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On the miscibility of liquid crystalline polymers

H. Hakemi

Snia Research, SNIA S.p.A. Group Via Borgonuovo 14, 20121 Milan, Italy

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Abstract

We report on the feasibility of the thermodynamic miscibility of liquid crystalline polymers (LCPs) and their use as a new material approach for the reinforcement of engineering thermoplastics (TPs). In this work, we present the preliminary results of the study on binary model systems consisting of both a wholly aromatic and an aromatic–aliphatic miscible LCP blend. The ultimate goal of this approach is to develop multi-component miscible LCP blends having TP-compatible components which could be useful as processing-aids and reinforcement of TP composites. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Although the technology and engineering of LCP-reinforced thermoplastics (TPs) have been rather well developed, [1–3] the knowledge of structure–property relations for optimization of the processing and prediction of the mechanical properties of LCP/TP composites are still far from complete. The scientific literature of LCP-reinforced TPs can be divided into two main categories; the mechanical approach [4–6] and the chemical approach [7–11]. While, the mechanical approach is based on direct mixing and blending of LCP with TP matrix, the chemical approach involves polymerization of LCP by either in situ molecular composites [7–9] or through the micro-composites methods [10,11]. However, the LCP-reinforced TP composites obtained by both these approaches suffer from a number of disadvantages. For example, the main drawback with the mechanical approach is the inherent thermodynamic incompatibility between the LCP and TP entities. This alone has been the major cause of uncertainty in the processing, and a limiting factor in the development of LCP-reinforced TPs. The chemical approaches, where the LCP moiety is either in situ polymerized (as graft, block or copolymer) with the matrix structure [7–9] or is solution polymerized in the matrix, [10,11] also suffer from other drawbacks, such as complex synthesis and lack of control of the LCP micro-domain orientations, which all result in an uncertainty in the reinforcement of the final composite.

Thus, a better understanding of thermodynamic compatibility and correlations between molecular and macroscopic parameters is an important issue for controlling and modifying the processing, morphology, order, dimensional stability, interfacial adhesion (interactions), as well as prediction of the mechanical properties of the LCP-reinforced TP composites.

The objective of the present work is to provide an alternative thermodynamic approach for the development of miscible LCP blends for processing-aids and reinforcement of the engineering TPs. In this respect, here we provide the preliminary results of our study on few TP-compatible and binary LCP blends as model systems, in order to substitute the conventional approach of utilizing single-component LCP [12] or immiscible binary LCP blends [13]. Basically, a thermodynamically miscible LCP blend would consist of, at least, a main reinforcing wholly aromatic or aliphatic–aromatic LCP component—LCP1. Other components would consist of a miscible and modified form of LCP1, where at least a second miscible component—LCP2—would have a TP-compatible chemical structure. The structure of LCP2 would consist of the residual functional groups that are molecularly similar to the TP matrix. The degree of compatibility between TP-compatible LCP and TP matrix itself can be optimized at the molecular level, preferably through random copolymerization. The main difference with the conventional (mechanical and chemical) approaches is that, the thermodynamic approach would consist of the intentionally miscible (binary or multi-component) LCP components, where their reinforcing wholly aromatic regime would also provide a pre-determined chemical compatibility, as well as the low processing temperature and viscosity. Intuitively, these criteria should also result in an enhanced interfacial adhesion through the TP-compatible aliphatic moieties and, consequently, improvement

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in the mechanical properties of the final (LCP)/TP composite system.

