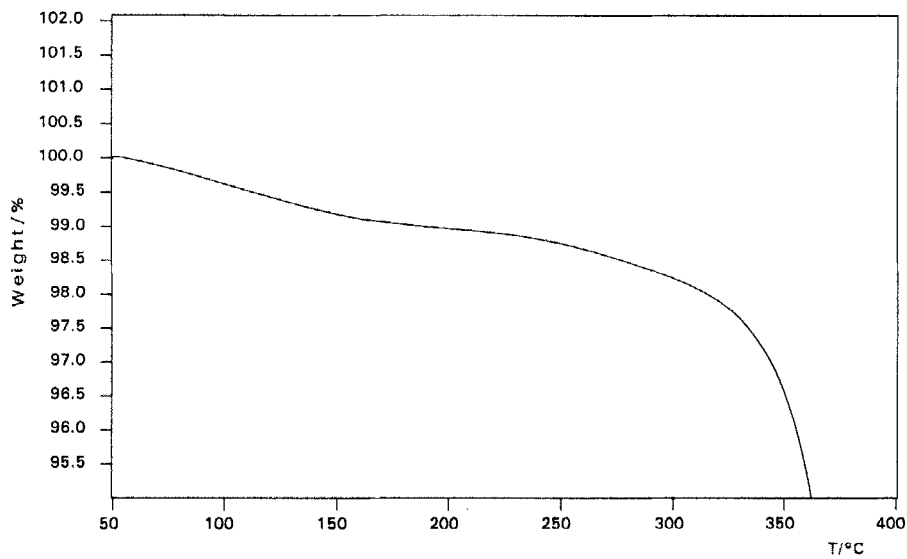


Figure 7. A TGA trace for the Et-6-12 copolymer showing its thermal stability up to 300°C.

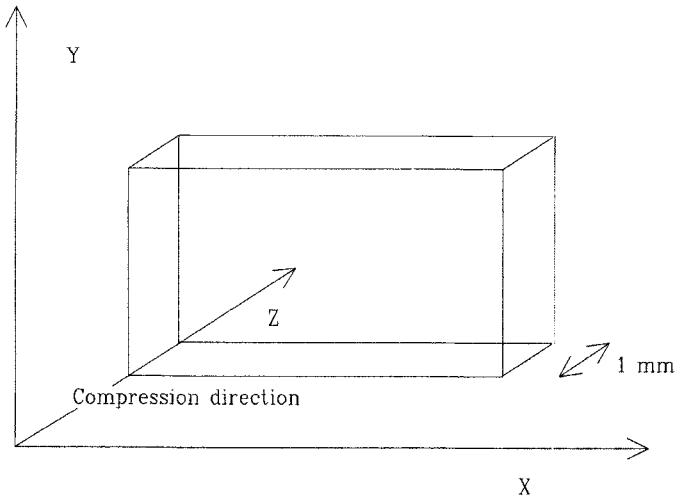


Figure 8. A coordinate system defining the axes of compression moulded specimens.

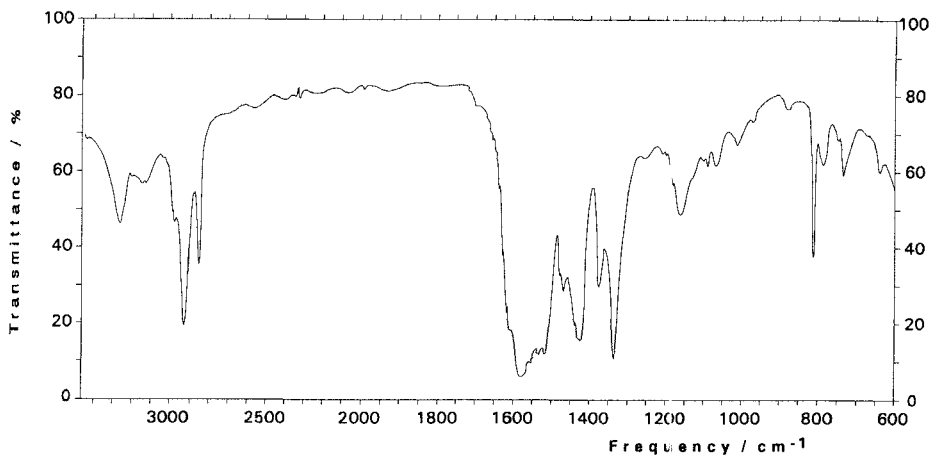


Figure 9. An infrared spectrum of a  $30\ \mu\text{m}$  film of the Et-6-12 copolymer with an air reference. Note the good transparency, i.e. lack of scattering, c. 80 per cent in the regions of the spectrum devoid of absorptions.

