Abstract: The non-isothermal kinetic analysis of the isotropic-melt to liquid crystalline phase transition of novel liquid crystalline ionogenic copolymers, LCI, the 10-(4-methoxyazobenzene-4'-oxy)decyl methacrylate-co-2-(acrylamido-2-methyl-1-propanesulfonic acid) and 10-MeOAzB/AMPS, copolymers, has been performed based on calorimetric experiments at different cooling rates. A classical non-isothermal crystallisation methodology, based on Avrami’s equations, was applied and it has shown that the formation of the mesophases from the isotropic state occurred close to the thermodynamic equilibrium and can be described with high accuracy by using different kinetic parameters. The results evidence the presence of several individual processes in the formation of liquid crystalline phases from the melt and a strong dependence of phase transition rates and activation energies with acid contents. In addition, the decrease in the phase transition rate is related to a decrease in orientational entropy and the final inhibition of the liquid crystal behaviour is ascribed to an exponential increase in the activation energy of the phase transition, promoted by strong acid aggregation. An optimum composition of the 10-MeOAzB/AMPS copolymers to achieve the dual characteristics of LCI (ionogenic and liquid crystalline behaviour) requires acid concentrations capable of promoting structure-forming effects on the LC phases and the evolution of phase separated morphologies.

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Valencia, 24th January 2012

Dear Editor:

I have submitted a manuscript entitled “A kinetic study of the formation of smectic phases in novel liquid crystal ionogens” for consideration for publication in the European Polymer Journal. The manuscript describes the melt-liquid crystal transition of a set of novel liquid crystal side chain copolymers containing sulfonic acid groups having application potential as anisotropic polymer electrolyte membranes. Due to the relevance of the structure-properties relations in these materials, it is important to describe the successive processes involved in the formation of the mesomorphic templates from the isotropic phase. The study of the non-isothermal calorimetric transition carried out in this paper has proved to be useful to describe the forming role of the acid groups on the stabilisation of the liquid crystal phase.

The manuscript contains original material which has not been published nor is being considered for publication elsewhere.

I look forward to hearing from you in due course.

Yours faithfully,

Prof. Amparo Ribes Greus
Institute of Materials Technology
Graphical Abstract

\[ X_t = \frac{\Delta h_t}{\Delta h_\infty} = \frac{\int_{t_0}^{t} \Delta h_t}{\int_{t_0}^{\infty} \Delta h_t} \]

\[ [\log(-\ln(1-X_t))] = \log Z + n \cdot [\log(t-t_0)] \]

Orientational movements

Translational effects

Side-chain packing
Highlights

Kinetic phase transition analysis of side-chain LC polymers containing acid groups

Nematic suppression in copolymers by orientational restrictions

Non-isothermal kinetic analysis of the isotropic to liquid crystal transition

Activation energies increase exponentially when acid aggregation occurs

Role of structure forming sulfonic acid groups in liquid crystals
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**Figure 6.** The dependence of the entropy change associated with the isotropic-liquid crystal phase transition ($\Delta S_c/R$) measured for differing cooling rates on the composition of the 10-MeOAzB/AMPS copolymers. For the homopolymer we see an isotropic-nematic-smectic A transition while the copolymers exhibit an isotropic-smectic A transition.

**Figure 7.** Calculation of the activation energy of the isotropic-smectic A process for the 10-MeOAzB/AMPS copolymers ($E_{a_{Tc}}$). Plots of the (a) Kissinger, (b) Flynn-Wall-Ozawa methods; (c) Evolution of $E_{a_{Tc}}$ for the two methods with the composition.
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A kinetic study of the formation of smectic phases in novel liquid crystal ionogens

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Abstract

The non-isothermal kinetic analysis of the isotropic-melt to liquid crystalline phase transition of novel liquid crystalline ionogenic copolymers, LCI, the 10-(4-methoxyazobenzene-4’-oxy)decyl methacrylate]-co-2-(acrylamido-2-methyl-1-propanesulfonic acid)s, 10-MeOAzB/AMPS, copolymers, has been performed based on calorimetric experiments at different cooling rates. A classical non-isothermal crystallisation methodology, based on Avrami’s equations, was applied and it has shown that the formation of the mesophases from the isotropic state occurred close to the thermodynamic equilibrium and can be described with high accuracy by using different kinetic parameters. The results evidence the presence of several individual processes in the formation of liquid crystalline phases from the melt and a strong dependence of phase transition rates and activation energies with acid contents. In addition, the decrease in the phase transition rate is related to a decrease in orientational entropy and the final inhibition of the liquid crystal behaviour is ascribed to an exponential increase in the activation energy of the phase transition, promoted by strong acid aggregation. An optimum composition of the 10-MeOAzB/AMPS copolymers to achieve the dual characteristics of LCI (ionogenic and liquid crystalline behaviour) requires acid concentrations capable of promoting structure-forming effects on the LC phases and the evolution of phase separated morphologies.

Keywords

Liquid crystal polymers (LCP), Differential scanning calorimetry (DSC), non-isothermal melt-crystallisation kinetic analysis
1. Introduction

Side chain liquid crystal polymers (SCLCP) exhibit a unique duality of properties combining those of low molar mass liquid crystals with those of polymers. This combination of properties arises from the structure of SCLCPs in which the mesogenic groups are covalently attached as pendants to a polymer backbone via a flexible spacer. The role of the flexible spacer is to decouple, at least to some extent, the relative tendencies of the mesogenic groups to self-assemble and form the liquid crystal phase from those of the polymer backbone to adopt random coil configurations [1]. The incorporation of nonmesogenic units along the backbone allows for additional functionalities to be endowed upon the polymer [2-4]. Of particular interest in recent years have been SCLCPs containing ionic and ionogenic units and these are also referred to as liquid crystal ionomers and iononogens (LCI). This interest stems not only from their considerable application potential in a range of quite diverse areas but perhaps most notably as anisotropic electrolytes, but also because they provide a demanding challenge to our understanding of self-assembly in polymeric systems [5, 6].

We recently reported the synthesis and phase behaviour of the 10-(4-methoxyazobenzene-4’-oxy)decyl methacrylate-co-2-(acrylamido-2-methyl-1-propanesulfonic acid)s, copolymers (1),

![Chemical Structure](image)

and refer to them using the acronym 10-MeOAzB/AMPS in which 10-MeOAzB refers to the liquid crystal side chain and AMPS to the sulfonic acid-based group. These copolymers exhibited smectic A phase behaviour over a broad range of compositions, specifically for copolymers containing 0.45 or greater mol fraction of 10-MeOAzB side chains [7]. This observation, in itself, is not unusual and may be accounted for by a compression of the backbone in the plane perpendicular to the liquid crystal director which enhances the
interactions between the mesogenic groups. Surprisingly, however, the smectic A-isotropic transition did not simply decrease on increasing the AMPS mol fraction but instead appeared to reach a limiting value. Such effect was accompanied by changes in the structure of the smectic A phase on increasing the AMPS mol fraction and this was attributed, at least in part, to hydrogen bonding between the sulfonic acid groups. In addition, a phase separated structure was observed consisting of regions of smectic A phase and acid-rich domains.