In view of the previous extensive studies on LCP/TP blends, as well as some recent attempts to utilize binary blends of wholly aromatic and semi-flexible LCPs, [1–3] no attempts have yet been made to utilize the thermodynamical blends of LCPs for TP reinforcement. Among the existing literature data on the thermodynamic compatibility of LCPs, we have already reported on the miscibility, eutectic behavior and extended mesomorphism in some binary homopolymer main-chain LCP mixtures [14]. We have also discovered the "induced" nematic phase in thermodynamically miscible main-chain/side-chain smectic copolymers, [15–17] and showed the effect of the network structure on reinforcement of their composites in TP matrix [18]. The enhancement of the mechanical properties has also been reported in the molecular composites, such as the rigid-rod polyimides and polyether–imide systems, due to the similarity of the imide structure in both LCP and TP moieties [19]. The available literature on the mechanical mixing of binary LCP blends, having both wholly aromatic and aliphtic–aromatic moieties, have shown either miscibility and matrix compatibility [20–23] or complete immiscibility and phase separation of the components [24,25]. The concept of thermodynamic miscibility has also been recently extended to study the homogeneous reinforcement of a low molecular weight LC with a nematic LCP [26].

Consequently, the main premises of the miscible LCP blends lies, at least, on the following criteria: (a) the enhancement of mesomorphic range and control of the crystal structure in eutectic LCP with respect to those of single-component LCPs; (b) the reduction of processing temperature and viscosity of the LCP/TP composites; (c) the enhancement and control of compatibility between LCP filler and TP matrix; and (d) the improvement of the interfacial adhesion and mechanical properties of the LCP/TP composites.

From this background, it should be clear that the selection of a proper TP-compatible LCP (random or block) copolymer and their miscible blends, would depend, at least, on the nature and chemical structure of LCP and TP components. Due to the potential thermodynamic miscibility of the properly selected LCP blends, their phase diagrams are expected to exhibit a "eutectic-type" behavior, indicating the lowest transition temperature, the widest mesomorphic range, the highest TP-compatibility and enhanced mechanical properties. These properties are expected to be improved over those in the conventional single-component or incompatible binary LCP systems.

In the present report, we provide the preliminary results of our study on the miscibility of a few binary LCP/LCP model systems, including the phase diagrams, thermal properties and optical microscopy. In the future, this study will be extended to the investigation of the multi-component LCP mixtures and their composites with TP matrix.

2. Experimental

2.1. Materials

The utilized LCP materials were all nematogenic copolymers consisting of two commercial wholly aromatic and three synthesized aromatic–aliphatic copolyesters and copolyester–amides.

The commercial nematic LCPs were Hoechst-Celanese copolyester Vectra-A950 (VA)) and copolyester–amide Vectra-B950 (VB), which contain the following functional groups

LCP	$-(-O-C_{10}H_6-CO-)-$ (HNA, %)	$-(-O-C_6H_4-CO-)-$ (HBA, %)	$-(-OC-C_6H_4-CO-)-$ (TA, %)	$-(-O-C_6H_4-NH-)-$ (AP, %)
Vectra-A950	30	70	–	–
Vectra-B950	50	–	30	20

VA was a copolyester consisting of 30% 2,6-dihydroxy-naphthoate (HNA) and 70% *para*-hydroxy-benzoate (HBA) mole ratio, whereas VB copolyesteramide contained a mole ratio of 50% HNA, 30% terephthalate (TA) and 20% *para*-amino-phenol (AP) moieties in its repeat units. The presence of the N–H group (from AP) and an extra C=O moiety (from TA) enhances the H-bonding tendencies in VB, which should increase its compatibility with polyamide and polyester-amide based engineering TPs.

The synthesized LCP model systems were the semi-flexible liquid crystal copolyester SBH (LCP1) [27] and its copolyester–amides BC124 and BC128 (LCP2), having the following chemical structure

LCP	$-(-O-C_6H_4-C_6H_4-O-)-$ (DBP, %)	$-(-OC-(CH2)_8-CO-)-$ (SA, %)	$-(-O-C_6H_4-CO-)-$ (HBA, %)	$-(-O-C_6H_4-NH-)-$ (AP, %)
SBH	25	25	50	0
BC124	23.75	25	50	1.25
BC128	25	25	43	7

SBH copolyester contained 25% *para*-dihydroxy-biphenyl (DBP), 25% sebasic acid (SA) and 50% *para*-hydroxy-bezophenoate (HBA) moieties with 25:25:50% mole ratio. BC124 copolyester-amide had chemical structure similar to SBH, where only 1.25% AP moiety was substituted at the expense of DBP. Instead, in BC128 copolyester–amide 7% AP was substituted for the HBA moiety. The thermal behavior of these polymers and their miscible blends are tabulated in Table 2. The details of the synthetic procedures of these polymers have been mentioned elsewhere [28–30].

