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N. Gogibus [a b], U. Maschke [a], B. Ewen [b], X. Coqueret [a] & M. Benmouna [c]

[a] Laboratoire de Chimie Macromoléculaire (UPRESA CNRS N° 8009), Bâtiment C6, Université des Sciences et Technologies de Lille, Villeneuve d'Ascq Cedex, F-59655, France

[b] Max-Planck-Institut für Polymer-forschung, Postfach 3148, Mainz, D-55121, Germany

[c] Laboratoire de Recherche sur les Macromolecules, Faculté des Sciences, Université Aboubakr Belkaïd, BP119, Tlemcen, 13000, Algeria

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Onset and End of Transitions in PDMS/5CB Blends as Revealed by Static Light Scattering

N. GOGIBUS[a,b], U. MASCHKE[*,a], B. EWEN[b], X. COQUERET[a] and M. BENMOUNA[c]

[a]*Laboratoire de Chimie Macromoléculaire (UPRESA CNRS N° 8009), Bâtiment C6, Université des Sciences et Technologies de Lille, F-59655 Villeneuve d'Ascq Cedex, France,*
[b]*Max-Planck-Institut für Polymer-forschung, Postfach 3148, D-55121 Mainz, Germany and*
[c]*Laboratoire de Recherche sur les Macromolecules, Faculté des Sciences, Université Aboubakr Belkaïd, BP119, 13000 Tlemcen, Algeria*

The phase diagram of poly(siloxanes) and low molecular weight liquid crystals as obtained by polarized optical microscopy have shown a peculiar behavior : Transitions from a nematic to an isotropic and from an isotropic miscibility gap to a single isotropic phase take place in two steps interpreted as onset and end of transitions. This behavior has been observed in various systems and particular in those involving poly(dimethylsiloxane) (PDMS) and 4-cyano-4′-*n*-pentyl-biphenyl (5CB). In order to confirm this behavior we performed static light scattering on blends of PDMS (M_w=45000g/mol) and 5CB at different compositions. These experiments covered a temperature range from 20 to 115°C and several scattering angles.

Keywords Light scattering, poly(dimethylsiloxane), nematic liquid crystal

INTRODUCTION

Recently[1,2], we reported results of the phase behavior of poly(dimethylsiloxane) (PDMS) and liquid crystal (LC) systems. Two

polymers of molecular weight M_w=45000g/mol and 5500g/mol were considered in combination with the LC 4-cyano-4′-*n*-pentyl-biphenyl (5CB) and the eutectic mixture of cyanoparaphenylene derivatives E7. The phase diagrams were established using Polarized Optical Microscopy (POM) and analyzed theoretically within classical models known in the literature. More details on these aspects can be found in references 1 and 2. For shortness, we focus here on the system PDMS (M_w=45000g/mol)/5CB and try to analyze the emergence of transitions in two distinct steps which are identified as the onset and end of transitions. A region where a nematic phase appears will be referred to by N while an isotropic phase is designated by I. A region where two of these phases are coexisting will be identified by the 2 corresponding letters (I or N) with the symbol +. Hence, as we shall see later our phase diagrams will exhibit the two types of miscibility gaps I+I and N+I. The central point of this paper is the emergence of transitions in two distinct steps. For example, two steps are indeed observed in various siloxane systems both in the transition from Nematic + Isotropic (N+I) to Isotropic + Isotropic (I+I) and from (I+I) to Isotropic (I). We demonstrate here that the temperature shift between these transitions depends strongly on the nature of the system under consideration, its miscibility and composition.

We find that this temperature shift could be as large as 75°C for PDMS (M_w=45000g/mol)/5CB with 10wt-% LC but it is considerably reduced as the concentration of LC increases. Our POM observations show that the shift disappears above 90 wt-% 5CB. The two-step phase transition behavior from (I+I) to I was clearly seen by looking at the evolution of the droplet size upon heating. However, with the POM

technique the observation is influenced by the eye's sensitivity of the observer and a substantial error can show up in the final results. To circumvent this problem, we performed static light scattering on the same systems to check whether similar onset and end of transitions could be found and try to assess the consistency between light scattering and POM results. This is the main object of the present study involving the system PDMS (M_w=45000g/mol)/5CB but noting that similar results are found in other siloxanes and the LC E7.