It appears therefore that the sulfonic acid groups play a central structure-forming role in determining the phase behaviour of these copolymers. Due to the relevance that processing conditions may have on the preparation of materials and membranes with liquid crystalline templates from the melt, this work investigates with more detail the structural formation of the smectic A phase from the isotropic melt for the 10-MeOAzB/AMPS copolymers. To achieve this we performed a calorimetric kinetic study of the non-isothermal isotropic melt-liquid crystal phase transition for the homopolymer (P10-MeOAzB) and the 10-MeOAzB/AMPS copolymers. A classical non-isothermal crystallisation approach has been used, based on Avrami’s equations and methods [8, 9, 10]. We note that such characterisation technique may be successful to determine accurately the lower enthalpy/entropy changes occurring during the transitions from the isotropic state to the mesophases and also between mesophases in low-ordered liquid crystal phases (such as nematic or some smectic phases) [11 – 22].
2. Experimental

The synthesis of the 10-MeOAzB/AMPS copolymers was performed by free radical copolymerisation of the monomers, using 1,1’-azobis(cyclohexane carbonitrile) as the initiator in dimethyl formamide (DMF), as has been described in detail elsewhere [7, 11]. The isotropic melt-liquid crystal transition kinetics were investigated using differential scanning calorimetry (DSC), by means of non-isothermal linear temperature-time programs. The DSC thermograms were obtained using a Mettler Toledo DSC 822° analyser (Columbus, OH, USA) and samples of around 5 mg. The thermal program consisted of alternating heating and cooling scans. An initial heating scan from 25 to 180ºC was applied to ensure the sample had entered the isotropic phase so deleting any thermal history. Subsequently, the samples were submitted to alternating cooling scans (with rate $\beta = 5, 7, 10, 15$ and $20$ ºC·min$^{-1}$) and heating scans (with rate $\beta = 10$ ºC·min$^{-1}$) between 0 and 180 ºC. All the thermograms were obtained under a nitrogen atmosphere and using an intracooler for temperature control (Haake EK90/mt). The STAR\textsuperscript{e} 9.2 software was used to obtain the experimental calorimetric parameters. All the experiments were performed at least three times and the averages and standard deviations of the thermodynamic parameters were obtained.

**DSC Phenomenological analysis [10]**

The isotropic-liquid crystal phase transitions of the copolymers were analysed using the methodology and equations shown in Figure 1. First, the specific enthalpy change associated with the isotropic-liquid crystal phase transition was calculated by integrating the DSC curves obtained in the cooling scan along the time axis ($\Delta H_t$). The fraction of liquid crystal phase at time $t$ ($X_t$) was obtained by normalising the $\Delta H_t$ values with respect to the enthalpy change corresponding to the complete isotropic-liquid crystal transition ($\Delta H_\infty$), following Eq 1, ranging from $X_{t,0}= 0$ (isotropic phase) to $X_{t,\infty} = 1$ (liquid crystal phase). The half-time of the formation of the liquid crystal phase ($\tau_{1/2}$) was defined as the time at which $X_t = 0.5$. The phase transition temperature ($T_c$) was taken to be the minimum of the exotherm. The phenomenological analysis was completed by calculating the so-called phase transition rate parameter, $\xi$, which in this case actually corresponds to the rate of formation of the liquid crystal phase, defined as the slope of the plots of the variable $(\tau_{1/2}^2T_c)^{-1}$ against the cooling rate, $\beta$ (Eq. 2).

*Kinetic analysis of the isotropic-liquid crystal phase transition*
The study of the bulk isotropic-liquid crystal phase transition of the copolymers was completed by calculating the apparent activation energy \((E_a T_c)\). The Kissinger [12] and the Flynn-Wall-Ozawa [13, 14] integral methods were applied at the maximum rate of the formation of the liquid crystal phase. The values of \(\ln(\beta T_c^{-2})\) and \(\log(\beta)\), respectively, were represented versus \(T_c^{-1}\) (Eq 3 and 4, respectively), and \(E_a T_c\) was calculated from the slopes of the curves.

In addition, the development of multiple individual processes occurring at the isotropic-liquid crystal transition was investigated by applying Avrami’s equations to the \(X_c\) data [8, 9]. The time-dependent probability of the formation of LC domains during the isotropic-liquid crystal transition can be then described by Eq. 5 in which \(t_0\) corresponds to the onset of the transition. The logarithmic form (Eq.6) allows for a linear fit of the phase transition data versus time. In order to consider the effect of the non-mesogenic units in the copolymers, Eq. 6 was corrected, to give Eq. 7, in which \(1-\lambda(\infty)\) is the weight fraction of the polymer potentially liquid crystalline at the termination of the process [15]. The parameter \(1-\lambda(\infty)\), was calculated as the ratio of the \(\Delta H_\infty\) values of the copolymers with respect to the homopolymer, at each cooling rate. Two empirical parameters can be obtained from the Avrami analysis for each DSC cooling curve, \(Z\) and \(n\), which describe the mechanism of the isotropic-liquid crystal transition processes. From these values, it is possible to calculate a rate parameter \(k = Z^{1/n}\) (Eq. 8), which describes the speed of the formation of the liquid crystal phase for each individual process.
Figure 1. Schematic representation of the methodology followed for the study of the non-isothermal isotropic-liquid crystal phase transition of the 10-MeOAzB/AMPS copolymers.
3. Results and discussion

3.1 Kinetic analysis of the isotropic-nematic-smectic A phase transition of the homopolymer P10-MeOAzB (Cop-1/0)

Figure 2 shows the non-isothermal isotropic melt-liquid crystal exotherms for the P10-MeOAzB homopolymer (Cop-1/0) at six different cooling rates. All the DSC traces contain two distinct events: a first order exothermic transition at high temperatures ($T_c \sim 134 - 136^\circ C$), associated with the isotropic-nematic phase transition, and a glass transition at lower temperatures ($T_g \sim 71 - 74^\circ C$) [4]. We have shown previously using polarised optical microscopy and small angle X-ray diffraction that on cooling from the isotropic phase, P10-MeOAzB forms a narrow temperature range nematic phase and on further cooling, a smectic phase.

The temperature corresponding to the minimum of the exothermic peak ($T_c$), and the associated enthalpy ($\Delta H_c$) and entropy ($\Delta S_c$) changes measured at different cooling rates are listed in Table 1. The values of $T_c$, $\Delta H_c$ and $\Delta S_c$ measured at $\beta = -10 \, ^{\circ}C \cdot min^{-1}$ are in good agreement with those reported elsewhere [4, 7, 16, 17]. On increasing the cooling rate, the isotropic-nematic transition exotherm becomes broader and shifts to slightly lower temperatures. The extent of supercooling is reproducible but very small ($\Delta T < 2^\circ C$) when the cooling rate is varied between 5 and 20$^\circ C/min$, suggesting that the transition occurs close to the thermodynamic equilibrium [10]. This observation is consistent with a thermodynamically weak transition such as a nematic-isotropic transition.
Figure 2. DSC cooling traces of P10-MeOAzB (Cop - 1/0) obtained at different cooling rates, β, from 5 to 20 °C/min.