2.2. Mixing and measurements

The transition temperatures of all the LCPs and the phase diagrams of LCP1/LCP2 blends were studied with both differential scanning calorimetry (DSC) and optical microscopy (OM) methods. The binary blending was carried out

Table 1
Thermal properties of Vectra-A/Vectra-B blends from DSC measurements (heating rate = 20°C/min; cooling rate = 5°C/min)

VA/VB, VB (wt%)	Crystal–nematic (°C)		Glass transition (°C)	
	T_{CN} (heating)	T_{NC} (cooling)	Heating	Cooling
0	286	230	136	127
25	262	215	136	127
28	259	213	135	125
47	257	211	134	125
75	252	205	136	127
100	273	215	136	126

in a DSC pan by direct weighing and mixing of the components through repeated heating and cooling cycles (usually 3–4 times) with rates of 20°/min, until no further changes were observed in the transition temperatures of the mixture. After the completion of DSC measurements, the same mixtures were used for the corresponding OM studies.

The DSC studies were carried out on 10–20 mg samples utilizing a Perkin–Elmer DSC-7 instrument. The OM investigations were done using a Leitz–Wetzaler polarizing Microscope equipped with a Linkam THM600 hot-stage and TMS90 temperature control unit. All OM studies in heating and cooling modes were carried out within the range of 5–80°/min rate under a nitrogen atmosphere.

3. Results and discussions

3.1. Vectra-A/vectra-B blends

In Table 1, we tabulated the glass transitions (T_g), the crystal-nematic (T_{CN}) and nematic-crystal (T_{NC}) transition temperatures of VA, VB and their blends within the whole concentration range of their phase diagram. From these data it is noted that the T_g of both components and their blends are almost identical and constant. However, the T_{CN} (or T_{NC}) transition of VB is 13°C (or 15°C) lower than that of VA. Evidently, this difference is the result of reduction in the crystalline structure of more random copolymer VB due to the presence of 20% AP in its repeat unit. The thermodynamic miscibility and indirect evidence of eutectic-type behavior through SEM, glass transition and heat of recrystallization studies, has also been reported for binary LCP blends of poly(HBA/HNA/TA/HQ) (Vectra/RD-501) and poly(ET/HBA) (Rodrun) blends [31]. The XRD spectra of these polymers (not reported here) demonstrate not only the similarity in the crystalline structures of VA and VB, but also a relatively broader crystalline diffraction peak and a more intense amorphous peak of the latter.

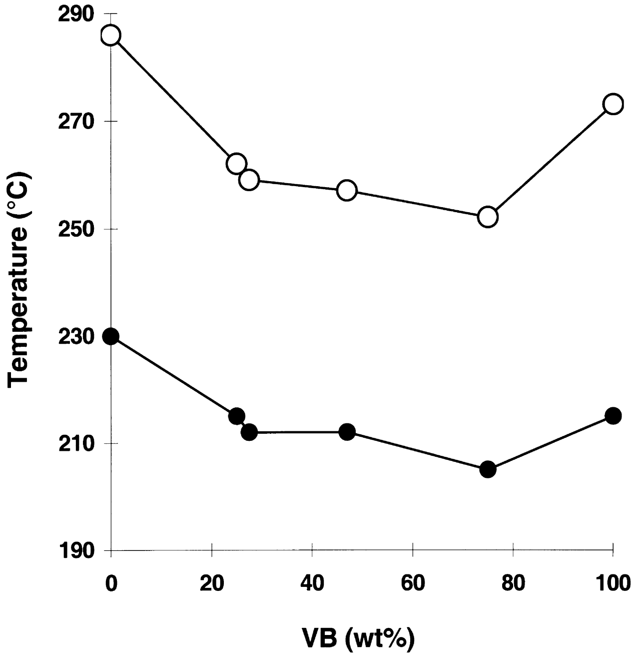

Fig. 1. Crystal–nematic transition temperatures of Vectra-A/Vectra-B blends on heating (open circles) and cooling (filled circles) modes.

