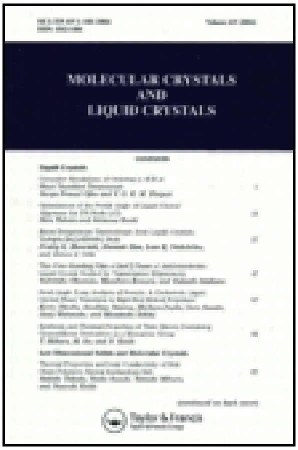

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Dynamics and Phase Transitions in Discotic and Calamitic Liquid Crystal Side-chain Polymers

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DYNAMICS AND PHASE TRANSITIONS IN DISCOTIC AND CALAMITIC LIQUID CRYSTAL SIDE-CHAIN POLYMERS

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We have investigated the effect of structure modification of various discotic liquid crystal side chain polymers on their phase transitions and the resulting dynamics. This has resulted in a better understanding of the structure of the various nematic phases that can be formed, in particular giving rise to the identification of supramolecular thermotropic nematic phases where the fundamental units comprise assemblies of molecules. In addition we have examined the dynamics of field-induced order parameters in the isotropic phase of calamitic side chain polymers using dielectric relaxation spectroscopy and dynamic Kerr effect measurements.

Keywords: dielectric spectroscopy; kerr effect; molecular dynamics; phase transitions; side-chain polymers; thermotropic liquid crystals

INTRODUCTION

Liquid crystal side-chain polymers consist of a polymer backbone with laterally attached, rod- or disk-shaped, mesogenic groups, see Figure 1.

These materials are ideal to investigate the effect of structure modification on the phase behaviour as there are multiple molecular parameters that can be varied systematically such as the degree of polymerisation, the level of substitution, the length of the aliphatic tails and the use of specific interactions e.g. via donor-acceptor interactions. Moreover these materials

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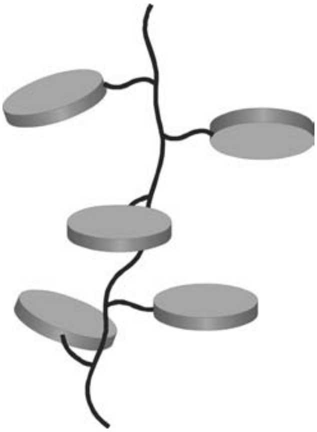


FIGURE 1 Schematic structure of a side-chain LCP with discotic mesogens attached to a flexible polymer backbone.

are ideal to investigate the effect of LC organisation on molecular dynamics. Here the advantage of the use of polymers is that the polymer backbone gives rise to a slowing down of the dynamics making it easier to access experimentally. Also, the presence of a glass transition can be used to vitrify the liquid crystalline organisation thereby avoiding crystallisation. Finally, the presence of the polymer backbone can lead to the frustration of long-range positional order giving rise to novel liquid crystalline phases such as the supramolecular nematic phases, N_{Col} and N_L. In this publication we give a brief overview of the various effects of structure modification on the phase diagrams and the dynamics of such side chain LC polymer materials.

NEMATIC-COLUMNAR TO NEMATIC-DISCOTIC TRANSITION

In this first example we will discuss the phase behaviour of the discotic side-chain liquid crystal polymers schematically shown in Figure 2 [1,2]. The details of the synthesis have been reported previously [3].

From the analysis of the phase behaviour we find relatively simple phase diagrams for the OCH_3 and OC_6H_{13} substituted disks, respectively G_{ND} 45°C N_D 200°C I(dec.) for OCH_3 and G_{ND} 25°C N_D 110°C I for OC_6H_{13}, where G_{ND} represents the glassy N_D phase. The polymers with discotic mesogens bearing CH_3 functionalities however show a richer and more interesting phase diagram as displayed in Figure 3.