The quantitative analysis of the non-isothermal isotropic-liquid crystal phase transition of P10-MeOAzB involved the calculation of the liquid crystal fraction (Xᵢ) as a function of time, φ(t) = t - t₀, using Eq. 1. The dependence of Xᵢ on φ(t) is shown in Figure 3a revealing sigmoidal plots, which can be understood as reminiscent of autocatalytic processes [10]. The values of apparent total phase transition period, Δtᵢ = t₀₀.99 - t₀₀.01, and half-phase transition time, τ₁/₂, were obtained from the Xᵢ curves, and are listed in Table 2. Figure 3a clearly shows the differences in the transitional process of P10-MeOAzB seen on varying the cooling rate. Specifically, the shift of the Xᵢ curves towards smaller φ(t) values on increasing β and the correspondingly lower Δtᵢ and τ₁/₂ values, reveal that isotropic-liquid crystal phase transition takes place more rapidly at higher cooling rates. Only a slight deviation is noted for β=15 and 20 °C/min at low φ. Similar observations are usually explained by more pronounced supercooling at higher cooling rates, promoting polymer crystallisation at temperatures more displaced from equilibrium (Tₑ). It appears reasonable to assume that a similar explanation accounts for the behaviour of the isotropic-liquid crystal phase transition, although we note that...
the extent of supercooling is small. A value of $\xi = 5.14 \cdot 10^{-3}$ K$^{-1}$ was calculated for P10-MeOAzB using Eq. 2.

Figure 3. Phenomenological and kinetic analysis of the isotropic-nematic phase transition shown by P10-MeOAzB: a) $X_t$ curves; b) Avrami plots.

The Avrami plots for the isotropic-nematic phase transition of P10-MeOAzB obtained using Eq. 5 and 7 are shown in Figure 3b. Each of these plots contains two distinct linear regions revealing the occurrence of a primary process (hereinafter, P1), at short transition times, and a secondary process (hereinafter, P2), at longer times. We suggest that these two processes could be assigned to the isotropic-nematic (P1) and nematic-smectic A (P2) transitions of the homopolymer, respectively [16, 17].

From the logarithmic representations of the two individual curves, the Avrami kinetic parameters related to the primary ($Z_1$, $n_1$, $k_1$) and secondary ($Z_2$, $n_2$, $k_2$) processes were obtained, according to Eq. 7 and 8, and are given in Table 3. The high $R^2$ values indicate that the two transition processes are well described by the Avrami model. It is also noteworthy that the Avrami rate constants for P10-MeOAzB, $k_i$, are of the same order of magnitude as seen for
anisotropic crystallisable polymers (~10^{-2} s^{-1}) [18, 19]. The slightly higher rates and \( n \) values seen for P10-MeOAzB may presumably be attributed to the morphological differences between the formation of ordered crystalline phases and transitions involving mesophases [20]. The differences in \( n \) and \( \ln(Z) \) for the two processes may be interpreted in terms of differences in the mechanisms associated with P1 and P2. Higher Avrami exponents and rate constants are found for P1 (\( n_1 > n_2; k_1 > k_2 \)), suggesting that the isotropic-nematic transition occurs more rapidly than the nematic-smectic A transition.
3.2 Kinetic analysis of the isotropic-smectic A transition for the 10-MeOAzB/AMPS-x/y copolymers

3.2.1 Bulk transition properties

Figure 4 shows the DSC cooling scans of the copolymers recorded at the lowest and highest cooling rates, namely, $\beta = 5$ and $\beta = 20 \, ^\circ\text{C}\cdot\text{min}^{-1}$, distinguishing non-isothermal isotropic melt-liquid crystal transition exotherms and glass transitions, $T_g$. Phase assignment was carried out on the basis of polarised optical microscopy and small angle x-ray diffraction studies [7]. The DSC traces measured at intermediate values of $\beta$ are essentially identical and fall between these limiting curves.

![Figure 4a](image1)

**Figure 4.** (a) DSC traces recorded at cooling rates, $\beta = 5$ and $20 \, ^\circ\text{C}\cdot\text{min}^{-1}$ and (b) the dependence of $X_i$ on $\phi(t)$ for the 10-MeOAzB/AMPS copolymers. Experimental points have not been shown for the sake of clarity.
The calorimetric parameters ($T_c$, $\Delta H_c$ and $\Delta S_c$) obtained from the DSC thermograms for the copolymers are listed in Table 4. The $T_c$ values initially decrease on increasing the AMPS mol fraction before reaching a limiting value at around $x_{\text{AMPS}} = 0.3$ (see Figure 5a). The values in Table 4 also suggest simultaneous reductions of $\Delta H_c$ and $\Delta S_c/R$ for the copolymers, at least for low AMPS concentrations.

![Figure 5. (a) $T_c$ values; (b) $\tau_{1/2}$; (c) $\xi$ values (Eq. 2) for the 10-MeOAzB/AMPS copolymers.](image)

The non-isothermal isotropic-smectic A phase transition of the copolymers was analysed using the same methodology described for the P10-MeOAzB homopolymer. The dependence of $X_t$ on $\phi(t)$ for the phase transition of the copolymers cooled at $\beta = 5$ and 20 °C-min$^{-1}$ is shown in Figure 4b. These curves are sigmoidal in shape similar to those observed for the homopolymer, and was understood as reminiscent of autocatalytic processes. The AMPS mol fraction has a marked effect on both the relative position and the shapes of the $X_t$ curves, suggesting variations in the phase transition process [10]. In order to quantify these differences, the kinetics parameters $\xi$, $\Delta t$, and $\tau_{1/2}$ were calculated for each of the copolymers (Figure 5b and 5c).

The introduction of AMPS units causes immediate reduction in the rate of the phase transition, which can be attributed to the introduction of heterogeneities or defects in these random copolymers [21]. At higher AMPS concentrations, $\xi$ seems to stabilise until reaching a plateau. These results can be related to the entropy changes calculated for the phase transition and plotted in Figure 6 as a function of the compositions of the polymers. The remarkable similarity between the evolution of $\xi$ and $\Delta S_c$ with composition, and the absence of nematic phases, underpin the role of orientational dynamics on the formation of the smectic A phase from the isotropic melt [22, 23].
Figure 6. The dependence of the entropy change associated with the isotropic-liquid crystal phase transition ($\Delta S_c/R$) measured for differing cooling rates on the composition of the 10-MeOAzB/AMPS copolymers. For the homopolymer we see an isotropic-nematic-smectic A transition while the copolymers exhibit an isotropic-smectic A transition.

The evaluation of the bulk isotropic-smectic A phase transition of the copolymers was completed by studying the apparent activation energy of the process. The Kissinger and Flynn-Wall-Ozawa models were applied to calculate the apparent activation energies of the phase transition ($E_{aT_c}$), from the plots of $\ln(\beta T_c^{-2})$ and $\log(\beta)$ against $T_c^{-1}$ (Figure 7a and Figure 7b, respectively). The apparent activation energies obtained by the two methods are similar and are shown in Figure 7c as a function of $x_{\text{AMPS}}$. At low AMPS concentrations, $E_{aT_c}$ remains nearly unaltered respect to P10-MeOAzB and a sudden increase in the absolute values occurs at $x_{\text{AMPS}} > 0.3$.

It is noteworthy in the previous results how the asymptotic behaviour of $\xi$ and $\Delta S_c$ coincides with the onset of the $E_{aT_c}$ increase. This effect occurs at composition ranges when the 10-MeOAzB/AMPS copolymers exhibit simultaneous formation of acid aggregation and liquid crystalline behaviour ($0.30 \leq x_{\text{AMPS}} \leq 0.56$) [7]. These results suggest that the combination of entropic and enthalpic effects may promote the forming role of the acid groups in the liquid crystal phase structure of the copolymers and the formation of pronounced microphase separated morphologies.