In Fig. 1, we show the crystal-to-nematic transitions of VA, VB and their blends within the whole phase diagram in heating (T_{CN}) and cooling (T_{NC}) modes. The data indicate that VA and VB are miscible at all concentrations. At the concentration range of about 75% VB, the blend shows a eutectic-type behavior, exhibiting the lowest transition temperature in the phase diagram. The transition temperature of this mixture on cooling ($T_{NC} = 205$°C) and on heating ($T_{CN} = 252$°C) are about 10 and 30°C lower than those of pure VB and VA, respectively. Clearly, as this miscible VA/VB blend provides the lowest processing temperature with respect to either single components, it should be a more appropriate LCP system as both processing-aid and TP compatibilizer than either VA or VB. In addition, the presence of a residual quantity of AP moiety in this eutectic-type mixture, is expected to further enhance the interfacial adhesion between the LCP filler and TP matrix.

3.2. SBH/BC124 blends

The transition temperatures of SBH/BC124 binary blends are tabulated in Table 2. Whereas the crystal-to-nematic transitions at both heating (T_{CN}) and cooling (T_{NC}) are obtained by DSC, the nematic–isotropic (T_{NI}) transitions are measured by OM method. Owing to the rapid degradation of these polymers at higher temperatures, their T_{NI}

Table 2
Thermal properties of SBH/BC124 and SBH/BC128 blends from DSC and OM measurements. Scanning rates are 5–20°C/min (crystal–nematic) and 80°C/min (nematic–isotropic)

	Crystal–nematic (°C)		Nematic–isotropic (°C)	
	T_{CN} (heating)	T_{NC} (cooling)	T_{NI} (heating)	T_{IN} (cooling)
SBH/BC124, BC124 (wt%)				
0	227	194	410	–
11.5	201	193	400	–
30	195	185	390	–
52.5	219	196	380	–
74	225	200	360	–
100	230	203	333	–
SBH/BC128, BC128 (wt%)				
0	227	194	410	–
16	194	183	–	–
25.5	200	185	–	–
45.5	204	188	–	–
52	206	189	–	–
66	208	195	–	–
81	214	205	–	–
100	249	230	–	–

could be measured only by OM at a fast heating rate of 80°/min. This transition could not be assessed properly even with OM for either SBH or the SBH-rich portion of the phase diagram.

In BC124 copolyester-amide, substitution of 1.25% of longer DBP rigid moiety with shorter AP moiety resulted in two opposite effects. The first effect is a strong destabilization of the nematic phase through the lowering of the T_{NI} (i.e. from >400°C for SBH to 333°C for BC124). The second effect is a moderate stabilization of the crystalline structure of BC124, which is manifested by its higher T_{CN} transition (230°C) with respect to that of SBH (227°C). The XRD spectra of BC124 (not reported here) indicate that this copolymer has a similar crystalline structure and relatively higher degree of crystallinity compared to that of SBH. We do not exclude the possibility that this may be due to the low molecular weight of BC124.

The textural analysis of the SBH/BC124 blends with optical microscopy has indicated complete mesomorphic miscibility. The trend and behavior of T_{NI} of the SBH/BC124 blends is a further support of complete miscibility of these polymers in their nematic phase.

