Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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First published on: 05 November 2010

To cite this Article Araya, Kotaro , Igeta, Koichi and Shimura, Masato(2009) 'Crystallisation of nematic liquid crystal mixtures', Liquid Crystals, 36: 5, 493 — 495, First published on: 05 November 2010 (iFirst)

To link to this Article: DOI: 10.1080/02678290903029746

URL: http://dx.doi.org/10.1080/02678290903029746

Liquid Crystals,
Vol. 36, No. 5, May 2009, 493–495

Crystallisation of nematic liquid crystal mixtures

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(Received 23 March 2009; final form 6 May 2009)

In this paper, we propose a method to accelerate the crystallisation of nematic liquid crystal mixtures based on crystallisation theory. This method is to hold a nematic liquid crystal sample at a temperature suitable for crystal growth after aging it at a temperature suitable for nucleation. After we specified these temperatures of a nematic liquid crystal mixture using differential scanning calorimetry, we demonstrate that the two-temperature aging method is effective for the crystallisation of other nematic liquid crystal mixtures in which the crystal-liquid crystal transition temperature has so far been undetectable.

Keywords: crystallisation; nucleation; crystal growth; nematic liquid crystal; glass transition

1. Introduction

Nematic liquid crystal mixtures are used as electro-optic liquid crystal devices (*1*) and liquid crystal solvents (*2–4*) due to their wide nematic range. Although such a wide temperature range is based on freezing point depression, the range can also be attributed to the stability of the supercooled nematic phase (*5, 6*). The supercooling behaviour of nematic liquid crystal mixtures is advantageous for these applications, but it has problems as well. For example, we cannot determine whether the liquid crystal phase we observed is in a stable or a metastable phase because the crystal–liquid crystal transition temperature is undetectable. Therefore, we have considered accelerating the crystallisation of nematic liquid crystal mixtures using differential scanning calorimetry (DSC). The crystallisation consists of two processes of nucleation and crystal growth, and its rate depends on the temperature in which the sample is held (*7, 8*). If we believe the crystallisation theory, we can expect that the procedure to hold a nematic liquid crystal sample at a temperature suitable for crystal growth after aging it at a temperature that is suitable for nucleation will be an effective one to accelerate the crystallisation. In this paper, we report that the two-temperature aging method is effective for the crystallisation of nematic liquid crystal mixtures.

2. Experimental

2.1 Materials

ZLI-1083 and ZLI-1132 were used as received from Merck. ZLI-1083 is a nematic liquid crystal mixture of *trans*-4-n-alkyl- (4′-cyanophenyl)cyclohexanes (*9*). ZLI-1132 is a nematic liquid crystal mixture of *trans*-4-n-alkyl- (4′-cyanophenyl)cyclohexanes and *trans*-4-n-pentyl- (4′-cyanobiphenyl)cyclohexane (*10*). The nematic liquid crystal–isotropic liquid transition of ZLI-1083 and ZLI-1132 is 52°C and 70°C, respectively.

2.2 Measurements

The calorimetric curves were recorded on a Perkin-Elmer Pyris-1 differential scanning calorimeter during the processes of heating and cooling. The temperatures were calibrated with the melting point of indium (156.6°C). The enthalpy was also calibrated with the latent heat of the melting of indium (28.45 J g^{-1}).

3. Results and discussion

To specify the temperature suitable for nucleation, we selected ZLI-1083 as a starting material. This is why the temperature suitable for crystal growth of the mixture is detected by chance. Figure 1 shows the DSC curve of ZLI-1083 for the heating and cooling process.

In Figure 1, the peaks at around 50°C in both processes are for the nematic liquid crystal–isotropic liquid transition. The mixture also shows a glass transition at around –70°C in both processes. In the heating process, the supercooled nematic liquid crystal mixture shows an exothermic peak of crystallisation at around –40°C and a fusion peak at around –20°C. From this DSC curve, we can assume that the temperature suitable for crystal growth could be around –40°C. The peak area around –20°C is 2.3 J g^{-1} and is smaller than the peak area (4.1 J g^{-1})

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ISSN 0267-8292 print/ISSN 1366-5855 online

DOI: 10.1080/02678290903029746
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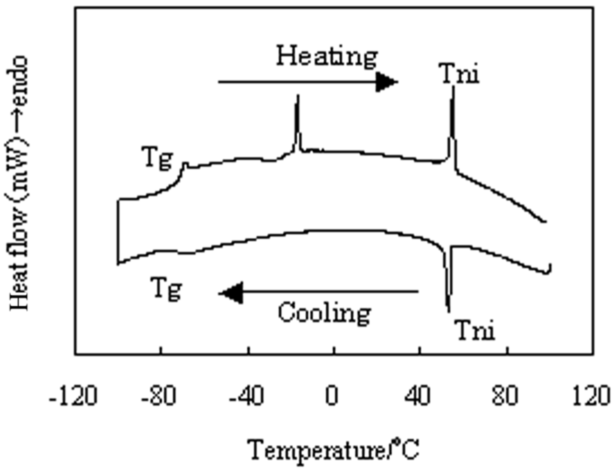

Figure 1. DSC curve of ZLI-1083 for both the heating and cooling processes.