The shapes of the $E_{aT_c}$ curves, which resemble exponential behaviour, also suggest that further additions of AMPS concentrations would represent a great increase in the activation energy.
Below a certain threshold 10-MeOAzB concentration, the rate of the phase transition ($\xi$) is possibly too slow to compensate the high intermolecular interactions in the melt caused by acid aggregation via hydrogen bonding. This accounts for the inhibition of the liquid crystallinity observed in the precedent studies for the 10-MeOAzB/AMPS copolymers with $x_{\text{AMPS}}>0.56$ [7].

**Figure 7.** Calculation of the activation energy of the isotropic-smectic A process for the 10-MeOAzB/AMPS copolymers (E$_{\text{act}}$). Plots of the (a) Kissinger, (b) Flynn-Wall-Ozawa methods; (c) Evolution of E$_{\text{act}}$ for the two methods with the composition.

### 4.2.2 Avrami analysis of the isotropic-smectic A phase transition for the 10-MeOAzB/AMPS copolymers

The phase transition kinetics of the copolymers were further analysed by applying the Avrami equations and following the methodology described for the 10-MeOAzB homopolymer (Eq. 5 to 8). It is possible to see how the copolymers with lower AMPS units (Figure 8a) clearly show the two linear regions observed for P10-MeOAzB (P1 and P2 processes in Figure 3b). On the other hand, the slopes of the two regions seem to equalise at higher concentrations of AMPS (Figure 8b). The kinetic parameters of the P1 and P2 processes are quantified by calculating the $n_i$, $Z_i$ and $k_i$ values as a function of the cooling rates and copolymer composition, and the results are included in Table 3.
Figure 8. Examples of Avrami plots obtained for the phase transition of the 10-MeOAzB/AMPS copolymers at high and low cooling rates. High (a) and intermediate (b) 10-MeOAzB concentrations

An increase in the $n$ values is observed in the case of the copolymers, respect to the homopolymer, for both processes. This variation could be indicative of a change in the phase transition mechanism by the presence of AMPS units, and is in coherence with the absence of the nematic phase in the copolymers observed by microscopy [11, 25]. The changes in the slopes observed in the Avrami curves and underlined in Figure 8 are also reflected in variations of the individual rate constants of $P_1 (k_1)$ and $P_2 (k_2)$. Lower values of $k_i$ are found in the copolymers respect to the homopolymer. This fact agrees with the reduction of the phase transition rate observed through the $\zeta$ values by the addition of AMPS units (see Figure 5c).
Moreover, while \( k_1 > k_2 \) in the case of \( P_{10}-\text{MeOAzB} \), \( k_1 \approx k_2 \) for \( \text{Cop}(0.7/0.3) \) and copolymers with higher AMPS concentrations. \( \text{Cop}(0.92/0.08) \) shows an intermediate behaviour and, finally, a sensitive increase on the \( k_i \) values is observed for \( \text{Cop}(0.54/0.46) \).

The equalising of the constant rates \((k_1, k_2)\) seems to indicate that the two individual processes, clearly visible in the homopolymer (\( P_1 \) and \( P_2 \)), are merging to a simple transition process for some of the copolymers. Figure 9 shows a proposed scheme of the LC phase formation from the isotropic melt in the \( 10\text{-MeOAzB/AMPS} \) copolymers. The formation of liquid crystal phases usually involves orientational, translational and configurational processes [22]. In the case of the homopolymer (\( P_{10}\text{-MeOAzB}, \text{Figure 9a} \)), the observance of the nematic phase (1D order) denotes an initial orientation process over a clear temperature range (\( P_1 \)). We can assume that the nematic template is nucleating the formation of the smectic layers (2D order) by the presence of pre-orientated mesogens. The smectic templates will then require backbone cooperative translational processes and side groups arrangements (to improve packing efficiency in interdigated Smectic phases) (\( P_2 \)). Such model fits well to previous findings in methacrylate azo-benzene-based homopolymers [16].

In the case of the \( 10\text{-MeOAzB/AMPS} \) copolymers, our kinetics results have indicated an initial decrease of the phase transition rate (\( \text{Figure 5c} \)), ascribed to a decrease in the entropy change (\( \text{Figure 6} \)). According to the model proposed in \( \text{Figure 9b} \), such decrease could be related to partial inhibition of the orientation of the mesogenic units, caused by the inclusion of ionic groups into the LC templates. This view is also consistent with the absence of nematic phases in the copolymers. However, the low concentration of AMPS will still allow for high mobility at long range and for the compression of the backbone to accommodate the non-mesogenic units into LC templates. Thus, it is possible that orientational processes are somehow overcooled and overlapping longer rate translational phenomena, and this may account for the decrease in the bulk phase transition temperature (\( \text{Figure 5a} \)) [7]. The recovery of the phase stability observed in the \( 0.30 \leq x_{\text{AMPS}} \leq 0.54 \) range could be then explained by a decrease in the actual concentration of AMPS units present in the LC templates, caused by phase separation. This can also explain the stabilisation of the entropic effects, due to a combination of lower local mobility hindrance and higher backbone compression to require effective packing. In this composition range, moreover, the formation of ionic aggregates may also promote stronger intermolecular interactions in the phase separated morphology. Such increase in enthalpic restrictions may act as structure forming at intermediate and high acid concentrations, and is coherent with the rise in the activation values obtained in this work and an increase in the viscosity of the copolymers.
(see Figure 7c). At the limit, the interactions will produce strong long-rate restrictions in the translational movements of the main chain, and final inhibition of the smectic behaviour (see Figure 9c) [7, 26, 27]. This hypothesis is also supported by the increase in the glass transition reported for these copolymers (Table 2, [7]).
4. Conclusions

The introduction of low amounts of acid groups (AMPS) units promotes an initial retardation of the phase transition rate (\(\xi\)) of the 10-MeOAzB/AMPS copolymers, due to a disrupting effect by the introduction of non-mesogenic units into the LC templates. At increasing acid groups concentrations, such destabilisation effects are compensated by a reduction in the effective concentration of AMPS units in the LC regions, driven by the occurrence of phase separation. Further additions of acid groups have structure-forming effects by increasing the rectification of the main chains and the viscosities, attributed to stronger ionic aggregation by hydrogen bonding. At the limit, the mobility restrictions in the backbone are so acute that may produce complete inhibition of the liquid crystal behaviour. In addition, the Avrami analysis showed that overcooling of the orientational processes may be the main reason for phase destabilisation and extinction of the nematic phase in the copolymers, and also for retardation of the phase transition at low acid contents. An equilibrium between entropic and ethalpic effects is achieved at intermediate compositions with phase separated morphologies which allow for simultaneous ionogenic and liquid crystalline behaviours typical of LCI.
8. Avrami, M. J. Chem. Phys. 7 (1939) 1103
10. Mandelkern, L. Crystallization of Polymers, 2nd ed.; Cambridge, University Press: Cambridge, UK, 2002; Chapter 8


21 Mandelkern, L. Crystallization of Polymers, 2nd ed.; Cambridge, University Press: Cambridge, UK, 2002; Chapter 8, pp 265


26 Zhao, Y.; Lei, H. Macromolecules 27 (1994) 4525

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A kinetic study of the formation of smectic phases in novel liquid crystal ionogens

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Abstract

The non-isothermal kinetic analysis of the isotropic-melt to liquid crystalline phase transition of novel liquid crystalline ionogenic copolymers, LCI, the 10-(4-methoxyazobenzene-4’-oxy)decyl methacrylate]-co-2-(acrylamido-2-methyl-1-propanesulfonic acid), **10-MeOAzB/AMPS**, copolymers, has been performed based on calorimetric experiments at different cooling rates. A classical non-isothermal crystallisation methodology, based on Avrami’s equations, was applied and it has shown that the formation of the mesophases from the isotropic state occurred close to the thermodynamic equilibrium and can be described with high accuracy by using different kinetic parameters. The results evidence the presence of several individual processes in the formation of liquid crystalline phases from the melt and a strong dependence of phase transition rates and activation energies with acid contents. In addition, the decrease in the phase transition rate is related to a decrease in orientational entropy and the final inhibition of the liquid crystal behaviour is ascribed to an exponential increase in the activation energy of the phase transition, promoted by strong acid aggregation. An optimum composition of the 10-MeOAzB/AMPS copolymers to achieve the dual characteristics of LCI (ionogenic and liquid crystalline behaviour) requires acid concentrations capable of promoting structure-forming effects on the LC phases and the evolution of phase separated morphologies.

