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Miscibility and free volume behaviour of a number of polymer blends containing only thermotropic liquid crystalline polymers

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Abstract

An extensive study has been undertaken on a number of blends containing only thermotropic liquid crystalline polymers (TLCPs) as only components. The effect of the structure of the TLCPs on their miscibility and free volume properties (probed by positron annihilation lifetime spectroscopy) is presented in this work. Although all TLCPs studied are nematic and the experience with low molecular weight liquid crystals is that a common mesophase ensures miscibility, blends of TLCPs with each other show a wide range of miscibilities. The polymeric aspects of TLCPs such as their molecular chemistry, structure and conformation are also found to be important in determining miscibility in blends of such materials. Regardless of their various miscibilities, TLCP blends tend to display smaller, fewer free volume sites than expected from a weighted average. This is ascribed to the intrinsic affinity of nematic TLCPs. This differs from thermoplastic blends where it has been found that degree of blend miscibility alters free volume behaviour as a function of blend composition. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Thermotropic liquid crystalline polymer; Miscibility; Positron annihilation

1. Introduction

Low molecular weight liquid crystals (LMWLCs) of the same mesophase (i.e. nematic) are generally miscible with each other, and indeed this criterion is often used to help classify new LMWLCs and LCPs [1,2]. Most TLCPs with commercial potential to date belong to the nematic class, showing molecular order in one dimension (molecular axial orientation). Compared with the miscibility expected from their low molecular weight counterparts, blends containing two nematic TLCPs appear to be not necessarily miscible [3–7]. Conversely, a nematic TLCP and a smectic TLCP, both containing flexible spacers of ten methylene chains, show partial miscibility [8]. The factors determining miscibility of such materials are not yet fully understood due to lack of a systematic investigation or a wide database of examples. This paper represents a summary of a large number of systems investigated in our laboratory recently. By processing blends in the same way and characterizing them using identical equipment and procedures allows us to go at least some of the way to recognizing factors essential in influencing blend properties. Note that further details of some of these blend systems have been previously reported [6,7]. We seek in this paper only to draw commonalties between blend behaviour of a wide range of samples.

In addition to determining miscibility using the standard technique of dynamic mechanical analysis, a major interest of this work is to measure free volume of such blends by using positron annihilation lifetime spectroscopy (PALS) and correlate miscibility and free volume behaviour of the blends.

The concept of free volume has been one of the most important postulations to interpret polymer characteristics in the glassy state. There are a number of techniques which are capable of providing direct [9–11] or indirect [12] estimation of free volume properties of polymers. PALS, however, has been shown to be a potent tool to study free volume characteristics of polymers as it can evaluate both the size and number concentration of nano sized free volume sites present in polymers [11,13]. This radioactive technique uses sub-atomic species (positrons and their derivatives, in particular, positroniums) to act as a molecular probe. This ability results from the positively-charged nature of positrons (they are the anti-particle of an electron) which leads them to being repelled by nuclei of surrounding atoms and thus residing and sampling areas of low electron density in a material. These can be crystalline defects in

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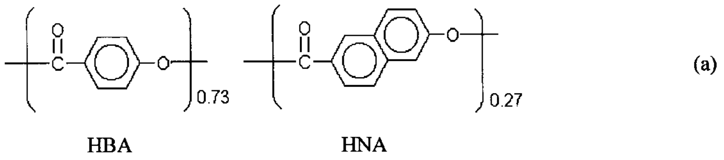
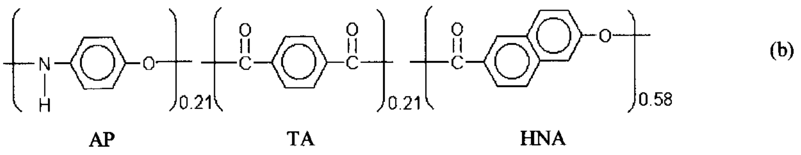


Vectra A950 (Vectra-A)