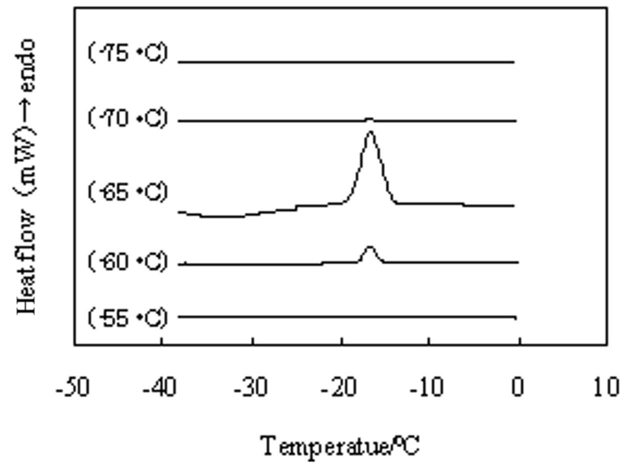

Figure 2. Some DSC curves of ZLI-1083. The aging temperatures are parenthesised. The aging time is 1 min.

for the nematic liquid crystal–isotropic transition. Because the latent heat for the nematic liquid crystal–isotropic transition is generally one-tenth that of the crystallisation (*11*), the small peak at around –20°C indicates that the sample of ZLI-1083 partially solidified in this temperature profile. This result is pertinent to the present study because we used the temperature dependence of the peak area to specify the temperature suitable for nucleation. Hereafter, we define two aging temperatures used for nucleation and crystal growth as T_1 and T_2, respectively. To find the temperature suitable for nucleation, we tried the next temperature profile. The crystal growth temperature (T_2) was fixed at –40°C, and T_1 was selected in the temperature range from –90°C to –50°C. The sample of ZLI-1083 was cooled to T_1 from 100°C at 500°C min^{-1}, and then it was held for 1 min. Next, the sample was heated to –40°C at 100°C min^{-1}, and then it was held for 1 min. Finally, the sample was heated to 20°C at 10°C min^{-1}. The selected DSC data are shown in Figure 2. The peak area of the fusion when T_1 was –65°C is 21.5 J g^{-1} and is larger than that of the other T_1. From this result, we can conclude that the temperature suitable for the nucleation is near –65°C for ZLI-1083. Another key finding is that the temperature suitable for the nucleation can be observed just above the glass transition temperature.

To test the effectiveness of the two-temperature aging method, we selected ZLI-1132. The supercooled nematic phase of this mixture is so stable that it can be used as a nematic liquid crystal solvent at temperatures between –40°C and 70°C (*12*). Figure 3 shows the DSC curve of ZLI-1132 for the heating and cooling process. The heating rate was 10°C min^{-1}. In Figure 3, the peaks at around 70°C in both processes are for the

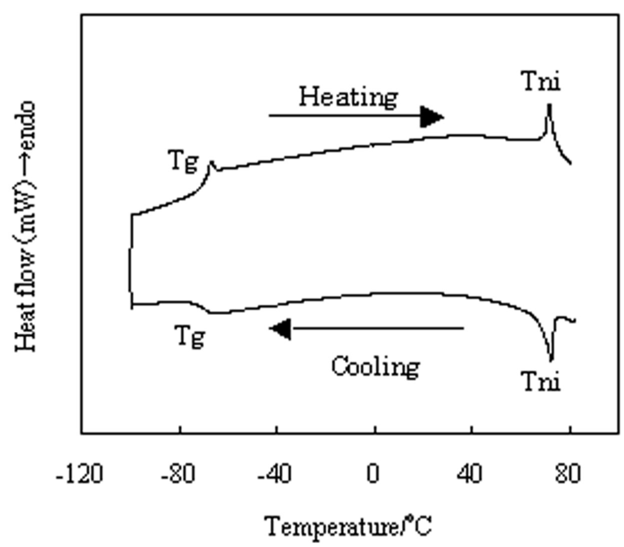

Figure 3. DSC curve of ZLI-1132 for both the heating and cooling processes.

nematic liquid crystal–isotropic liquid transition. The mixture also shows a glass transition at around –70°C in both processes. We did not observe any peak with the crystallisation in this temperature profile. In fact, the crystallisation takes more than 24 h in a freezer with a constant temperature of –40°C.