Keywords

Liquid crystal polymers (LCP), Differential scanning calorimetry (DSC), non-isothermal melt-crkystallisation kinetic analysis
1. Introduction

Side chain liquid crystal polymers (SCLCP) exhibit a unique duality of properties combining those of low molar mass liquid crystals with those of polymers. This combination of properties arises from the structure of SCLCPs in which the mesogenic groups are covalently attached as pendants to a polymer backbone via a flexible spacer. The role of the flexible spacer is to decouple, at least to some extent, the relative tendencies of the mesogenic groups to self-assemble and form the liquid crystal phase from those of the polymer backbone to adopt random coil configurations [1]. The incorporation of nonmesogenic units along the backbone allows for additional functionalities to be endowed upon the polymer [2-4]. Of particular interest in recent years have been SCLCPs containing ionic and ionogenic units and these are also referred to as liquid crystal ionomers and iononogens (LCI). This interest stems not only from their considerable application potential in a range of quite diverse areas but perhaps most notably as anisotropic electrolytes, but also because they provide a demanding challenge to our understanding of self-assembly in polymeric systems [5, 6].

We recently reported the synthesis and phase behaviour of the 10-(4-methoxyazobenzene-4′-oxy)decyl methacrylate]-co-2-(acrylamido-2-methyl-1-propanesulfonic acid)s, copolymers (1),

![Chemical structure of 10-MeOAzB/AMPS](image)

and refer to them using the acronym **10-MeOAzB/AMPS** in which 10-MeOAzB refers to the liquid crystal side chain and AMPS to the sulfonic acid-based group. These copolymers exhibited smectic A phase behaviour over a broad range of compositions, specifically for copolymers containing 0.45 or greater mol fraction of 10-MeOAzB side chains [7]. This observation, in itself, is not unusual and may be accounted for by a compression of the backbone in the plane perpendicular to the liquid crystal director which enhances the
interactions between the mesogenic groups. Surprisingly, however, the smectic A-isotropic transition did not simply decrease on increasing the AMPS mol fraction but instead appeared to reach a limiting value. Such effect was accompanied by changes in the structure of the smectic A phase on increasing the AMPS mol fraction and this was attributed, at least in part, to hydrogen bonding between the sulfonic acid groups. In addition, a phase separated structure was observed consisting of regions of smectic A phase and acid-rich domains.

It appears therefore that the sulfonic acid groups play a central structure-forming role in determining the phase behaviour of these copolymers. Due to the relevance that processing conditions may have on the preparation of materials and membranes with liquid crystalline templates from the melt, this work investigates with more detail the structural formation of the smectic A phase from the isotropic melt for the 10-MeOAzB/AMPS copolymers. To achieve this we performed a calorimetric kinetic study of the non-isothermal isotropic melt-liquid crystal phase transition for the homopolymer (P10-MeOAzB) and the 10-MeOAzB/AMPS copolymers. A classical non-isothermal crystallisation approach has been used, based on Avrami’s equations and methods [8, 9, 10]. We note that such characterisation technique may be successful to determine accurately the lower enthalpy/entropy changes occurring during the transitions from the isotropic state to the mesophases and also between mesophases in low-ordered liquid crystal phases (such as nematic or some smectic phases) [11 – 22].
2. Experimental

The synthesis of the 10-MeOAzB/AMPS copolymers was performed by free radical copolymerisation of the monomers, using 1,1’-azobis(cyclohexane carbonitrile) as the initiator in dimethyl formamide (DMF), as has been described in detail elsewhere [7, 11]. The isotropic melt-liquid crystal transition kinetics were investigated using differential scanning calorimetry (DSC), by means of non-isothermal linear temperature-time programs. The DSC thermograms were obtained using a Mettler Toledo DSC 822e analyser (Columbus, OH, USA) and samples of around 5 mg. The thermal program consisted of alternating heating and cooling scans. An initial heating scan from 25 to 180ºC was applied to ensure the sample had entered the isotropic phase so deleting any thermal history. Subsequently, the samples were submitted to alternating cooling scans (with rate $\beta = 5, 7, 10, 12, 15$ and 20 ºC·min$^{-1}$) and heating scans (with rate $\beta = 10$ ºC·min$^{-1}$) between 0 and 180 ºC. All the thermograms were obtained under a nitrogen atmosphere and using an intracooler for temperature control (Haake EK90/mt). The STAR$^9$ 9.2 software was used to obtain the experimental calorimetric parameters. All the experiments were performed at least three times and the averages and standard deviations of the thermodynamic parameters were obtained.

**DSC Phenomenological analysis [10]**

The isotropic-liquid crystal phase transitions of the copolymers were analysed using the methodology and equations shown in Figure 1. First, the specific enthalpy change associated with the isotropic-liquid crystal phase transition was calculated by integrating the DSC curves obtained in the cooling scan along the time axis ($\Delta H_t$). The fraction of liquid crystal phase at time t ($X_t$) was obtained by normalising the $\Delta H_t$ values with respect to the enthalpy change corresponding to the complete isotropic-liquid crystal transition ($\Delta H_\infty$), following Eq 1, ranging from $X_{t,0} = 0$ (isotropic phase) to $X_{t,\infty} = 1$ (liquid crystal phase). The half-time of the formation of the liquid crystal phase ($\tau_{1/2}$) was defined as the time at which $X_t = 0.5$. The phase transition temperature ($T_c$) was taken to be the minimum of the exotherm. The phenomenological analysis was completed by calculating the so-called phase transition rate parameter, $\xi$, which in this case actually corresponds to the rate of formation of the liquid crystal phase, defined as the slope of the plots of the variable $\left(\tau_{1/2} T_c\right)^{-1}$ against the cooling rate, $\beta$ (Eq. 2).

**Kinetic analysis of the isotropic-liquid crystal phase transition**
The study of the bulk isotropic-liquid crystal phase transition of the copolymers was completed by calculating the apparent activation energy ($E_aT_c$). The Kissinger [12] and the Flynn-Wall-Ozawa [13, 14] integral methods were applied at the maximum rate of the formation of the liquid crystal phase. The values of $\ln(\beta T_c^2)$ and $\log(\beta)$, respectively, were represented versus $T_c$ (Eq 3 and 4, respectively), and $E_aT_c$ was calculated from the slopes of the curves.