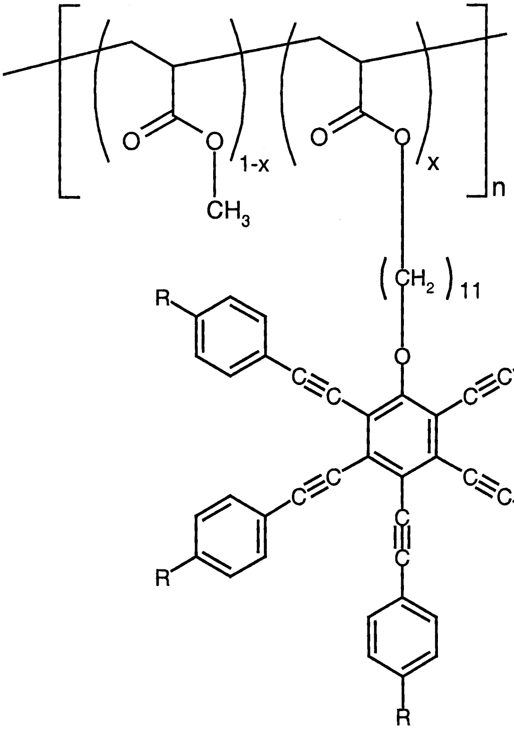


FIGURE 2 This shows a polymer with discotic mesogenic groups where the tails can be CH_3, OCH_3 and OC_6H_{13}. The level of substitution of the mesogens can be varied between about $x = 0.3$ to 0.95. The co-monomer is methyl-, pentyl- or dodecyl- substituted to block the remaining acid chloride functionalities after the attachment of the mesogens using a polymer analogous reaction.

As shown in this figure the mesogen weight fraction has a large influence on the occurrence of various nematic phases. At low [M] values only the nematic columnar phase N_{Col} occurs while at higher [M] also the more traditional N_D phase is observed at elevated temperatures. This gives rise to the occurrence of a clear N_{Col} to N_D transition ($\Delta H = 8.1\,kJ\,mol^{-1}$ for the polymer in which the degree of substitution x is 0.64) where the difference between these phases is that the N_D phase has a structure where the individual disks show orientational order while in the N_{Col} phase the mesogens are arranged in columnar stacks, see Figure 4. The columns in the N_{Col} phase do not possess columnar long-range (hexagonal or rectangular) order but instead are arranged similar to the rods in a standard calamitic nematic phase. Therefore the N_{Col} phase may be considered to be a supramolecular thermotropic nematic phase. The observed N_{Col} to N_D phase

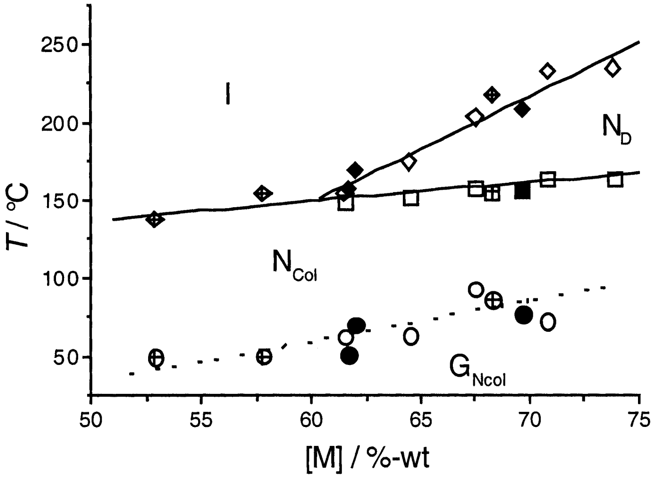


FIGURE 3 Phase diagram of the methyl substituted disk SCLCP from Figure 2 as a function of the mesogen weight fraction. The drawn curves are the result of applying the McMillan theory.

transition is due to the disintegration of the supramolecular columns into single discs that subsequently form the N_D phase. The latent-heat observed at the transition we believe is due to the loss of translational entropy when the individual disk join together to form the columnar aggregates.[3] The question of course is whether this should be classified as a real first-order transition – as the overall symmetry of the phase does not change.