For ZLI-1132, we can assume that the temperature of nucleation is –65°C because the glass transition temperature of ZLI-1132 is almost equal to that of ZLI-1083. After much trial and error, we detected the peak of crystallisation when the aging time was more than 30 min. The selected DSC data are shown in Figure 4. The nucleation temperature (T_1) was fixed at –65°C, and T_2 was selected in the

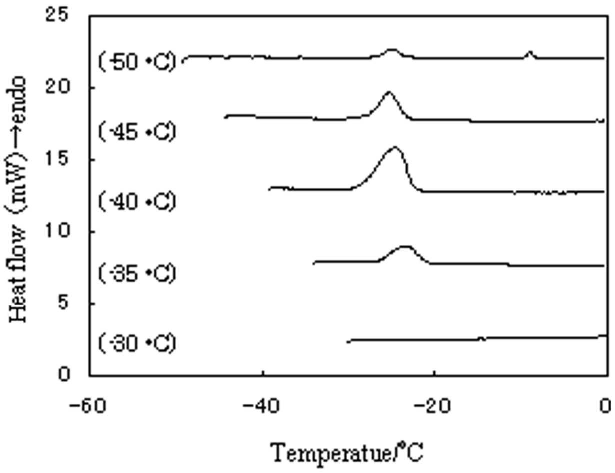

Figure 4. Some DSC curves of ZLI-1132 aged at T_1 = –65°C. The first aging temperatures (T_2) are parenthesised. The aging time of T_1 and T_2 is 60 min.

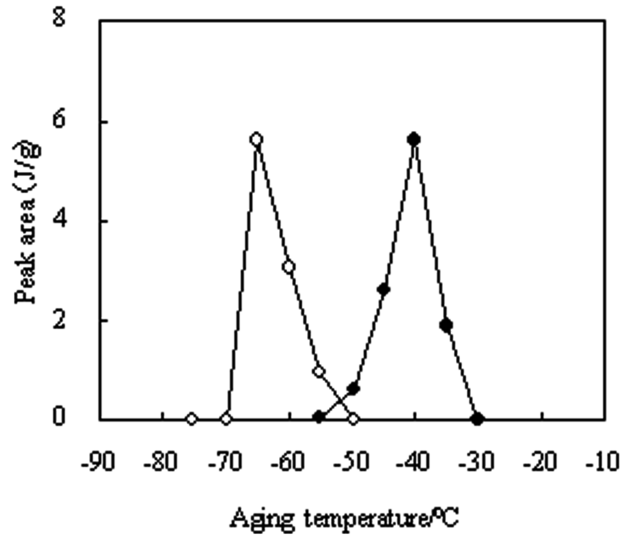

Figure 5. Relationship between the aging temperature and the peak area of the fusion. ○: T_2 was fixed at –40°C. ●: T_1 was fixed at –65°C.

temperature range from –30°C to –50°C. The aging time of T_1 and T_2 is 60 min. The peak of fusion was observed at around –20°C. As expected, the crystallisation occurred within 2 h using this two-temperature aging method. The peak area of the fusion when T_2 was –40°C is larger than that of the other T_2. Figure 5 plots the relationship between the peak area of the fusion and T_2. These results lead us to conclude that the temperature suitable for crystal growth is near –40°C for ZLI-1132. On the contrary, T_1 was changed in the range from –75°C to –55°C to confirm the temperature suitable for nucleation. Figure 5 plots the relationship between the peak area of the fusion and T_1, and we can conclude that the temperature suitable for nucleation is –65°C. Moreover, it is easily understood that the crystallisation consists of two processes of nucleation and crystal growth as described above.

4. Conclusions

We demonstrated that a two-temperature aging method is effective for the crystallisation of nematic liquid crystal mixtures. This indicates that the crystallisation theory is applicable to liquid crystal materials. Moreover, we also found that the temperature suitable for nucleation is just above the glass transition temperature for both ZLI-1083 and ZLI-1132. This finding can be useful for detecting the fusion temperature of other nematic liquid crystal mixtures that easily form a glassy phase.

Acknowledgments

We would like to thank Dr. H. Kagawa for supplying references on liquid crystals and Mr. K. Iwasaki for assisting with the DSC measurements.

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