In addition, the development of multiple individual processes occurring at the isotropic-liquid crystal transition was investigated by applying Avrami’s equations to the $X_c$ data [8, 9]. The time-dependent probability of the formation of LC domains during the isotropic-liquid crystal transition can be then described by Eq. 5 in which $t_0$ corresponds to the onset of the transition. The logarithmic form (Eq.6) allows for a linear fit of the phase transition data versus time. In order to consider the effect of the non-mesogenic units in the copolymers, Eq. 6 was corrected, to give Eq. 7, in which $1-\lambda(\infty)$ is the weight fraction of the polymer potentially liquid crystalline at the termination of the process [15]. The parameter $1-\lambda(\infty)$, was calculated as the ratio of the $\Delta H_\infty$ values of the copolymers with respect to the homopolymer, at each cooling rate. Two empirical parameters can be obtained from the Avrami analysis for each DSC cooling curve, $Z$ and $n$, which describe the mechanism of the isotropic-liquid crystal transition processes. From these values, it is possible to calculate a rate parameter $k = Z^{1/n}$ (Eq. 8), which describes the speed of the formation of the liquid crystal phase for each individual process.

**Figure 1.** Schematic representation of the methodology followed for the study of the non-isothermal isotropic-liquid crystal phase transition of the 10-MeOAzB/AMPS copolymers.
3. Results and discussion

3.1 Kinetic analysis of the isotropic-nematic-smectic A phase transition of the homopolymer P10-MeOAzB (Cop-1/0)

Figure 2 shows the non-isothermal isotropic melt-liquid crystal exotherms for the P10-MeOAzB homopolymer (Cop-1/0) at six different cooling rates. All the DSC traces contain two distinct events: a first order exothermic transition at high temperatures (T_c ~ 134 - 136°C), associated with the isotropic-nematic phase transition, and a glass transition at lower temperatures (T_g ~ 71 - 74°C) [4]. We have shown previously using polarised optical microscopy and small angle X-ray diffraction that on cooling from the isotropic phase, P10-MeOAzB forms a narrow temperature range nematic phase and on further cooling, a smectic phase.

The temperature corresponding to the minimum of the exothermic peak (T_c), and the associated enthalpy (ΔH_c) and entropy (ΔS_c) changes measured at different cooling rates are listed in Table 1. The values of T_c, ΔH_c and ΔS_c measured at β = -10 °C-min⁻¹ are in good agreement with those reported elsewhere [4, 7, 16, 17]. On increasing the cooling rate, the isotropic-nematic transition exotherm becomes broader and shifts to slightly lower temperatures. The extent of supercooling is reproducible but very small (ΔT < 2°C) when the cooling rate is varied between 5 and 20°C/min, suggesting that the transition occurs close to the thermodynamic equilibrium [10]. This observation is consistent with a thermodynamically weak transition such as a nematic-isotropic transition.

Figure 2. DSC cooling traces of P10-MeOAzB (Cop - 1/0) obtained at different cooling rates, β, from 5 to 20 °C/min.

The quantitative analysis of the non-isothermal isotropic-liquid crystal phase transition of P10-MeOAzB involved the calculation of the liquid crystal fraction (X_i) as a function of time, φ(t) = t – t₀, using Eq. 1. The dependence of X_i on φ(t) is shown in Figure 3a revealing sigmoidal plots, which can be understood as reminiscent of autocatalytic processes [10]. The values of apparent total phase transition period, Δt_c = t_φ=0.99 - t_φ=0.01, and half-phase transition time, τ_{1/2}, were obtained from the X_i curves, and are listed in Table 2. Figure 3a clearly shows the differences in the transitional process of P10-MeOAzB seen on varying the cooling rate. Specifically, the shift of the X_i curves towards smaller φ(t) values on increasing β and the
correspondingly lower $\Delta t_c$ and $\tau_{1/2}$ values, reveal that isotropic-liquid crystal phase transition takes place more rapidly at higher cooling rates. Only a slight deviation is noted for $\beta=15$ and 20 °C/min at low $\phi_t$. Similar observations are usually explained by more pronounced supercooling at higher cooling rates, promoting polymer crystallisation at temperatures more displaced from equilibrium ($\bar{T}_S^0$). It appears reasonable to assume that a similar explanation accounts for the behaviour of the isotropic-liquid crystal phase transition, although we note that the extent of supercooling is small. A value of $\xi = 5.14 \cdot 10^{-3}$ K$^{-1}$ was calculated for P10-MeOAzB using Eq. 2.

**Figure 3.** Phenomenological and kinetic analysis of the isotropic-nematic phase transition shown by P10-MeOAzB: a) X curves; b) Avrami plots.

The Avrami plots for the isotropic-nematic phase transition of P10-MeOAzB obtained using Eq. 5 and 7 are shown in Figure 3b. Each of these plots contains two distinct linear regions revealing the occurrence of a primary process (hereinafter, P1), at short transition times, and a secondary process (hereinafter, P2), at longer times. We suggest that these two processes could be assigned to the isotropic-nematic (P1) and nematic-smectic A (P2) transitions of the homopolymer, respectively [16, 17].

From the logarithmic representations of the two individual curves, the Avrami kinetic parameters related to the primary ($Z_1$, $n_1$, $k_1$) and secondary ($Z_2$, $n_2$, $k_2$) processes were obtained, according to Eq. 7 and 8, and are given in Table 3. The high $R^2$ values indicate that the two transition processes are well described by the Avrami model. It is also noteworthy that the Avrami rate constants for P10-MeOAzB, $k_i$, are of the same order of magnitude as seen for anisotropic crystallisable polymers ($\approx 10^{-2} \text{ s}^{-1}$) [18, 19]. The slightly higher rates and $n$ values seen for P10-MeOAzB may presumably be attributed to the morphological differences between the formation of ordered crystalline phases and transitions involving mesophases [20]. The differences in $n$ and $\ln(Z)$ for the two processes may be interpreted in terms of differences in the mechanisms associated with P1 and P2. Higher Avrami exponents and rate constants are found for P1 ($n_1 > n_2; k_1 > k_2$), suggesting that the isotropic-nematic transition occurs more rapidly that the nematic-smectic A transition.
3.2 Kinetic analysis of the isotropic-smectic A transition for the 10-MeOAzB/AMPS-x/y copolymers

3.2.1 Bulk transition properties

Figure 4 shows the DSC cooling scans of the copolymers recorded at the lowest and highest cooling rates, namely, $\beta = 5$ and $\beta = 20 ^\circ\text{C} \cdot \text{min}^{-1}$, distinguishing non-isothermal isotropic melt-liquid crystal transition exotherms and glass transitions, $T_g$. Phase assignment was carried out on the basis of polarised optical microscopy and small angle x-ray diffraction studies [7]. The DSC traces measured at intermediate values of $\beta$ are essentially identical and fall between these limiting curves.

Figure 4. (a) DSC traces recorded at cooling rates, $\beta = 5$ and $20 ^\circ\text{C} \cdot \text{min}^{-1}$ and (b) the dependence of $X_t$ on $\phi(t)$ for the 10-MeOAzB/AMPS copolymers. Experimental points have not been shown for the sake of clarity.

The calorimetric parameters ($T_c$, $\Delta H_c$ and $\Delta S_c$) obtained from the DSC thermograms for the copolymers are listed in Table 4. The $T_c$ values initially decrease on increasing the AMPS mol fraction before reaching a limiting value at around $x_{\text{AMPS}} = 0.3$ (see Figure 5a). The values in Table 4 also suggest simultaneous reductions of $\Delta H_c$ and $\Delta S_c/R$ for the copolymers, at least for low AMPS concentrations.

