

FORMATION OF MESOPHASE MONO-DOMAINS AND MICRO-STRUCTURES IN THIN FILMS OF A SERIES OF COPOLYETHERS CONTAINING BOTH ODD-NUMBERED METHYLENE UNITS*

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Abstract The structural and morphological evolution of mono-domains in thin films has been investigated for a series of liquid crystalline (LC) copolyethers. The copolyethers studied were synthesized by the reaction of 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxyl-phenyl)propane (TPP) with 1,7-dibromoheptane and 1,11-undecane at different compositions (coTPPs-7/11). In contrast to the solution-cast thin films without annealing, which exhibit the isotropic homogeneous molecular orientation, mono-domains with a homeotropic alignment were found in coTPP-7/11(5/5) after the thin films were annealed in the high-temperature columnar phase (Φ). Similar to the nucleation process in polymer crystallization, transmission electron microscopic observations show that small mono-domains appear in the initial stage of annealing, where molecules form a uniaxial in-plane chain orientation. With increasing annealing time, the molecular orientation gradually became tilted with respect to the substrate surface, and finally, a uniaxial homeotropic molecular orientation was achieved after a prolonged annealing time. The lateral size of mono-domains was found to increase continuously with annealing time and grew into a circular shape, indicating an isotropic lateral growth scheme which implies a hexagonal molecular packing proved by the electron diffraction experiments.

Keywords Main-chain liquid crystalline polymer, Structure, Morphology

INTRODUCTION

Highly ordered smectic phases such as smectic F (S_F), smectic crystalline G (SC_G) and H (SC_H) phases have been reported for a series of main-chain liquid crystalline (LC) polyethers based on 1-(4-hydroxy-4'-biphenyl)-2-(4-hydroxylphenyl)-propane (TPP) and various numbers of methylene units. The phase structures and phase behaviors are different for these TPP homopolymers containing odd- and even-numbered methylene units^[1-3]. For example, the TPP ($n = 7$) exhibits the phase transition sequences of $f^{[2]}$:

$$\text{Glassy state} \leftrightarrow SC_G \leftrightarrow S_F \leftrightarrow N \leftrightarrow I$$

where as for the TPP ($n = 11$), a SC_H phase is added at low temperatures^[3]:

$$\text{Glassy state} \leftrightarrow SC_H \leftrightarrow SC_G \leftrightarrow S_F \leftrightarrow N \leftrightarrow I$$

The chain orientation in the S_F and SC_G phases of TPP ($n = 7$) possesses the molecular axis tilted approximately 14° and 16° from the fiber direction, respectively^[2]. In the case of ($n = 11$), this tilted angle

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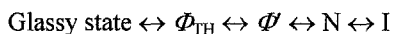
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becomes 7° in the S_F phase, but the molecular orientation becomes parallel to the fiber direction in the SC_G and SC_H phases^[2]. Their transition thermodynamic properties^[1-6], molecular dynamics in different phases have also been investigated^[7].

Recently, TPP copolyethers (coTPPs- n/m) with an equal comonomer molar ratio of various odd-numbers ($n = 5, 7, 9, 11$) and a fixed even-number of methylene units ($m = 12$) have been studied^[8]. The SC_G phase with a three-dimensionally ordered structure has been found in coTPP-11/12. When the mismatch of numbers of the methylene units increases, the smectic phases are suppressed and a hexagonal columnar phase (Φ_H) with a two-dimensional lateral order appears in coTPPs-5/12 and -7/12. A S_F to Φ_H phase transition is observed in coTPP-9/12^[8] when the temperature increases. We have also reported a series of coTPPs-7/12 with different comonomer compositions, where the highly ordered smectic, Φ_H , and tilted hexagonal columnar (Φ_{TH}) phases were composition dependent^[9]. The chain orientation is tilted with respect to the hexagonal normal in a Φ_{TH} phase.

In the bulk samples of coTPPs-7/11, the low-temperature phase can be identified as a Φ_{TH} phase with multiple tilt angles between the molecular axes and the normal of the hexagonal lattice. However, the lateral lattice dimensions with various tilt angles were identical^[10]. During heating, this Φ_{TH} phase transforms to another columnar (Φ) phase, accompanied by discontinuous changes in both lateral dimensions and tilt angles. Further heating of the samples leads to transitions from the Φ to the N phase, and from the N phase to the isotropic melt^[10]. For the samples of coTPPs-7/11, disregarding the composition change, their transition sequence is:

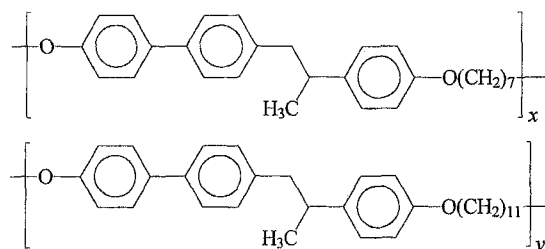


The surface-induced structural ordering has been studied on the thin films of homopolymers^[11, 12]. Highly ordered mono-domains and a metastable phase with orthorhombic chain packing were surface-induced and stabilized. The morphology and the ordering evolution of mono-domains in homopolymers were found to be related to the structural symmetry, temperature, component, and molecular mobility. Since copolymers possess lower structural symmetry and higher molecular mobility, their formation and ordering of mono-domains may differ from that of the homopolymers. The structural evolution and molecular orientation of mono-domains of the coTPPs-7/11 were studied in this work.

EXPERIMENTAL

Materials

The syntheses of coTPPs-7/11 involve the random copolymerization of TPP mesogen with 1,7-dibromoheptane and 1,11-dibromoundecane. The detailed synthetic procedure was described in an earlier publication^[13]. Their number-average molecular weights ranged between 20,000 to 30,000 g/mol based on GPC measurements with polystyrene standards. The chemical structure of the copolymer is:



The compositions (x/y) of the coTPPs-7/11 varied from 1/9 to 9/1. The samples were kindly supplied by Prof. V. Percec at Case Western Reserve University.

CoTPPs-7/11 thin films were cast from a 0.1% (W/W) coTPPs-7/11/chlorobenzene solution on an amorphous carbon-coated surface. After the solvent was evaporated in vacuum for 24 h, the resulting thin films had a thickness ranging from 50 to 100 nm. These films were annealed for the structure and chain orientation determinations.

Characterization

The dried samples were heated to different LC phases, followed by isothermal annealing under a nitrogen atmosphere for 15 h before being cooled slowly to room temperature. On the other hand, different annealing times were also used. Transmission electron microscopy (TEM) was performed with a JEOL 2010 instrument at an accelerating voltage of 200 kV. The films were shadowed with Pt and gold and were used for the spacing calibration of the electron diffraction (ED).

Fiber WAXD patterns were obtained using an 18 kW rotating anode X-ray generator with an imaging plate (Rigaku automated imaging system with 3000×3000 pixel resolution). Calibration was conducted using silicon powder and silver behenate. Fibers were prepared by drawing the samples from the N phase. Samples were then heated and illuminated with a point-focusing X-ray beam. A typical exposure time for fiber samples was 30 min.

RESULTS AND DISCUSSION

Structures and Morphology of Mono-Domains

Three mesophases i.e., N, Φ' and Φ_{TH} phases, were identified in coTPPs-7/11 bulk samples as described previously. All the coTPPs-7/11 samples possess the same phase structure and transition sequence as shown in the phase diagram (Fig. 1). No copolymer composition dependence of the phase transition sequence was found^[10].

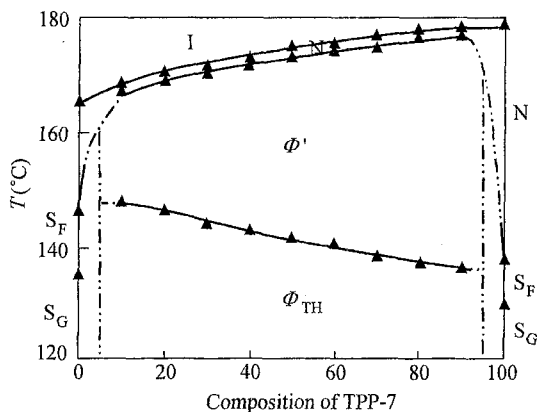


Fig. 1 Phase diagram of the coTPP-7/11 series

When the coTPPs-7/11(5/5) thin films were annealed at 153°C for 15 h in the Φ' phase, highly ordered mono-domains with single-crystal-like ED patterns can be obtained as shown in Fig. 2. The domains look like a circular shape (see Fig. 2a), reflecting a hexagonal symmetry where chain orientation is more or less perpendicular to the surface. The hexagonal ED pattern shown in Fig. 2(b) is close to the $[00l]$ zone, indicating a homeotropic chain alignment in mono-domains. The value of $a = b = 0.53$ nm can be calculated from the ED patterns and this is consistent with the WAXD experiments of the powder and fiber samples^[10].

Highly ordered mono-domains are formed in TPP ($n = 7$) thin films when they are annealed in or cooled down slowly from the N phase^[11]. No mono-domains could be formed in the smectic F or smectic crystal G phase since chain mobility would be restricted due to the solid-state-like characters of the highly ordered smectic phases. However, for TPP ($m = 12$), such mono-domains were observed when thin films were annealed in the S_F phase. The number of methylene units may be critically associated with molecular mobility to form mono-domains^[12]. Both the chemical structure of molecules as well as the phase structures and orders determine the molecular mobility and, thereby, the ability to form the mono-domains. This can also be proved by the sample annealed in the Φ_{TH} phase. The low chain mobility in this phase at low temperatures does not generate the ordered mono-domains.