director, i.e. larger domain sizes, even in polydomain specimens [13]. Alternatively scattering or turbidity arises from the amplitude of the orientational fluctuations which are controlled by the elastic moduli. For polymers the elastic moduli are increased relative to those of small molecules and the enhanced viscous interactions can result in overdamped oscillations [12]. These are all factors which lead to reduced scattering and hence greater transparency. Turbidity, therefore, is not an inherent feature of the liquid crystalline state.

Very long, thin, resistant fibres were also spun from a melt of the polymer.



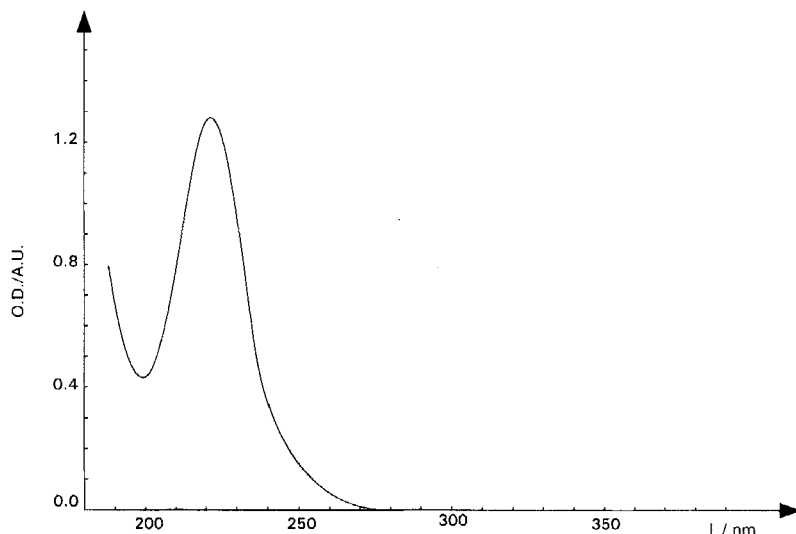


Figure 10. An ultraviolet–visible portion of the spectrum of a 30  $\mu\text{m}$  film of the Et-6-12 copolymer with an air reference. Here the transmission in the non-absorbing region in the visible and near-UV is also very high.

#### 4. Device application

The study of the non-linear optical properties of the compounds discussed above, a new class of liquid crystalline polymers, could be of interest for the following reasons:

- (i) High values of the third harmonic intensities have been reported for nitrogen containing heterocyclic compounds, for example, pyridine and pyrazine rings [14]. In fact triazine, may be naively considered to be an imine trimer.
- (ii) Orientational order through liquid crystallinity. In fact, a preliminary measurement [15] showed that such polymers have a very large temperature coefficient of refractive index, i.e.  $\delta n/\delta T \sim 10^{-3}$  instead of  $10^{-5}$ , normally associated with liquid crystals. Such a large temperature coefficient is generally associated with large values of the third harmonic intensity.
- (iii) Complete transparency because of the glassy mesophase.
- (iv) Good mechanical properties.
- (v) Readily available starting materials and ease of synthesis.

#### 5. Conclusions

Polymers based on the s-triazine ring show a propensity to form mesophases, even in cases where the polymer is quite flexible and an obvious mesogenic unit with the expected aspect ratio is lacking. Presumably a supramolecular structure is involved as previously suggested for the low molar mass analogues. A new polymer synthesis involves the unusual but advantageous concept of exploiting the diamine comonomer as proton acceptor in the formation of triazine/diamine polymers.

A new family of triazine based polymers is shown to behave as liquid crystalline glasses. Birefringence was observed continuously by polarizing microscopy from room temperature to over 100°C beyond the glass transition temperatures, indicating persistence of the organization. DSC analysis shows only a glass transition. The diffuse nature of the X-ray reflections clearly indicates a lack of crystallinity and suggests

nematic ordering as previously suggested for the low molar mass analogues. This new class of liquid crystalline polymer is particularly interesting as the materials can be easily processed due to their low transition temperatures. They have good mechanical properties, are highly transparent, and could find application in electro-optical systems.

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