Figure 5. (a) $T_c$ values; (b) $\tau_{1/2}$; (c) $\xi$ values (Eq. 2) for the 10-MeOAzB/AMPS copolymers:

The non-isothermal isotropic-smectic A phase transition of the copolymers was analysed using the same methodology described for the P10-MeOAzB homopolymer. The dependence of $X_t$ on $\phi(t)$ for the phase transition of the copolymers cooled at $\beta = 5$ and $20 ^\circ\text{C} \cdot \text{min}^{-1}$ is shown in Figure 4b. These curves are sigmoidal in shape similar to those observed for the homopolymer, and was understood as reminiscent of autocatalytic processes. The AMPS mol fraction has a marked effect on both the relative position and the shapes of the $X_t$ curves, suggesting variations in the phase transition process [10]. In order to quantify these differences, the kinetics parameters $\xi$, $\Delta t_c$ and $\tau_{1/2}$ were calculated for each of the copolymers (Figure 5b and 5c).
The introduction of AMPS units causes immediate reduction in the rate of the phase transition, which can be attributed to the introduction of heterogeneities or defects in these random copolymers [21]. At higher AMPS concentrations, \( \xi \) seems to stabilise until reaching a plateau. These results can be related to the entropy changes calculated for the phase transition and plotted in Figure 6 as a function of the compositions of the polymers. The remarkable similarity between the evolution of \( \xi \) and \( \Delta S_c \) with composition, and the absence of nematic phases, underpin the role of orientational dynamics on the formation of the smectic A phase from the isotropic melt [22, 23].

**Figure 6.** The dependence of the entropy change associated with the isotropic-liquid crystal phase transition (\( \Delta S_c/R \)) measured for differing cooling rates on the composition of the 10-MeOAzB/AMPS copolymers. For the homopolymer we see an isotropic-nematic-smectic A transition while the copolymers exhibit an isotropic-smectic A transition

The evaluation of the bulk isotropic-smectic A phase transition of the copolymers was completed by studying the apparent activation energy of the process. The Kissinger and Flynn-Wall-Ozawa models were applied to calculate the apparent activation energies of the phase transition (\( E_{aT_c} \)), from the plots of \( \ln(\beta T_c^{-2}) \) and \( \log(\beta) \) against \( T_c^{-1} \) (Figure 7a and Figure 7b, respectively). The apparent activation energies obtained by the two methods are similar and are shown in Figure 7c as a function of \( x_{AMPS} \). At low AMPS concentrations, \( E_{aT_c} \) remains nearly unaltered respect to P10-MeOAzB and a sudden increase in the absolute values occurs at \( x_{AMPS} > 0.3 \).

It is noteworthy in the previous results how the asymptotic behaviour of \( \xi \) and \( \Delta S_c \) coincides with the onset of the \( E_{aT_c} \) increase. This effect occurs at composition ranges when the 10-MeOAzB/AMPS copolymers exhibit simultaneous formation of acid aggregation and liquid crystalline behaviour (0.30 \( \leq x_{AMPS} \leq 0.56 \)) [7]. These results suggest that the combination of entropic and enthalpic effects may promote the forming role of the acid groups in the liquid crystal phase structure of the copolymers and the formation of pronounced microphase separated morphologies.
The shapes of the $Ea_{Tc}$ curves, which resemble exponential behaviour, also suggest that further additions of AMPS concentrations would represent a great increase in the activation energy. Below a certain threshold $10$-MeOAzB concentration, the rate of the phase transition ($\xi$) is possibly too slow to compensate the high intermolecular interactions in the melt caused by acid aggregation via hydrogen bonding. This accounts for the inhibition of the liquid crystallinity observed in the precedent studies for the $10$-MeOAzB/AMPS copolymers with $x_{AMPS}>0.56$ [7].

Figure 7. Calculation of the activation energy of the isotropic-smectic A process for the $10$-MeOAzB/AMPS copolymers ($Ea_{Tc}$). Plots of the (a) Kissinger, (b) Flynn-Wall-Ozawa methods; (c) Evolution of $Ea_{Tc}$ for the two methods with the composition.

### 4.2.2 Avrami analysis of the isotropic-smectic A phase transition for the $10$-MeOAzB/AMPS copolymers

The phase transition kinetics of the copolymers were further analysed by applying the Avrami equations and following the methodology described for the $10$-MeOAzB homopolymer (Eq. 5 to 8). It is possible to see how the copolymers with lower AMPS units (Figure 8a) clearly show the two linear regions observed for $P10$-MeOAzB ($P1$ and $P2$ processes in Figure 3b). On the other hand, the slopes of the two regions seem to equalise at higher concentrations of AMPS (Figure 8b). The kinetic parameters of the $P1$ and $P2$ processes are quantified by calculating the $n$, $Z$, and $k$ values as a function of the cooling rates and copolymer composition, and the results are included in Table 3.
Figure 8. Examples of Avrami plots obtained for the phase transition of the 10-MeOAzB/AMPS copolymers at high and low cooling rates. High (a) and intermediate (b) 10-MeOAzB concentrations

An increase in the $n$ values is observed in the case of the copolymers, respect to the homopolymer, for both processes. This variation could be indicative of a change in the phase transition mechanism by the presence of AMPS units, and is in coherence with the absence of the nematic phase in the copolymers observed by microscopy [11, 25]. The changes in the slopes observed in the Avrami curves and underlined in Figure 8 are also reflected in variations of the individual rate constants of P1 ($k_1$) and P2 ($k_2$). Lower values of $k_i$ are found in the copolymers respect to the homopolymer. This fact agrees with the reduction of the phase transition rate observed through the $\xi$ values by the addition of AMPS units (see Figure 5c). Moreover, while $k_1 > k_2$ in the case of P10-MeOAzB, $k_1 \approx k_2$ for Cop(0.7/0.3) and copolymers with higher AMPS concentrations. Cop(0.92/0.08) shows an intermediate behaviour and, finally, a sensitive increase on the $k_i$ values is observed for Cop(0.54/0.46).

The equalising of the constant rates ($k_1$, $k_2$) seems to indicate that the two individual processes, clearly visible in the homopolymer (P1 and P2), are merging to a simple transition process for some of the copolymers. Figure 9 shows a proposed scheme of the LC phase formation from the isotropic melt in the 10-MeOAzB/AMPS copolymers. The formation of liquid crystal phases usually involves orientational, translational and configurational processes [22]. In the case of the homopolymer (P10-MeOAzB, Figure 9a), the observance of the nematic phase (1D order) denotes an initial orientation process over a clear temperature range (P1). We can assume that the nematic template is nucleating the formation of the smectic layers (2D order) by the presence of pre-orientated mesogens. The smectic templates will then require backbone cooperative translational processes and side groups arrangements (to improve packing efficiency in interdigitated Smectic phases) (P2). Such model fits well to previous findings in methacrylate azo-benzene-based homopolymers [16].