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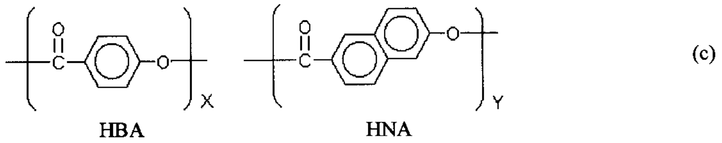
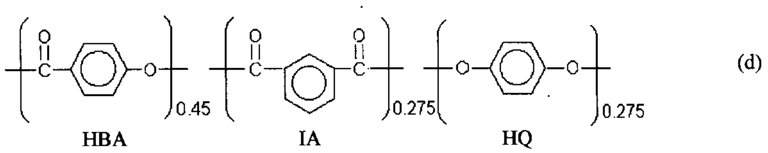
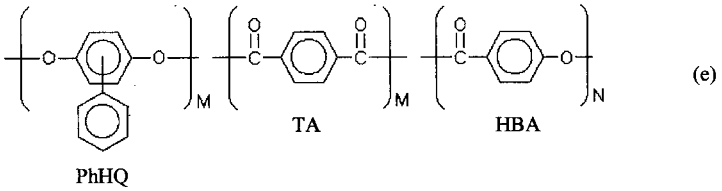


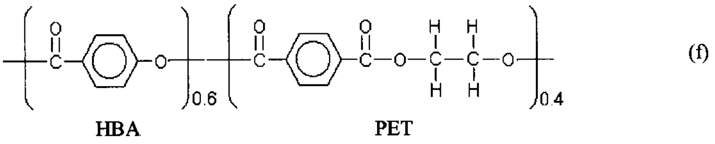
Vectra C950 (Vectra-C) (X ≅ 0.85)



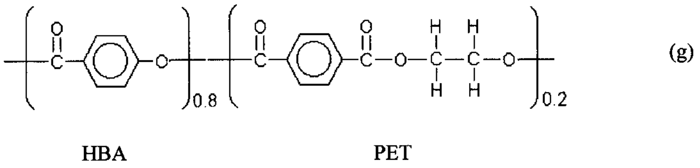
HIQ45



HX2000



Rodrun LC3000 (LC3000)



Rodrun LC5000 (LC5000)

Fig. 1. Chemical structures of the TLCPs used.

Table 1
Processing conditions of the TLCP + TLCP blends

Blend constituents		Blending conditions	Moulding
Vectra-A	HX2000	Extruder, 30 rpm	330°C, 5 min
Vectra-A	Vectra-C	Mixer, 350°C, 30 rpm, 5 min	330°C, 5 min
Vectra-A	Vectra-B	Mixer, 310°C, 20 rpm, 5 min	310°C, 5 min
Vectra-A	HIQ45	Mixer, 320°C, 20 rpm, 5 min	320°C, 5 min
Vectra-A	LC3000	Mixer, 310°C, 20 rpm, 5 min	310°C, 5 min
Vectra-A	LC5000	Mixer, 310°C, 20 rpm, 5 min	310°C, 5 min
Vectra-B	Vectra-C	Mixer, 350°C, 30 rpm, 5 min	330°C, 5 min
Vectra-B	LC5000	Mixer, 310°C, 20 rpm, 5 min	310°C, 5 min
LC5000	LC3000	Mixer, 310°C, 20 rpm, 5 min	310°C, 5 min

metals and ceramics or free volume in polymers. PALS work on polymeric materials to date has been predominantly limited to thermoplastics (TPs) [14,15] and their blends [13,16–18]. Only very few studies have been made using PALS on the free volume properties of TLCPs [19] and blends containing TLCPs [6,7,19].

2. Experimental

TLCPs chosen in the study include a wide selection of commercial or semi-commercial materials. They are Vectra A950 (labelled Vectra-A hereafter), Vectra B950 (Vectra-B), Vectra C950 (Vectra-C) and HIQ45 of Ticona (USA) (formerly Hoechst–Celanese), HX2000 of DuPont (USA) and Rodrun LC3000 (LC3000) and LC5000 (LC5000) of Unitika (USA). Wholly aromatic TLCPs are regarded as rigid TLCPs, whilst TLCPs with flexible moiety such as ethylene terephthalate unit in the Rodrun materials are semi-flexible TLCPs [20]. Their chemical compositions are shown in Fig. 1. Blends of these TLCPs were prepared in a Haake mixer. Transesterification commonly takes place in processing polymer blends containing polyesters and/or polycarbonates. It has been often reported that such reaction is not an issue in blends containing only TLCPs [3,4]. Nonetheless, an antioxidant (Irganox 1098, Ciba–Geigy) was added to further prevent any likelihood of transesterification. The full details of the blend pairs and their preparation can be found in Table 1.