The overall phase diagram of SBH/BC124 blends are shown in Fig. 2. The important observation from the phase diagram in Fig. 2a is the complete miscibility of the components in the nematic phase—which is observed from the linear trend of the T_{NI} transition—and the occurrence of a eutectic-type (or solid solution) behavior (Fig. 2b) of T_{CN} transition in the SBH-rich region of the phase diagram (i.e. 20–30% BC124). At the eutectic composition, the T_{NC} transition (cooling curve) is about 10 and 20°C lower than those of pure SBH and BC124, respectively. This effect is much more stronger in the heating curve, where the T_{CN} of this

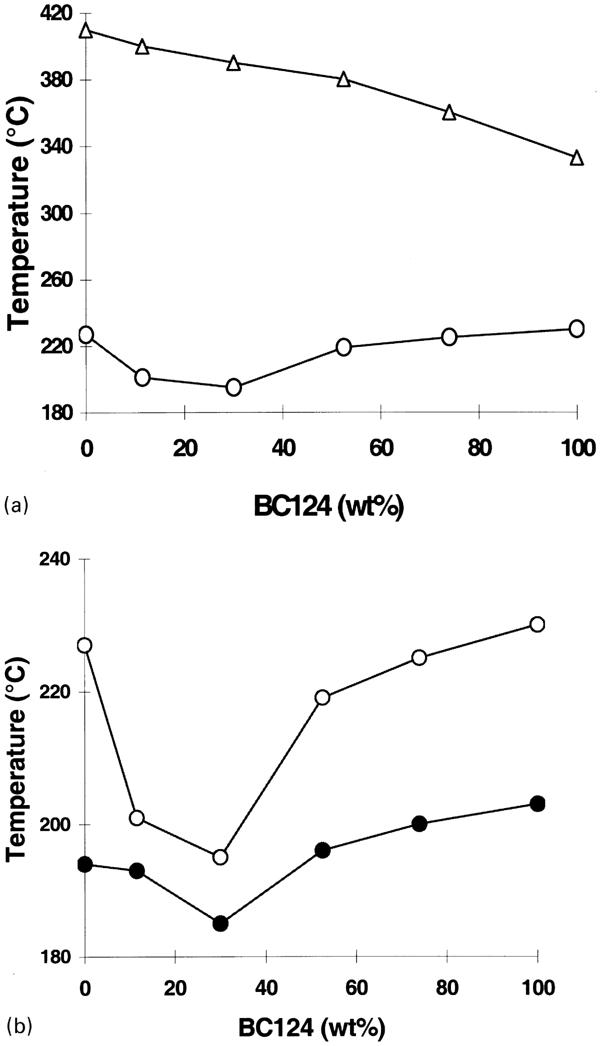

Fig. 2. Transition temperatures of SBH/BC124 blends: (a) crystal–nematic (open circles) and nematic–isotropic (open triangle) transitions on heating mode; and (b) crystal–nematic transition on heating (open circles) and cooling (filled circles) modes.

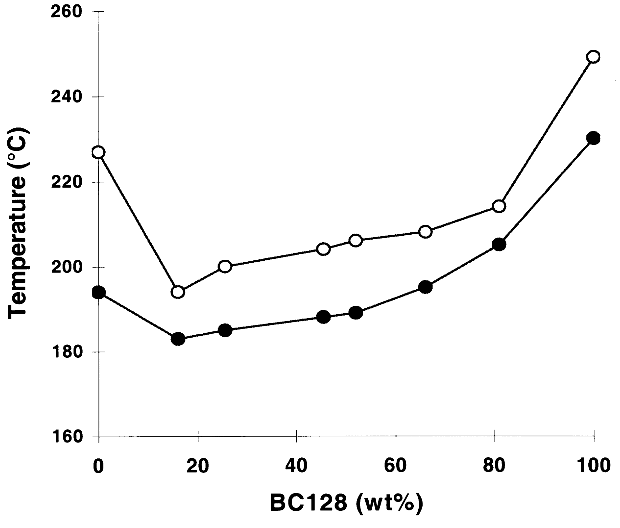

Fig. 3. Crystal–nematic transition temperatures of SBH/BC128 blends on heating (open circles) and cooling (filled circles) modes.

eutectic point is lowered by as much as 22°C (relative to SBH) and 35°C (with respect to BC124).