To model the phase diagram we make use of the two-dimensional variant of the McMillan model, usually employed for the Col_h-N_D phase transition [4,5]. Here we are implicitly assuming that the N_{Col} phase from a thermodynamic point of view actually is a columnar phase but where the

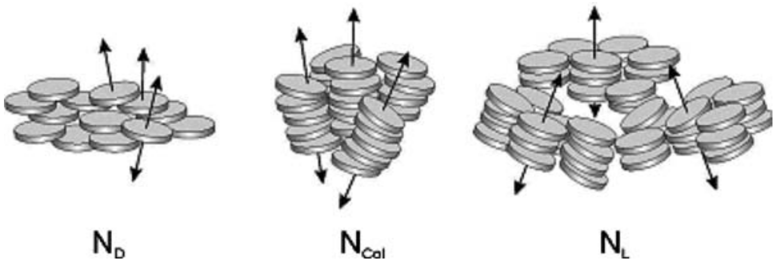


FIGURE 4 This shows the local structure of a nematic discotic (N_D) and the nematic columnar (N_{Col}) phase.

long-range order is frustrated by the presence of the polymer backbone. The mean-field potential for the McMillan model is given by:

$$U(\beta, \mathbf{r}) = -V_0[S + \alpha\sigma V(\mathbf{r})]P_2(\cos\beta) \tag{1}$$

This expression contains two order-parameters: S (or $\langle P_2 \rangle$) which describes the orientational order (S = 0 isotropic, S > 0 orientational order) and σ that describes the degree of columnar order ($\sigma = 0$ no columns, $\sigma > 0$ columnar order), the position dependent potential V($\mathbf{r}$) acts to align the columns in a hexagonal fashion:

$$V(\mathbf{r}) = \cos(\mathbf{A} \cdot \mathbf{r}) + \cos(\mathbf{B} \cdot \mathbf{r}) + \cos(\mathbf{C} \cdot \mathbf{r}) \tag{2}$$

The potential is formed by superimposing three sinusoidal standing waves where the governing vectors **A**, **B**, and **C** are aligned at angles of 60° in the xy plane:

$$\mathbf{A} = \frac{4\pi}{\sqrt{3}d}\hat{\mathbf{x}} \qquad \mathbf{B} = \frac{4\pi}{\sqrt{3}d}\left(\frac{\sqrt{3}}{2}\hat{\mathbf{y}} - \frac{\mathbf{1}}{\mathbf{2}}\hat{\mathbf{x}}\right) \qquad \mathbf{C} = \mathbf{A} + \mathbf{B} \tag{3}$$

The phase diagram that results from this potential is shown in Figure 5 as a function of the parameters V_0 and α respectively describing the overall strength of the mean-field interaction and the relative contribution of the position dependent part of the expression. Note that for a sufficiently high

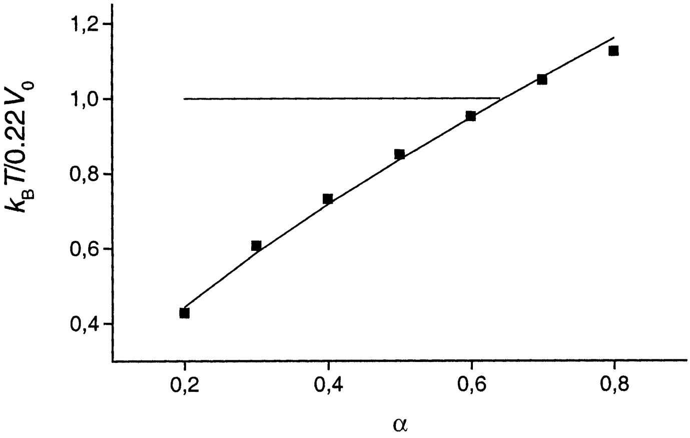


FIGURE 5 Phase diagram for the extended McMillan theory. The symbols match the exact results, the drawn horizontal line represents the N_D to I transition at $T_{NI} = 0.22\,V_0/k_B$. The drawn curve is a power law fit to $k_B T_{Col}/V_0 = \kappa\alpha^{0.69}$, with $\kappa = 0.30$.