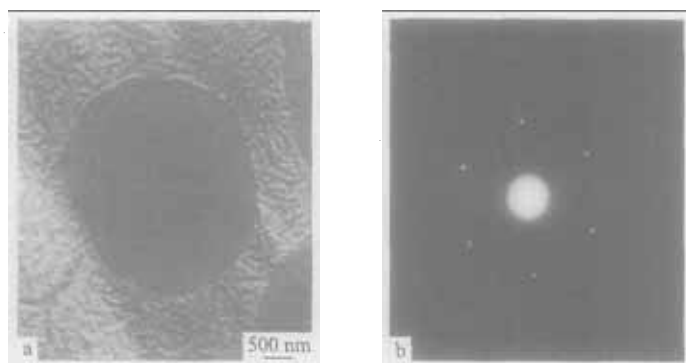


Fig. 2 TEM micrograph of coTPP-7/11(5/5) monodomains formed after annealing in the Φ phase for 15 h (a); and the corresponding ED pattern (b)

Formation of Mono-Domains and Molecular Reorientation

Figure 3 presents the WAXD fiber pattern of coTPP-7/11(5/5). Compared with the homoTPPs that exhibit highly ordered smectic phases, the sharp low-angle layer reflections do not appear but the multiple wide-angle reflections appear in the quadrants. These multiple WAXD spots are almost aligned on a pair of “lines” nearly parallel to the meridian direction. The structural analysis suggests a Φ_{TH} phase possessing various tilt angles based on the LC classification^[14–17].

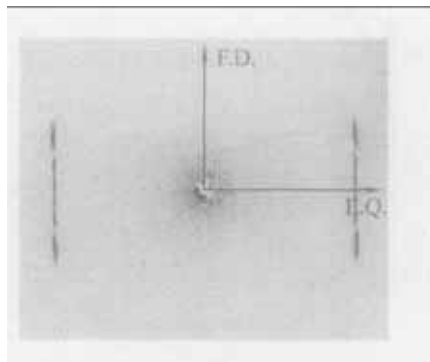


Fig. 3 Room temperature WAXD fiber pattern of coTPP-7/11(5/5)

The formation of mono-domains and their growth are illustrated in Fig. 4 for the coTPP-7/11(5/5) thin films annealed at 153 °C. The randomly distributed network morphology is observed with a ring ED pattern (see Fig. 4a). This indicates that the as-cast samples are poly-domains and the in-plane chain orientation is isotropic. Based on the optical principle, this type of chain orientation generates a uniaxial negative optical ellipsoid^[18]. At the early stage of annealing (10 min), the molecules start to self-aggregate as shown in Fig. 4(b). The ED pattern shows multiple diffraction spots and is similar to the WAXD fiber pattern of Fig. 3. In this case, chains are uniaxially and homogeneously aligned, where molecular axes are oriented parallel to the substrate surface.

The chain reorientation within the mono-domains can be more clearly observed in the ED patterns of Fig. 4(c) and 4(d). With increasing annealing time, mono-domains gradually transfer into tilted hexagonal phase as evidenced by the ED pattern with two sets of diffraction spots (Fig. 4c), which are attributed to the sets of (110) reflections of a hexagonal lateral packing. The d spacings of these reflections are consistent with the WAXD results. The chains may tilt along the direction parallel to the (110) plane, which leads to the extinction of (200) reflection. On the other hand, domains with different tilt angles will gradually align towards one direction, corresponding to a narrower distribution of tilt angles. This is proved by the (110) reflections in

Fig. 4(c) which become closer with increasing annealing time. The chain orientation therefore changes from the in-plane homeotropic to a tilted alignment. When the annealing time exceeds 5 h, three sets of ED spots are observed and the angles formed between the neighboring spots are approximately close to 60° (see Fig. 4d). This reveals a gradual change of a tilted to a normal hexagonal packing with chain orientation near to the homeotropic alignment. When thin films were annealed for 15 h, a completely homeotropic alignment of mono-domains was found, as shown in Fig. 2(b). This type of chain orientation provides a uniaxial positive optical ellipsoid^[18]. The process of chain reorientation is similar to a surface-freezing transition^[19].