Blend miscibility was determined by dynamic mechanical thermal analysis (DMTA) by using a Rheometrics dynamic analyser II (RDAII) equipped with torsion rectangular fixtures from 40 to 180°C at 1 Hz with a constant strain of 0.4%. Blend samples of $50 \times 5 \times 2\ \mathrm{mm}^3$ were tested in 2°C steps with a soak time of 1 min at each temperature for thermal equilibrium.

Free volume properties were measured by positron annihilation lifetime spectroscopy (PALS) and were carried out on an automated EG and G Ortec fast–fast coincidence system using a ^{22}Na spot source at 22 ± 1°C. Theories and details of PALS can be found elsewhere [13,21]. In the context of this work, the two main parameters of interest are τ_3 (ns), the average lifetime for *ortho*-positronium (*o*-Ps) annihilation, and I_3 (%), the intensity of the τ_3 component (since there are a number of mechanisms leading to annihilation of the original incoming positrons [13,15]). τ_3 is related to the size or volume of the free volume cavities and I_3 to a combination of the number concentration of free volume cavities and the probability of *o*-Ps formation.

3. Results and discussion

Before discussing the correlation between molecular structure, miscibility and free volume based on the results summarized in Table 2, examples of a miscible blend system and an immiscible blend system, respectively, are presented. This will allow the tabulated summary to be better understood and interpreted.

Fig. 2 shows the tan δ spectra of the Vectra-B + Vectra-C blends by DMTA. Vectra-C is a copolyester of *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) (Fig. 1). The detailed compositions of Vectra-C have not been revealed by the supplier nor are available in the literature. By comparing its dielectric relaxation spectra with that of Vectra-A (which consists of 73 mol% HBA and 27 mol% HNA), it is clear that Vectra-C has a higher content of HBA [21]. Vectra-C is estimated to consist of 85 mol% of HBA by comparing its melting point (325°C) with the relationship of melting point of HBA/HNA TLCP and HBA composition [22]. HBA/HNA TLCPs with low

Table 2
Summary of miscibility compositional dependence of PALS free volume behaviour of various TLCP + TLCP blends (“ − “: negative deviation”, ±”: rule of mixture, “ + ”: positive deviation, three symbols: 25, 50 and 75% of the second component, five symbols: 20, 40, 50, 60, and 80% of Vectra-A)

	Blend pairs	τ_3	I_3
Miscible blends	Vectra-A + Vectra-C blends	− ± −	− − −
	Vectra-A + HIQ45 blends	− − +	− − ±
	Vectra-B + Vectra-C blends	± − −	− − −
	LC3000 + LC5000 blends	+ − +	− + −
Immiscible blends	Vectra-A + Vectra-B blends	± ± +	− ± ±
	Vectra-A + LC3000 blends	− − −	− − −
	Vectra-A + LC5000 blends	− − −	− − −
	Vectra-B + LC5000 blends	− − −	± + +
	HX2000 + Vectra-A	+ + + + +	− − − − −

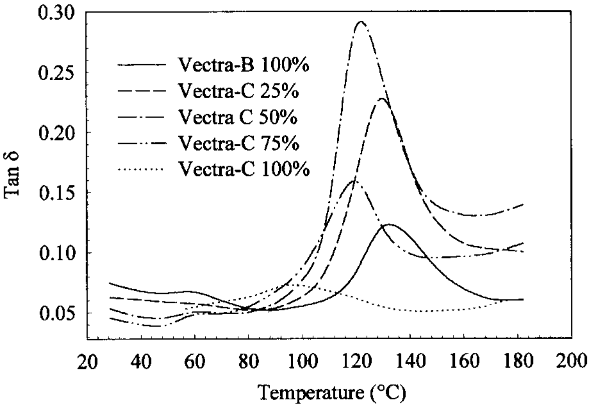


Fig. 2. Tan δ spectra of the Vectra-B + Vectra-C blends by RDAII at 1 Hz.

HNA contents generally have T_gs at about 100°C [19] and the T_g of Vectra-C is determined to be 98°C. Vectra-B is a terpolymer and polyesteramide which consists of 60 mol% HNA, 20 mol% terephthalic acid (TA) and 20 mol% aminophenol (AP) (Fig. 1). Vectra-B has a higher T_g of 130°C as it has been found that the existence of amide links in an ester environment can increase T_g of TLCPs. With the addition of Vectra-C, a single blend T_g shifts from the temperature location of Vectra-B towards that of Vectra-C, with the peak height being much greater than either Vectra-B or Vectra-C. No tan δ peak relating to the Vectra-C component can be observed in the blends and thus Vectra-B and Vectra-C appear to form a miscible blend, although not in a typical way. In thermoplastic blends which are miscible, the single T_g is generally found to move monotonically in temperature location between those of the neat constituents, as does the peak height. It has been reported that miscible TLCP + TLCP blends may show greater tan δ peak heights than their constituents [6], this being ascribed to changes in LC alignment of the blends compared with that of the neat components.