value of α, the N_D phase disappears and a direct N_{Col}-I transition is predicted. The topology of the experimental phase diagram is therefore nicely confirmed using this theory. By taking scaling law expressions for the functional dependence of V_0 and α on the mesogen fraction [M], i.e. as $V_0 = c1[M]^{c2}$ and similarly for α it is possible to derive how the various potential terms depend on the mesogen content. We find that $V_0 \sim [M]$ and $\alpha \sim [M]^{-1.16}$. This means that the strength of the mean-field potential increases linearly with mesogen content while the tendency for column formation becomes smaller as [M] increases. In retrospect the latter result is logical as with increasing [M] the gains to be had from column formation decrease due to the increasingly aromatic nature of the environment. In Figure 3 the drawn curves are the result of using the McMillan theory together with the scaling laws for V_0 and α mentioned above, showing that quite good quantitative agreement is possible via this rather simple approach. Clearly though this model is only a first step and a full description of the N_{Col} phase should include taking the presence of the polymer backbone into account explicitly, including the complications involved with the packing of the mesogens and the restrictions imposed by the backbone. Also, the mean-field approach given above uses order parameters that describe long-range order while of course in the N_{Col} phase such long-range order does not exist – so that for a proper description clearly a formalism would have to be used that is based on the local interparticle correlations.

THE NEMATIC-LATERAL PHASE

In the section above we implicitly assumed that the polymer backbone in some way is frustrating the formation of true long-range positional order thus giving rise to the N_{Col} phase where the hexagonal packing disappears altogether. In fact another possibility was recently found by us where the hexagonal order is formed locally but where the positional order fails to become long-range in nature. We have designated this the nematic lateral phase (N_L) as there is both columnar as well as lateral hexagonal packing of the mesogens [6]. The N_L phase was found from X-ray diffraction studies on donor-acceptor complexes as formed by a polymer discotic donor similar to those shown in Figure 2 and molecular acceptors derived from trinitrofluorenone. In summary the N_L phase optically has all the characteristics of a normal nematic phase such as a schlieren texture and a rather low viscosity while the X-ray patterns show remarkably sharp peaks that would normally be associated with a Col phase. Examples for 2-D XRD patterns of the N_D, N_{Col} and N_L phases are given in Figure 6.

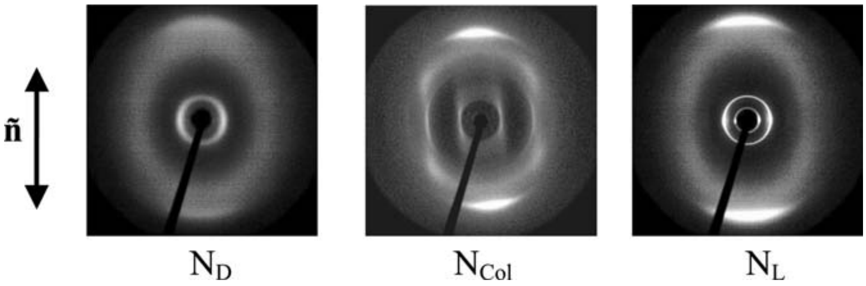


FIGURE 6 Characteristic XRD diffraction patterns for the N_D, N_{Col} and N_L phase. The director is randomly oriented in the plane perpendicular to the applied magnetic field.

The characteristics of the various phases can be analysed further in terms of relative correlation lengths as derived using the Scherrer equation. This results in correlation lengths of about 2.5 molecular dimensions in the N_D phase while the N_{Col} and N_L phase show correlation lengths of at least 8.5 times the respective molecular dimensions. Here the difference is that in the N_{Col} phase this only occurs on the meridian i.e. along the column axis while in the N_L phase this also takes place in the lateral direction, giving rise to rather sharp equatorial peaks. Figure 7 shows the schlieren texture and the birefringence (as the retardation Γ) versus temperature for a system that exhibits an N_L to N_D transition. The birefringence curve might suggest a second-order transition, as no discontinuity of the order parameter is evident.

However, this is probably due to the polymeric nature of the sample as the latent heat of the transition in fact is quite high at about 5 kJ mol^{-1} i.e. fully comparable to a Col-N_D transition. From this observation it appears that we are clearly dealing with a first-order process.

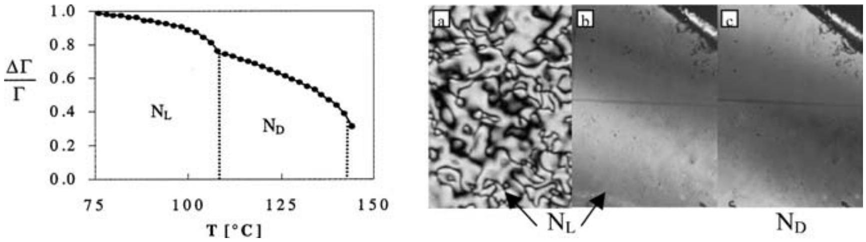


FIGURE 7 Optical retardation $\Gamma = d\Delta n$ versus temperature (left) and schlieren and uniform planar textures of the N_L and N_D phases (right).