Further, the data of Table 2 and Fig. 3 indicate that, whereas the crystalline structures of SBH and BC124 are similar, they are relatively more stable in BC124, probably due to the presence of the small quantity (1.25%) of AP moiety in its repeat unit. But the existence of AP moiety in BC124 copolyester–amide resulted in a strong reduction of its nematic stability, by as much as 100°C (with respect to that of SBH). This effect can be explained by a decrease in the overall chain rigidity of BC124 relative to SBH due to the substitution of DBP by a shorter AP moiety and a more random copolymer nature of the former.

3.3. SBH/BC128 blends

In the third binary SBH/BC128 mixture, BC128 is also a nematogenic copolyester–amide, having a higher mesomorphic stability than BC124. The higher mesophase and crystalline order of BC128 are clearly attributed to the presence of higher content (7.5%) of AP group. However, the presence of larger quantity of AP does not affect the rigidity of this copolymer backbone as much as it promotes the H-bonding effect. Consequently, the larger content of H-bonding promoter AP moiety seems to be responsible for the inaccessible T_{NI} transitions of BC128, as well as for the stability of its crystalline structure in the blends. The crystalline structure of BC128 from its XRD spectra (not shown here) also indicates that like BC124, this copolyester–amide has a similar crystalline structure and relatively higher degree of crystallinity compared to that of SBH.

The SBH/BC128 blends were prepared in the same manner as those in the SBH/BC124 system. The thermal transition data of these blends are also tabulated in Table 2. As the T_{NI} of BC128 and SBH/BC128 blends are above their degradation temperatures, we were not able to measure them with either the DSC or the OM method, even at heating rates higher than 80°C/min. In Fig. 3, we plotted the crystal–nematic transitions of SBH/BC128 blends at both heating and cooling modes. From Fig. 3, it is also evident that the SBH-rich portion of the phase diagram, namely at the concentration range of 10–30% BC128, the miscible blends exhibit a eutectic-like behavior. This behavior is observed in both heating and cooling modes and exhibits 10°C (T_{NC}) to 30°C (T_{CN}) depressions with respect to those of single components. As the substitution of HBA moiety of SBH by 7.5% of AP should not affect the overall rigidity of the BC128 copolymer chain, this eutectic-type blend is also expected to be useful as a processing-aid, self-reinforcing LCP and TP-compatible system in composites with engineering TPs.

4. Conclusion

The phase behavior and miscibility of the three studied binary LCP blends are qualitatively similar. From the thermal behavior and phase diagrams of these copolyester/copolyester–amide blends, we deduce that all three binary systems are thermodynamically miscible and exhibit a eutectic-like behavior with the lowest transition temperature at certain interim composition. The miscibility of these binary LCP blends was confirmed by thermal and optical studies. The overall results suggest, a eutectic-type LCP blend to be a more useful system than the single-component LCP as processing-aid, TP-compatibilizer and TP-reinforcement but the extent of its effect need to be established experimentally.

Obviously, not only the processing temperatures of such miscible blends are lowest at certain interim composition, but also due to the presence of residual TP-compatible and H-bonding promoter moieties, they may provide a further means of controlling their molecular compatibilities with the corresponding engineering TPs. Namely, instead of a single-component LCP, by selecting a TP-compatible thermodynamic LCP blend, not only the processing temperatures, but also the interfacial adhesion and mechanical properties of their composites with TPs could be improved and better controlled.

The validity of the present approach, which is beyond the scope of this study, would require a further experimental verification. This will require a systematic development of multi-components LCP blends, their processing with TP matrices and determining the processing and mechanical properties of their composites. Once the correlations between their chemical structure, thermodynamic compatibility, rheology, morphology and mechanical properties in the binary LCP/TP composite are established, the investigations could be extended to a wider range of multi-component LCP blends and engineering TP systems.