When blending polyesters, the possibility of transesterification has to be taken into account. Although such reaction commonly occurs for flexible polyesters, the literature to date supports the fact that transesterification is absent or negligible for blends containing only thermotropic polyesters [3,4]. A previous study regarding the effects of possible transesterification on behaviour of TLCP + TLCP blends shows that transesterification (if any) does not effect solid properties such as miscibility by DMTA and PALS, whilst blend properties in the molten state are different for blends with and without the addition of an inhibitor [23].

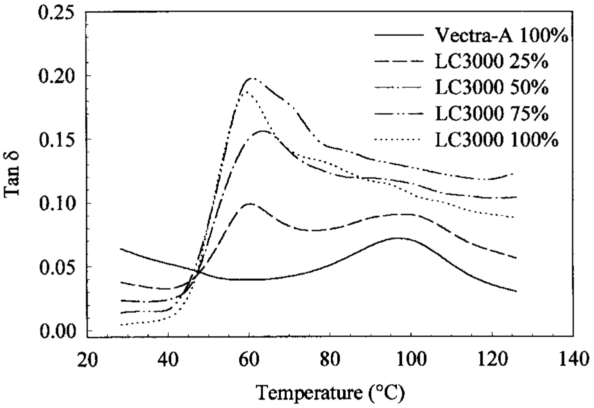


Fig. 3. Tan δ spectra of the Vectra-A + LC3000 blends by RDAII at 1 Hz.

Conversely, Fig. 3 depicts tan δ spectra of the immiscible blends of Vectra-A and LC3000. Both polymers have a common monomer, HBA, of which Vectra-A has 73 mol% and LC3000 has 60 mol%, as shown in Fig. 1. Vectra-A is a rigid-chain TLCPs because its comonomer is the aromatic HNA, whilst LC3000 is a semi-flexible TLCP since it incorporates the flexible PET moiety. T_g of Vectra-A is measured to be around 100°C and LC3000 has a T_g of 58°C. In the case of LC3000 which was found to phase separate into PET-rich and HBA-rich phases, the liquid crystalline HBA-rich phase is considered to be dispersed in the matrix of PET-rich phase [24]. The T_g found in LC3000 is attributed to its PET phase (the HBA phase T_g is never seen as clearly [24]). With the addition of 25% LC3000, the blend shows distinct tan δ peaks of both components. The intensity of the LC3000 T_g peak increases in strength with the addition of LC3000, changing little in location. It becomes even greater in height than that of neat LC3000 at, for example, the 75% LC3000 content. By contrast, the weak tan δ peak of Vectra-A is gradually diluted with the addition of LC3000, becoming undetectable at 75% LC3000 content. The T_gs of the blends relating to the LC3000 component did move slightly towards T_g of neat Vectra-A when the Vectra-A content is not greater than 50%, indicating possible partial miscibility in the LC3000-rich phase even though they are largely immiscible. This partial miscibility is likely due to chemical similarity of these two TLCPs (both contain a large amount of HBA) rather than molecular conformation (Vectra-A and LC3000 have different molecular rigidities). Lin and Winter [5] studied a similar blend system (Vectra-A and Eastman PET/60PHB) and the occurrence of gross phase separation within blends was confirmed from the appearance of the endothermic peaks of the individual components in the cooling DSC thermograms. The heat of crystallization of each component was in proportion to the concentration of the blend, as expected if there is little miscibility, or even interaction, between each component [5].

Table 1 summarizes the miscibility of the TLCP + TLCP blends studied in this work, derived mainly from DMTA results. All TLCPs studied are the nematic type, but miscibility of their blends ranges from miscible and partially miscible to immiscible. To simplify the terminology and allow ease of comparison, either “miscible” or “immiscible” will be assigned to describe the blend miscibility hereafter. However, some blends labelled immiscible in fact demonstrate more complicated behaviour [21].