DIELECTRIC RELAXATION SPECTROSCOPY AND KERR EFFECT DYNAMICS

Apart from giving rise to interesting phase behaviour side chains polymers are also very suitable for systematic investigation of dynamic phenomena. As a first example Figure 8 shows the dynamics and the relaxation strength from dielectric relaxation spectroscopy. In this technique the orientational mobility of the permanent dipole of the mesogen located along the phenolic oxygen in the mesogen is investigated by application of an AC electric field. It is observed from Figure 8 that at the N_D to N_{Col} transition two processes take place (i) the system slows down by about 1 decade, and (ii) the relaxation strength increases by a factor of about 4. Both the slowing down, as well as the increased relaxation strength, are in good agreement with the concept of columns occurring in the N_{Col} phase. The resulting picture that emerges is of a slow motion of the columns, where several dipoles are performing collective rotations. Note that the factor of 4 in the relaxation-strength agrees very nicely with the X-ray results where the correlation length increases by about the same factor.

Finally, it is also worth examining the dynamics of field-induced order parameters in side-chain polymer systems. We have investigated the field induced $\langle P_1 \rangle$ and $\langle P_2 \rangle$ order parameters in the isotropic phase of several calamitic liquid crystal side chain polymers. The $\langle P_1 \rangle$ dynamics was determined via dielectric relaxation spectroscopy, while the $\langle P_2 \rangle$ response was investigated via Kerr effect dynamics, i.e. by measuring the in phase and out of phase field induced birefringence under application of an AC field. From the maxima of the relaxation peaks of ε'' and K'' we can determine the characteristic response time of the various field-induced order

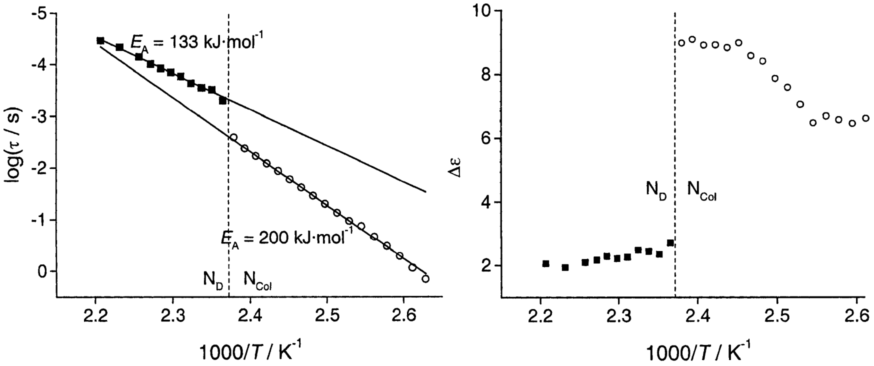
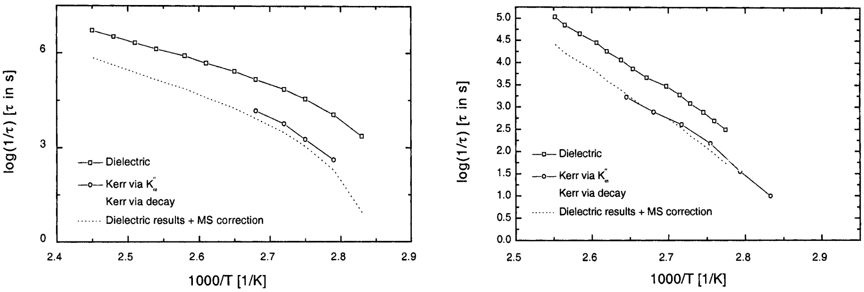


FIGURE 8 This shows the relaxation time (left) and strength (right) versus reciprocal temperature for a material with a N_{Col}-N_D transition.



