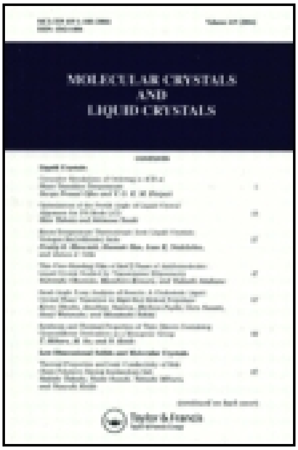

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RE-ENTRANT POLYMORPHISM IN BINARY MIXTURES CONTAINING A SIDE CHAIN POLYSILOXANE

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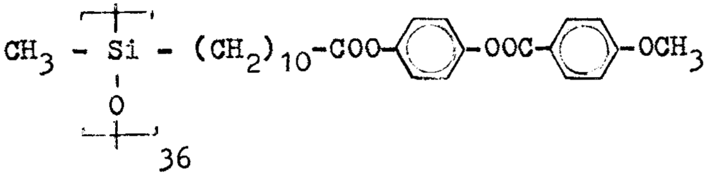
Abstract The miscibility behaviour of the liquid crystalline side chain polysiloxane with low-molecular-weight mesogene was investigated using optical microscopy and X-ray diffraction techniques. A s_{ARe}- n - s_A re-entrant polymorphism of appropriate mixtures is clearly demonstrated.

INTRODUCTION

The first case of a nematic-smectic-nematic re-entrance was observed with pure polar compounds and with binary mixtures of them [1]. Some binary mixtures of nonpolar components show also this strange phase behaviour [2]. Further, in the last time re-entrance was observed in binary systems with polar or nonpolar liquid crystalline (LC) polymers and low-molecular-weight (LMW) compounds [3,4]. In this paper we describe the occurence of the smectic-nematic-smectic re-entrance in three binary systems containing a LC side chain polysiloxane. The results were supported by X-ray investigations.

EXPERIMENTAL

The polymer used in this study was a polysiloxane (P1) of the following structure:



P_{cr} 57°C P_{sE} 96°C P_{sA} 144°C P_{is}.

With respect to the phase symbols in case of LC polymers see ref. [5]. The preparative procedure for the polymer has been described previously [6].

As LMW compounds we have chosen 4-n-pentanoyloxyphenyl 4-n-dodecyloxybenzoate (M1; cr 58°C (s_B 48°C) s_C 62°C s_A 75°C n 82.5°C is), 4-n-butanoyloxyphenyl 4-n-dodecyloxybenzoate (M2; cr 56°C (s_B 51°C) s_C 62°C s_A 68°C n 82°C is), and 4-n-pentanoyloxyphenyl 4-n-decyloxybenzoate (M3; cr 62°C s_B 65°C s_A 82°C n 95°C is)[7].

The textures and transition temperatures of the samples were observed using a polarizing microscope fitted with a heating stage. The phase diagrams were constructed using the contact method and by investigation of samples of definite compositions.

The Ni-filtered CuK$_\alpha$-radiation and a flat film camera were used to investigate samples oriented by a magnetic field. A Guinier equipment was applied to study unoriented specimens.

RESULTS AND DISCUSSION

Figures 1,2 and 3 show the isobaric phase diagrams for the binary systems M1-P1, M2-P1, and M3-P1. In all three cases we observed the unusual s_{ARe}-n-s_A sequence in mixtures containing an excess of the LMW components.

By cooling the homogeneous mixtures from the isotropic phase we found the focal conic s_A textures.