EXPERIMENTAL PART

Materials

PDMS was prepared by anionic living polymerization using n-butyllithium as initiating species and trimethylchlorosilane as end-capper. The obtained polymer was purified and characterized by gel permeation chromatography (GPC). The molecular weight and the degree of polydispersity (M_w/M_n) are obtained from toluene solutions at 25°C giving M_w=45000g/mol (PDMS) with M_w/M_n=1.1. The LC 4-cyano-4′-*n*-pentyl-biphenyl (5CB) was purchased from Merck Eurolab GmbH (Germany) and is characterized by the crystalline to nematic transition temperature T_{KN}=23°C, and the nematic to isotropic transition temperature at T_{NI}=35.3°C[3].

Sample preparation

The sample preparation was made with a combination of the solvent induced phase separation (SIPS) and the thermally induced phase separation (TIPS)[4,5] methods. The polymer and the LC were dissolved in a common organic solvent THF at 70 weight-percent (wt-%) and room temperature. These mixtures were stirred mechanically for two

hours before a small quantity was cast on a clean glass slide. Then THF was evaporated completely at room temperature for 24 hours. The samples prepared with this method exhibit a swiss-cheese type of morphology.

POM measurements

The thermo-optical studies were performed on a POM ZEISS equipped with a heating/cooling stage Linkam temperature control unit. Samples were heated from room temperature to approximately 15 degrees above the transition temperature leading to the isotropic phase. Then they were left for about 15 min in the isotropic state. The subsequent thermal processes applied to the samples depend on the kinetics of reaching the thermodynamic equilibrium state. Further details on the experimental procedure and data recording can be found elsewhere[1,2,6]. At least two samples were prepared independently with the same composition to check reproducibility of the transition temperatures.

Light scattering

Light scattering measurements were performed at room temperature using a He-Ne Laser (λ=632.8 nm) which was polarized perpendicular to the scattering plane. The optical set-up is arranged in such a way that both polarizer and analyzer are in the vertical position (i.e. normal to the scattering plane). In this case we measure the polarized component of the scattering intensity denoted I_{VV}. A beam stop prevents the transmitted beam from reaching the screen. The scattering pattern was recorded by a CCD camera. A circular intensity pattern independent of the azimuthal angle ϕ was found allowing to perform radial averages of the I_{VV} scattered intensity. Further experimental details are described in reference [7].

RESULTS AND DISCUSSION

Figure 1 shows the phase diagram in the temperature/ LC volume fraction (T, φ_{LC}) frame obtained from microscopy (POM for Polarized Optical Microscopy) observations and by light scattering. The latter technique was used only for samples with 30 wt-% and 70 wt-% 5CB. The agreement between the two techniques is good. In both cases, the temperature gap between onset and end of transitions is 30°C at the lower concentration of 5CB (i.e.10 wt-% 5 CB) but reduces to 10°C at 70 wt-% 5CB. The light scattering measurements were made in a wide range of the wave vector q but we select only few values to illustrate the phenomenon

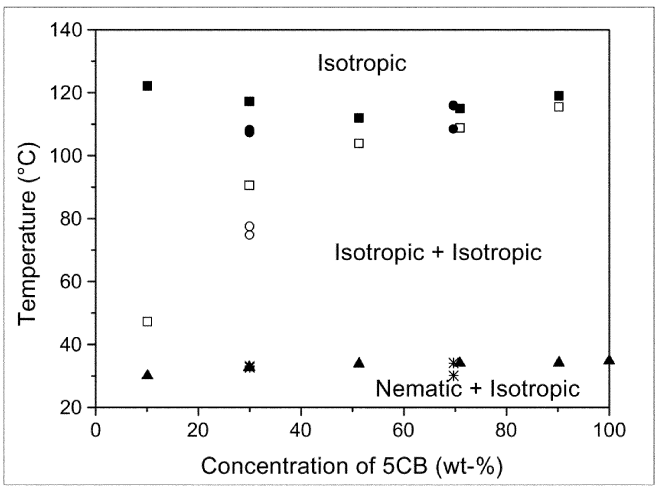

FIGURE 1 The phase diagram of PDMS (M_w=45000g/mol)/5CB system as obtained by POM (squares and triangles) and by light scattering (other symbols). Filled symbols represent onset of transitions while empty ones are for the end of transitions.

under consideration. The results shown in this figure demonstrate unambiguously the existence of two steps in various transitions. The techniques used here rely on different physical processes (transmission and scattering of light), hence the observed consistency of the results is certainly not forticious and confirm the view that one is indeed dealing with onset and end of transitions. To our knowledge, this phenomenon has not been reported before for similar systems. Figure 2 shows the variation of the scattered intensity as a function of temperature for the sample corresponding to 30 wt-% 5CB and three values of q only.