References

[1] Carfagna C, editor. Liquid crystalline polymers. Oxford: Pergamon, 1993.

[2] La Mantia FP, editor. Thermotropic liquid crystal polymer blends. Lancaster: Technomic, 1995.

[3] Isayev AI, Kyu T, Cheng SZD, editors. Liquid-Crystalline Polymer Systems ACS Symposium Series. Washington, DC: American Chemical Society, 1996.

[4] Cogswell FN et al. US4,386,174 (1981).

[5] Cogswell FN et al. US4,438,236 (1984).

[6] Froix MF. US4,460,735 (1984).

[7] Tagayanagi M, et al. J Macromol Sci, Phys B 1980;17:591.

[8] Helminak IE et al. US4,207,407 (1980)

[9] Hwang WF, et al. J Macromol Sci, Phys B 1983;22:231.

[10] Ogata N, Sanui K, Itaya H. Polym J 1990;22:85.

[11] Kamitani K, Watanabe M, Sanui K, Ogata N. J Polym Sci, Polym Chem Ed 1993;31:597.

[12] Magagnini PL. In: La Mantia FP, editor. Thermotropic liquid crystal polymer blends. Lancaster: Technomic, 1995 chap. 1.

[13] Isayev AI. In: Isayev AI, Kyu T, Cheng SZD, editors. Liquid-crystalline polymer systems, ACS Symposium Series. Washington, DC: American Chemical Society, 1996 chap. 1.

[14] Krigbaum WR, Hakemi H, Kotek R. Macromolecules 1985;18:965.

[15] Hakemi H, Rasoul HAA. Polym Commun 1990;31:82.

[16] Hakemi H, Rasoul HAA, Stackman RW. US4,842,754 (1989).
[17] Hakemi H, Rasoul HAA, Stackman RW. US4,952,334 (1990).
[18] Cheng WM, Rasoul HAA, Stackman RW. Polym Reprints 1991; 32:50.
[19] Fukai A, Yang JC, Kyu T, Cheng SZD, Hsu SLC, Harris FW. Polymer 1999;33:3621.
[20] DeMeuse, MT, Jaffe M. Mol Cryst Liq Cryst Inc Nonlin Optics 1988;157:535.
[21] DeMeuse MT, Jaffe M. Polym Prepr 1989;30:540.
[22] DeMeuse MT, Jaffe M. In: Weiss RA, Ober CK, editors. Liquid crystalline polymers, ACS Symposium Series 435Washington, DC: American Chemical Society, 1990.
[23] DeMeuseMT. SPE ANTEC’93, 1993. p. 1722.
[24] Lin YG, Winter HH. Polym Engng Sci 1992;32:773.
[25] Ding R, Isayev AI. SPE ANTEC’93, 1993. p. 1176.
[26] Krigbaum WR, Hakemi H, Ciferri A. Liq Cryst 1998.
[27] Maganini PL, Pedretti U, Perego G,Bresci B, Carrozzino S, Roggero A. US Patent 4,833,299 (1989).
[28] Magagnini PL, Bresci B, Paci M, Roggero A, Pedretti U, La Mantia FP. In: Saraf DN, Kunzru D, editors. Recent advances in chemical engineering, New York: McGraw-Hill, 1999.
[29] La Mantia FP, Valenza A, Paci M, Magagnini PL, Pedretti U, Roggero A. Polym Engng Sci 1992.
[30] Pedretti U, Bonfanti C, Hakemi H, Montani E, Roggero A. Proceedings of the twelfth International Liquid Crystal Conference, Freiburg, Germany, 1988.
[31] Stachowski, DiBenedetto AT. In: Isayev AI, Kyu T, Cheng SZD, editors. Liquid-crystalline polymer systems, ACS symposium series1996 chap. 5.