In the case of the 10-MeOAzB/AMPS copolymers, our kinetics results have indicated an initial decrease of the phase transition rate (Figure 5c), ascribed to a decrease in the entropy change (Figure 6). According to the model proposed in Figure 9b, such decrease could be related to partial inhibition of the orientation of the mesogenic units, caused by the inclusion of ionic groups into the LC templates. This view is also consistent with the absence of nematic phases in
the copolymers. However, the low concentration of AMPS will still allow for high mobility at long range and for the compression of the backbone to accommodate the non-mesogenic units into LC templates. Thus, it is possible that orientational processes are somehow overcooled and overlapping longer rate translational phenomena, and this may account for the decrease in the bulk phase transition temperature (Figure 5a) [7]. The recovery of the phase stability observed in the 0.30 ≤ x_{AMPS} 0.54 range could be then explained by a decrease in the actual concentration of AMPS units present in the LC templates, caused by phase separation. This can also explain the stabilisation of the entropic effects, due to a combination of lower local mobility hindrance and higher backbone compression to require effective packing. In this composition range, moreover, the formation of ionic aggregates may also promote stronger intermolecular interactions in the phase separated morphology. Such increase in enthalpic restrictions may act as structure forming at intermediate and high acid concentrations, and is coherent with the rise in the activation values obtained in this work and an increase in the viscosity of the copolymers (see Figure 7c). At the limit, the interactions will produce strong long-rate restrictions in the translational movements of the main chain, and final inhibition of the smectic behaviour (see Figure 9c) [7, 26, 27]. This hypothesis is also supported by the increase in the glass transition reported for these copolymers (Table 2, [7]).

**Figure 9.** Schematic representation of the isotropic–melt to liquid crystalline transitions in the P10-MeOAzB (a), P10-MeOAzB/AMPS copolymers showing liquid crystal behaviour (b) and amorphous P10-MeOAzB/AMPS copolymers (c)
4. Conclusions

The introduction of low amounts of acid groups (AMPS) units promotes an initial retardation of the phase transition rate ($\xi$) of the 10-MeOAzb/AMPS copolymers, due to a disrupting effect by the introduction of non-mesogenic units into the LC templates. At increasing acid groups concentrations, such destabilisation effects are compensated by a reduction in the effective concentration of AMPS units in the LC regions, driven by the occurrence of phase separation. Further additions of acid groups have structure-forming effects by increasing the rectification of the main chains and the viscosities, attributed to stronger ionic aggregation by hydrogen bonding. At the limit, the mobility restrictions in the backbone are so acute that may produce complete inhibition of the liquid crystal behaviour. In addition, the Avrami analysis showed that overcooling of the orientational processes may be the main reason for phase destabilisation and extinction of the nematic phase in the copolymers, and also for retardation of the phase transition at low acid contents. An equilibrium between entropic and ethalpic effects is achieved at intermediate compositions with phase separated morphologies which allow for simultaneous ionogenic and liquid crystalline behaviours typical of LCI.
8. Avrami, M. J. Chem. Phys. 7 (1939) 1103
10. Mandelkern, L. Crystallization of Polymers, 2nd ed.; Cambridge, University Press: Cambridge, UK, 2002; Chapter 8

15


21 Mandelkern, L. Crystallization of Polymers, 2nd ed.; Cambridge, University Press: Cambridge, UK, 2002; Chapter 8, pp 265


26 Zhao, Y.; Lei, H. Macromolecules 27 (1994) 4525

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Table 1. Parameters obtained from the DSC analysis of \textbf{P10-MeOAzB}

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<th>Cooling rate $\beta$ ($^{\circ}$C·min$^{-1}$)</th>
<th>$T_g$ (ºC)</th>
<th>$T_c$ (ºC)</th>
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Table 2. Phenomenological analysis of the crystallization of the 10-MeOAzB/AMPS copolymers: $\Delta T_c$ and $\tau_{1/2}$ values.

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Table 3. Kinetic analysis of the crystallization of the 10-MeOAzB/AMPS copolymers: fitting parameters corresponding to the Avrami’s model.

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Table 3. Kinetic analysis of the crystallization of the 10-MeOAzB/AMPS copolymers: fitting parameters corresponding to the Avrami’s model (cont.)

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## Table 4

Parameters obtained from the DSC analysis of the 10-MeOAzB/AMPS copolymers

| Cooling rate $\beta$ ($^{\circ}\text{C} \cdot \text{min}^{-1}$) | Cop (0.92/0.02) | | | | | | Cop (0.76/0.24) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | $T_g$ | $T_c$ | $\Delta H_c$ | $\Delta H_m$ | $\Delta S_c/R$ | $\Delta H_m$ | $T_g$ | $T_c$ | $\Delta H_c$ | $\Delta H_m$ | $\Delta S_c/R$ | $\Delta H_m$ |
| 5 | 71.3 | 134.4 | 10.98 | 4.78 | 1.41 | 11.17 | 72.4 | 132.8 | 7.67 | 3.04 | 0.90 | 8.28 |
| 7 | 71.0 | 133.9 | 11.11 | 4.84 | 1.43 | 11.03 | 73.1 | 132.0 | 8.26 | 3.27 | 0.97 | 8.12 |
| 10 | 70.1 | 133.7 | 10.96 | 4.77 | 1.41 | 10.91 | 70.2 | 131.4 | 7.87 | 3.12 | 0.93 | 7.96 |
| 12 | 70.7 | 133.0 | 10.96 | 4.77 | 1.41 | 10.73 | 70.2 | 131.0 | 7.74 | 3.06 | 0.91 | 7.97 |
| 15 | 71.1 | 132.1 | 10.90 | 4.74 | 1.41 | 10.67 | 70.8 | 130.5 | 7.86 | 3.11 | 0.93 | 7.94 |
| 20 | 70.0 | 132.1 | 10.88 | 4.74 | 1.41 | 11.33 | 70.7 | 129.7 | 7.79 | 3.08 | 0.92 | 7.94 |
Table 4. Parameters obtained from the DSC analysis of the 10-MeOAzB/AMPS copolymers (cont.)

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DSC thermograms (at different cooling rates $\beta$)

$q\left(\frac{mW}{g}\right)$ vs T, t → $X_t = \frac{\Delta h_t}{\Delta h_\infty} = \frac{\int_{t_0}^{t} \Delta h_t}{\int_{t_0}^{\infty} \Delta h_t}$ (Eq 1)

$X_t$ vs T, t, $\forall \beta$

Phenomenological analysis

$T_c$ (phase transition peak)

$t_{1/2}$ (half-time crystallisation)

$\zeta$ (phase transition rate parameter)

$[\tau_{1/2} \cdot T_c]_n = C - \zeta \beta_k$ (Eq 2)

Kinetic analysis

Activation energy

Kissinger

$[\ln(\beta T_c^2)]_n = C - (Ea/R) [T_c^{-1}]_n$ (Eq 3)

Flynn-Wall-Ozawa

$[\log(\beta)]_n = C - (Ea/R) [T_c^{-1}]_n$ (Eq 4)

Avrami’s model

$1-X_t = \exp(-Z \cdot (t-t_0)^\lambda)$ (Eq 5)

$[\log(-\ln(1-X_t))]_n = \log Z + n [\log(t-t_0)]_n$ (Eq 6)

$\ln\left(\frac{1 - \frac{X_t}{1 - \lambda(\infty)}}{1 - \lambda(\infty)}\right) = \frac{1}{1 - \lambda(\infty)} K \cdot t^n$ (Eq 7)

$\log(Z)$, $n$$\rightarrow k = \frac{Z^n}{n}$ (Eq 8)

$Z_1$, $n_1$, $k_1$

$Z_2$, $n_2$, $k_2$
Figure 3b
Click here to download high resolution image
Figure 6

\[ \frac{\Delta S}{R} \text{ vs. } X_{10-\text{MeOAzB}} \]

\[ \beta \text{ (°C·min}^{-1}) \]

- □ 2
- ● 5
- ▲ 7
- ▼ 10
- ◀ 12
- ◀ 15