Instead of following miscibility rules derived from

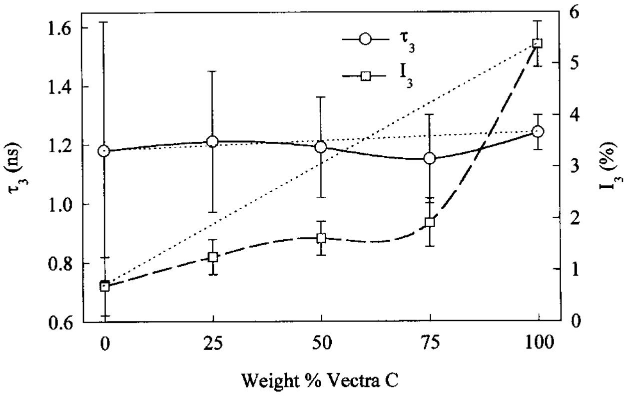


Fig. 4. PALS free volume parameters (τ_3 and I_3) of the Vectra-B + Vectra-C blends.

LMWLCs where the same type of mesophase generally ensures miscibility, miscibility between TLCPs predominantly relies on their macromolecular aspects, i.e. molecular chemistry and molecular conformation. TLCPs with the same comonomers but different composition ratios were found to be miscible, such as Vectra-A + Vectra-C blends and LC3000 + LC5000 blends, due to the similarity in both molecular chemistry and chain packing. Blends of rigid TLCPs and semi-flexible TLCPs are largely immiscible, for instance, Vectra-A + LC3000 blends, and Vectra-B + LC5000 blends. Semi-flexible TLCPs with higher rigid moiety content show better miscibility with rigid TLCPs, such as the better miscibility observed in Vectra-A + LC5000 blends than in Vectra-A + LC3000 blends [21]. The miscible behaviour observed in Vectra-A + HIQ45 blends may be a result of both chemical similarity (each contains a large proportion of HBA) and the loosely packed nature of HIQ45 molecules which allows the Vectra-A component to be readily incorporated within it. By contrast, more poorly packed HX2000 only has limited miscibility with Vectra-A, most likely due to their chemical dissimilarity (they do not contain a significant amount of a common comonomer). It is thus clear that similarity in comonomer units and similarity in rigidity (and a mixture of both) determines miscibility of these nematic materials.

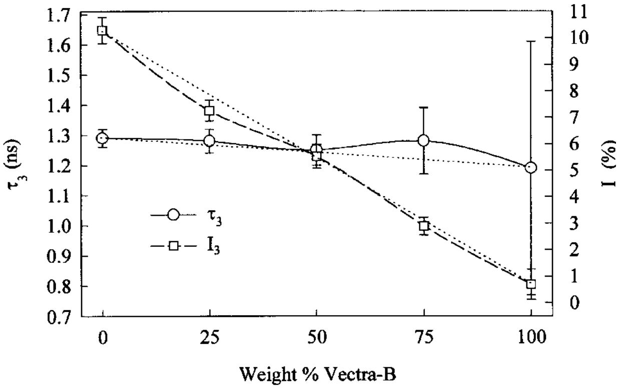


Fig. 5. PALS free volume parameters (τ_3 and I_3) of the Vectra-A + LC3000 blends.

Fig. 4 shows PALS parameters (τ_3 and I_3) of the miscible Vectra-B + Vectra-C blends as a function of Vectra-C concentration. As mentioned previously, τ_3 is a measure of the size of free volume site (the greater τ_3, the larger size) in polymers. Rigid TLCPs, Vectra-B and Vectra-C have very similar values of τ_3. The τ_3 value of the 25% Vectra-C blend is almost equivalent to the weighted average, whilst the 50 and 75% Vectra-C blends have τ_3 values smaller than additivity. A negative deviation in the plot of τ_3 versus blend composition is often observed in miscible TP + TP blends due to chain affinity and thus closer packing in such blends [13]. I_3 is indicative of the number concentration of free volume sites in polymers (the higher I_3, the greater concentration of free volume sites). I_3 results for the blends show a distinct, negative deviation. Although these results correlate well with the fact that Vectra-B + Vectra-C blends are miscible, some other aspects are worth considering. For blends containing polymers which are able to inhibit or quench *o*-Ps (such as Vectra-B due to its amide group), free volume behaviour of the blends probed by *o*-Ps relies not only on physical aspects such as chain packing. Chemical aspects of the blends play an important role in determining formation and annihilation of *o*-Ps and thus free volume probed by *o*-Ps. I_3 values of the blends are rather closer to that of pure Vectra-B, clearly indicating that inhibition to *o*-Ps formation is strongly influenced by the Vectra-B component. This is especially in this miscible blend system as the *o*-Ps inhibiting component will be more finely distributed throughout the blend in a miscible, rather than immiscible blend system.