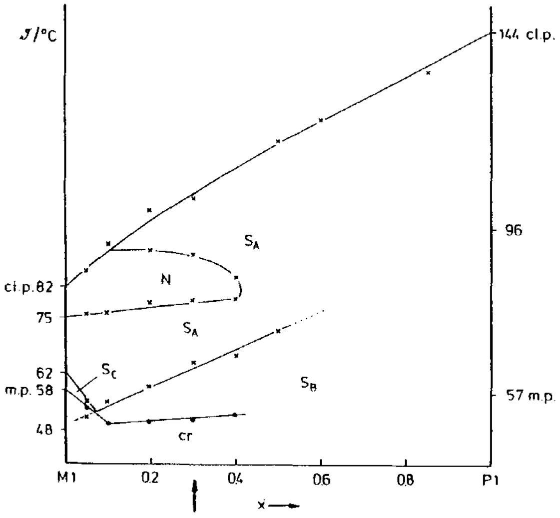


FIGURE 1 Phase diagram of the compounds P1 and M1

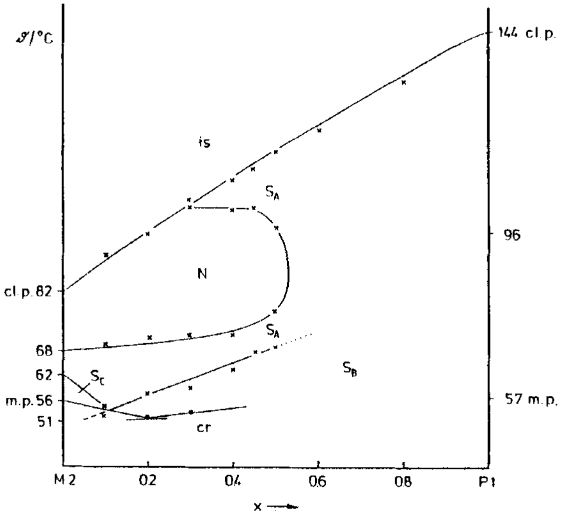


FIGURE 2 Phase diagram of the compounds P1 and M2

With decreasing temperatures this texture transforms into the nematic schlieren texture and at lower temperatures we observed the transition into the focal conic

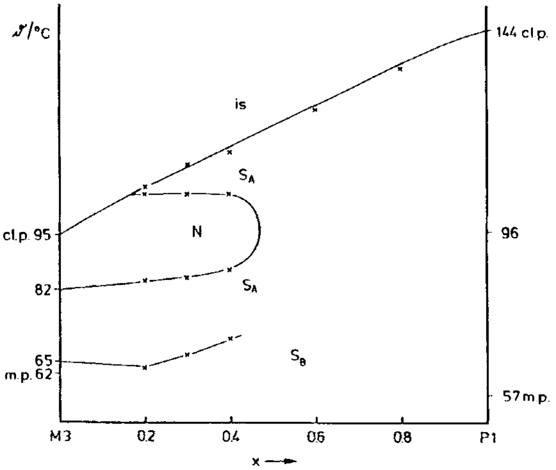


FIGURE 3 Phase diagram of the components P1 and M3

s_A texture. Due to the lack of specific textures, in mixtures with more than 60 mole% of the polymer, the microscopic phase identification was impossible.

The arrow in Figure 1 indicates the mixture which was investigated by means of X-ray experiments at different temperatures.

Figure 4 shows the half width at full maximum (HWFM) of the 001-reflexes in dependence on the temperature. The increase of the HWFM between 80°C and 90°C proves the existence of a nematic phase between the two smectic phases.

Figure 5 shows the spacings of more or less perfectly ordered layers in the mixture derived from Bragg reflections (smectic phases) or diffuse lines (nematic phase) in dependence on the temperature. The spacing increases from 3.4 nm at 75°C to 4.2 nm at 95°C in the high temperature s_A phase. The first value is in accordance with the length of the extended LMW-compound