Polymer A

Polymer B

FIGURE 9 Dynamic relaxation spectroscopy and Kerr-effect dynamics relaxation times from the isotropic phase of the two polymers shown in Figure 10. The dashed curve is from the shifting of the dielectric results onto the Kerr effect values which yields the divergence temperature T* from the Maier-Saupe term in the Smoluchowski equation.

parameters as a function of temperature. From our experiments we find that the $\langle P_1 \rangle$ dynamics is substantially faster than that of $\langle P_2 \rangle$, this is shown in Figure 9 for two polymers – one of these polymers has a nematic phase, while the other does not. For the polymer structures concerned, see Figure 10.

To explain the difference in the dynamics of the order parameters we make use of the Smoluchowski equation that describes the rotational diffusion of rods in the presence of external fields:

$$\frac{d\Psi}{dt} = \overline{D_r}\mathbf{R}\cdot\left(\mathbf{R}\Psi + \frac{1}{k_B T}\Psi\mathbf{R}U\right). \tag{4}$$

Here Ψ is the (time dependent) orientational distribution function, $\mathbf{R} = \mathbf{u} \times \frac{d}{d\mathbf{u}}$ is the rotational derivative, and $\overline{D_r}$ is the rotational diffusion

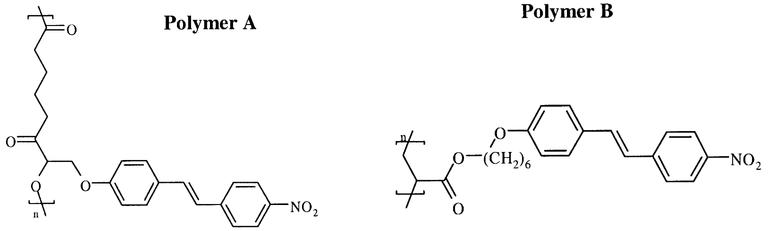


FIGURE 10 The structure of the nematic polymer A (G_N 50°C N 80°C I) and isotropic side-chain polymer B (G_I 55°C I).

constant. The potential U contains both the applied E field as well as a Maier-Saupe like term, which takes the mesogenic character of the materials into account.

$$U = \mu_0 u_i E_i + \varepsilon S_{ij} u_i u_j \tag{5}$$

Here μ_0 is the permanent dipole moment of the mesogen, E_i are the components of the applied electric field **E**, **u** is the unit vector describing the molecular long axis, **S** is the (Saupe) ordering matrix, and ε is the strength of the mean-field (nematic) potential. From a detailed analysis of this equation as given in the book of Doi and Edwards [7] it is found that the $\langle P_1 \rangle$ dynamics does not show any special behaviour while the presence of the Maier-Saupe term causes the $\langle P_2 \rangle$ dynamics to diverge at a critical temperature T^* which is situated just below the T_{NI}. Using this it is possible to determine the value of T^* from the difference in the dynamic response of the order parameters, the resulting values are found to be close to T_{NI} for the nematic polymer A while for polymer B the T^* value is substantially below the glass transition temperature. This means that the dynamics allows us to determine the T_{NI} value for the non-liquid crystalline side-chain polymer using measurements performed in the isotropic phase. Clearly the governing principle here is the fact that the symmetry of the order parameter involved is the same as that of the corresponding term of the free-energy and it is also to be anticipated that this method can be generalised to investigate other transitions e.g. if a biaxial perturbation is applied it should be possible to dynamically determine the location of a biaxial-nematic to uniaxial-nematic phase transition $T_{N_B\text{-}N_U}$ even if the material does not have an equilibrium biaxial phase. Possibly suitable biaxial perturbations to use in this specific case may involve dynamic shear flow or the application of cylindrically symmetric electric field gradients, and this is a topic we hope to explore further in the near future.

SUMMARY AND CONCLUSIONS

From our results we conclude that side-chain liquid crystal polymers are useful materials to investigate the structure property relations and the dynamics in liquid crystalline materials. Discotic side-chain polymers can show interesting new supramolecular nematic phases where the fundamental units are assemblies of mesogens rather than individual mesogenic units. In addition the use of polymer systems allows a detailed investigation of the influence of the various liquid crystal phases on the dynamics. In particular it appears to be possible to use the dynamics of field-induced order parameters to locate the presence of phase transitions that are not visible in the equilibrium phase diagram.

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