Fig. 5 shows PALS parameters (τ_3 and I_3) of Vectra-A + LC3000 blends as a function of LC3000 concentration. This blend system was confirmed to be immiscible by DMTA (Fig. 3). However, both τ_3 and I_3 results display negative deviation from the ROM (rule of mixture) behaviour. This indicates that the size and number density of free volume cavities sampled by *o*-Ps, of the Vectra-A + LC3000 blends do not increase, despite the immiscibility. In TP + TP blends, immiscible systems have been shown to exhibit a positive deviation of free volume size from ROM due to larger free volume cavities formed at the interface [17]. The immiscibility between Vectra-A and the PET-rich region of LC3000 might create voids too large to be detected by *o*-Ps, supported by the observation of a less-than-average density for these blends [21]. The chemical affinity between Vectra-A and the HBA-rich regions of LC3000 due to the similarity in the molecular chemistry may lead to the negative deviations found in τ_3 and I_3.

Table 1 also summarizes free volume behaviour of the TLCP + TLCP blends determined by PALS. Other than the LC3000 + LC5000 blends and the 75% HIQ45 blend, miscible TLCP + TLCP blends predominantly show negative deviations from ROM or the weighted averages of τ_3, as generally found for miscible TP + TP blends [13,16–18].

Compositional dependence of blend I_3 has not been found to show any clear trend for either miscible or immiscible blends from PALS studies on polymer blends to date. In this work, negative deviations seem to be a dominant feature for miscible TLCP + TLCP blends, with the only exception being the 50% LC5000 blend in the LC3000 + LC5000 system. In fact, compositional dependence of PALS free volume parameters, including both τ_3 and I_3, of most of the TLCP + TLCP blends studied in this work shows either a negative deviation from ROM or at least weighted average behaviour. This suggests that even though some TLCP + TLCP blends demonstrate two-phase behaviour using macroscopic characterization such as DMTA, TLCPs possessing the same mesophase may have sufficient intrinsic molecular affinity to result in blends of smaller and/or less free volume sites. However, this affinity does not necessarily result in the complete miscibility, as for their low MW counterparts. The intrinsic affinity of LC materials of the same mesophase may counteract the immiscible nature of different macromolecules. This leads to better molecular packing in the blends containing two TLCPs, regardless of the miscibility.

4. Conclusions

Miscibility behaviour of TLCP + TLCP blends was examined over a number of blend systems containing nematic TLCPs. Although LMWLCs of the same mesophasic class often show miscibility, TLCPs forming the same mesophase (usually nematic) do not necessarily exhibit complete miscibility. TLCPs with few comonomers and/or with very different rigidities are generally found to be immiscible. Miscibility behaviour of the TLCP + TLCP blends studied in this work indicates that polymeric aspects such as molecular chemistry and molecular packing are more decisive than the mesophasic aspects (i.e. the fact that both constituents are nematic). It is found that, for miscibility to occur, both components should be of similar molecular rigidity (rigid or semi-flexible) and preferably contain some common comonomer(s).

In this work, free volume behaviour of the most extensive range of TLCP + TLCP blends produced to date was also studied using PALS. In miscible TP + TP blends, free volume cavities of the blends have been reported to be smaller than or equal to the weighted average of the components due to better packing of the molecules. With few exceptions, it is found that the miscible TLCP + TLCP blends also generally show negative deviations in τ_3 from linear additivity of the pure components. Even fairly immiscible blends appear to pack well and have at least average behaviour (or a slightly negative deviation) with regards τ_3. Compositional dependence of I_3 of the miscible TLCP + TLCP blends also mostly exhibits negative deviations, not always observed in the TP + TP blends. Although the miscibility criteria drawn from LMWLCs are not necessarily obeyed by TLCPs, TLCPs possessing the same mesophase may have some intrinsic molecular affinity, which need not lead to complete miscibility. Since the TLCPs used were all commercial or semi-commercial products and tend to be nematic, the effect of the type of TLCP phase could theoretically be an issue but cannot be readily tested here.

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