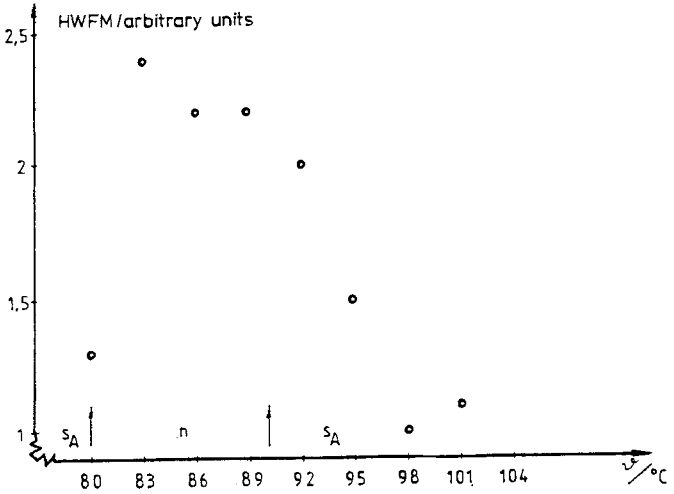


FIGURE 4 HWFM of the 001-reflexes in dependence on the temperature

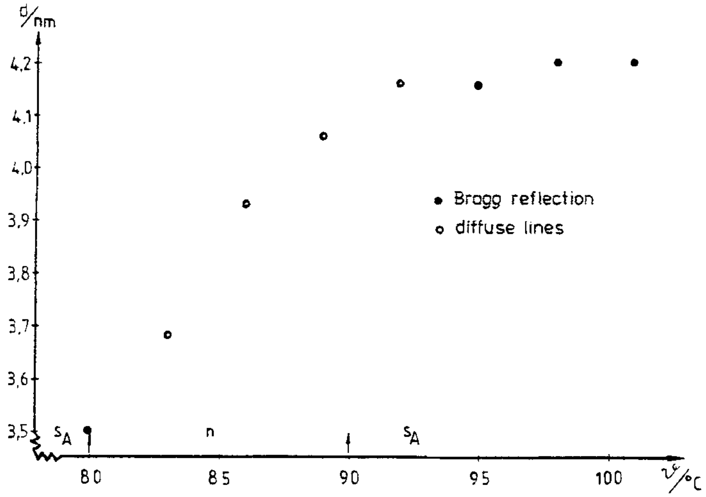


FIGURE 5 d-values of the mixture in dependence on the temperature

measured by means of CPK-models. The layer thickness increases in the region of the nematic phase. At higher temperature a nearly constant d-value was found for the s_A phase.

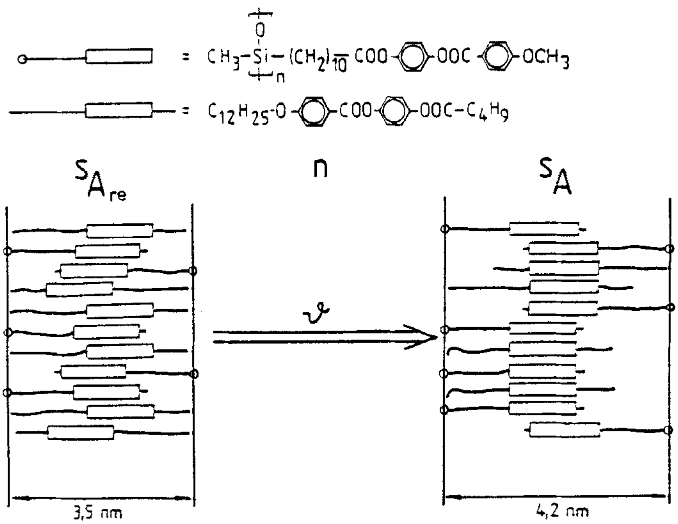


FIGURE 6 Structural model of the s_A phases

In Figure 6 we try to give an interpretation of the results from the X-ray measurements. At lower temperatures the length of the LMW-compound (M1) determines the layer thickness. The smectic high temperature phase shows a packing similar to that of the pure polymer compound (P1) in the P_{sA} phase [8]. This structure allows one a more intensive contact between neighbouring aromatic cores.

ACKNOWLEDGMENT

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