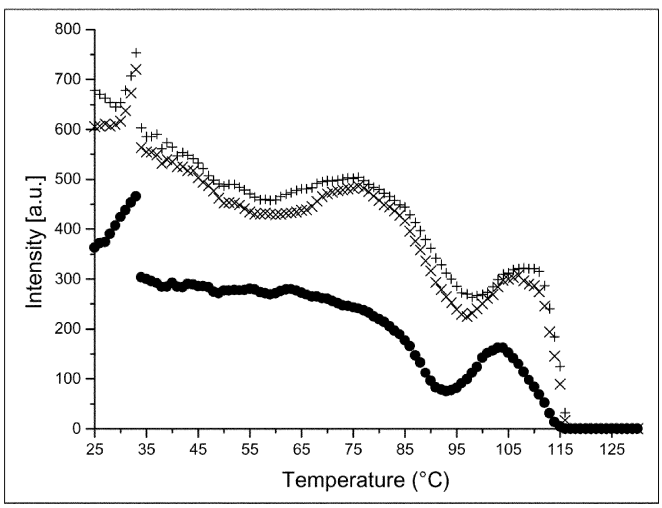

FIGURE 2 The scattered intensity versus temperature for the 30 wt-% 5CB/70wt-% PDMS mixture at three amplitudes of the scattering vector q (+: q=1.05279 μm^{-1}; x: q=1.09627 μm^{-1}; • : q=1.31289 μm^{-1}.

This figure indicates clear transitions at the temperatures 34.5, 93 and 116°C. The first one is related to the (N+I)/(I+I) transition which seems to take place in one step slightly below 35°C. The difference with the

(N)/(I) transition of pure 5CB is within the errors of the measurements which is of the order of one degree. The minimum of Figure2 at 93°C is the onset of transition from (I+I) to (I). A large number of droplets melts down in the single phase region but few of them remain dispersed in the polymer matrix through 115°C. These trends are found at all wavevectors but the temperature shift between onset and end of transition decreases as q increases. Most importantly, these features depend crucially upon LC concentration as shown in Figure 3 which reproduces similar plots as Figure 2 for the 70 wt-% LC sample.

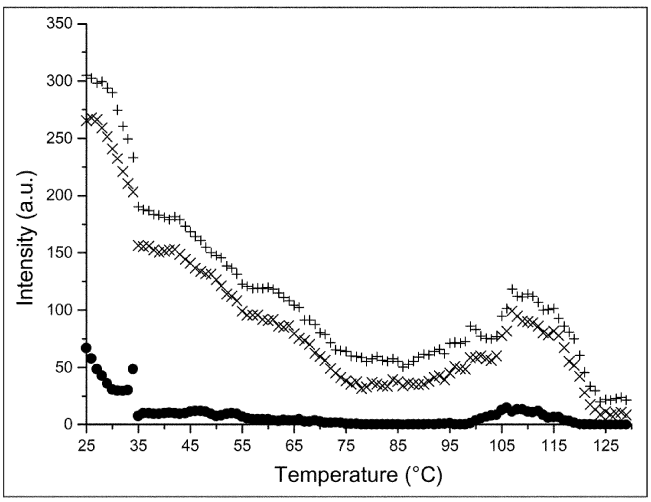

FIGURE 3 The scattered intensity versus temperature for the 70 wt-% 5CB/30 wt-% PDMS mixture at three amplitudes of the scattering vector q (+: q=1.05279 μm^{-1}; x: q=1.09627 μm^{-1}; • : q=1.31289 μm^{-1}.

The striking difference with Figure 2 is that the onset and end of transitions from (I+I) to (I) are extremely close to each other. Both POM and light scattering confirm these trends and give us confidence

on the argument justifing the phase transitions observed in siloxane/LC systems.

CONCLUSIONS

The results reported here indicate that the transition (I+I) to (I) takes place in two steps which are quite distinct at low LC composition. This phenomenon has been found previously by POM observation and corroborated here using static light scattering. It is further enhanced when the miscibility of polymer and LC decreases as in the case of the eutectic mixture E7. Preliminary light scattering data of PDMS/E7 have indeed shown similar results consistent with the POM observation. Reports of these results and related investigations will be the subject of a future communication.

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