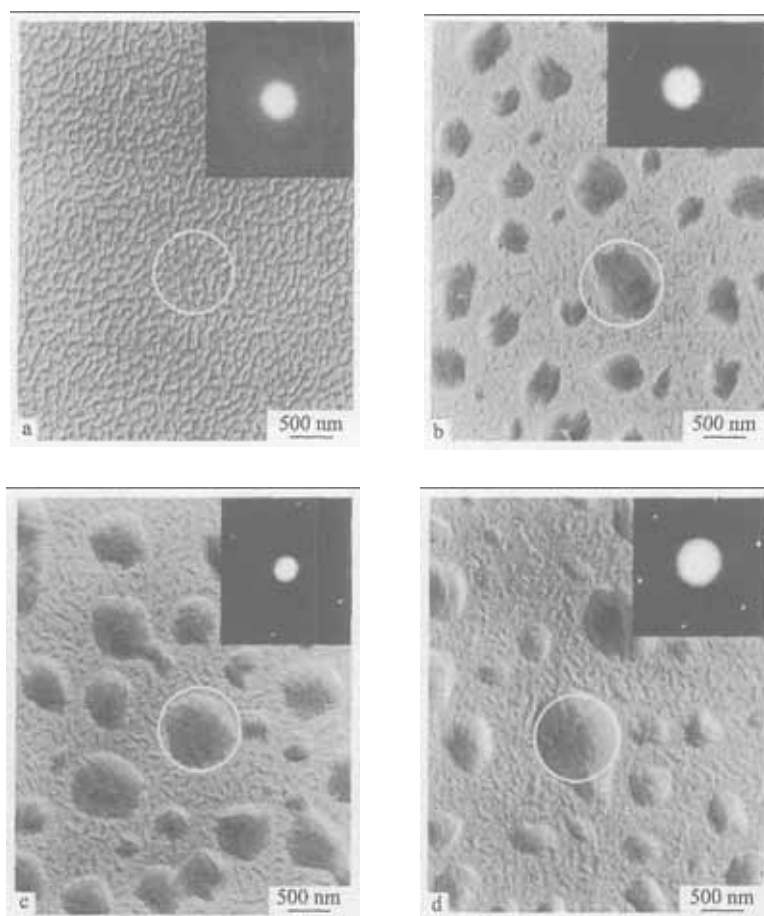


Fig. 4 TEM micrographs and ED patterns of the coTPP-7/11(5/5) mono-domains formed at 153°C for different annealing times: (a) without annealing; (b) 10 min; (c) 2 h; (d) 5 h. The ED patterns originate from the circled mono-domains and are shown with the correct orientation.

Nucleation and Self-Assembly Processes

The formation of the mono-domains may be analogous to a nucleation and self-assembled process. The chain orientation is isotropic in-plane before annealing. During the annealing process, it becomes a tilted homeotropic alignment within the nuclei of mono-domains; while outside of the mono-domains, the chains are in-plane uniaxially oriented towards the nuclei, indicating a chain diffusion during this self-assembly process. Further annealing causes the lateral size and thickness to grow with time, and the chain orientation becomes more or less homeotropic within the domains. We speculate that the area in which chains diffuse towards nuclei is associated

with the molecules transferring from randomly oriented poly-domains to uniaxially oriented mono-domains. No birefringence can be observed under PLM within the domains, since the chain orientation within the domains is parallel to the light beam.

Composition-Dependence of Morphology

As mentioned above the formation of mono-domains is related to the structural symmetry, temperature, molecular mobility and component. The composition may also slightly affect the molecule mobility and therefore, the component-dependence of morphology was studied. The coTPPs-7/11 thin films annealed at 153°C in the Φ phase form the circular mono-domains only when the TPP-7 composition is below 70% (see Fig. 5), because the homoTPP ($n = 7$) can only form mono-domains in the N phase. When the TPP-7 composition increases, the ability to form mono-domains decreases in the Φ phase. It was also found that the lateral size of mono-domains increases from coTPPs-7/11(1/9) to coTPPs-7/11(6/4). It is noteworthy that the molecular mobility is temperature-dependent rather than undercooling-dependent. On the other hand, the formation of mono-domains is nucleation controlled and thus it is undercooling-dependent. In Fig. 1, it is evident that the transition temperature for the Φ to N transition slightly increase with the TPP-7 composition. Therefore, at a constant temperature of 153°C, undercooling increases with the increasing of TPP-7 content. It has been known that the growth velocity of crystals increases with the increasing of undercooling, which in turn increase the lateral size of circular mono-domains with increasing of TPP-7 content. Meanwhile, the composition-dependence of the formation of mono-domains suggests that in this series of samples the long-range molecular diffusion is near its lower limit in the Φ phase. Only when comonomers generate enough disturbance for the chain structure, the long-range diffusion occurs. The effect of such disturbances is different for comonomers, namely, the TPP-7 comonomer exerts a greater effect than the TPP-11.

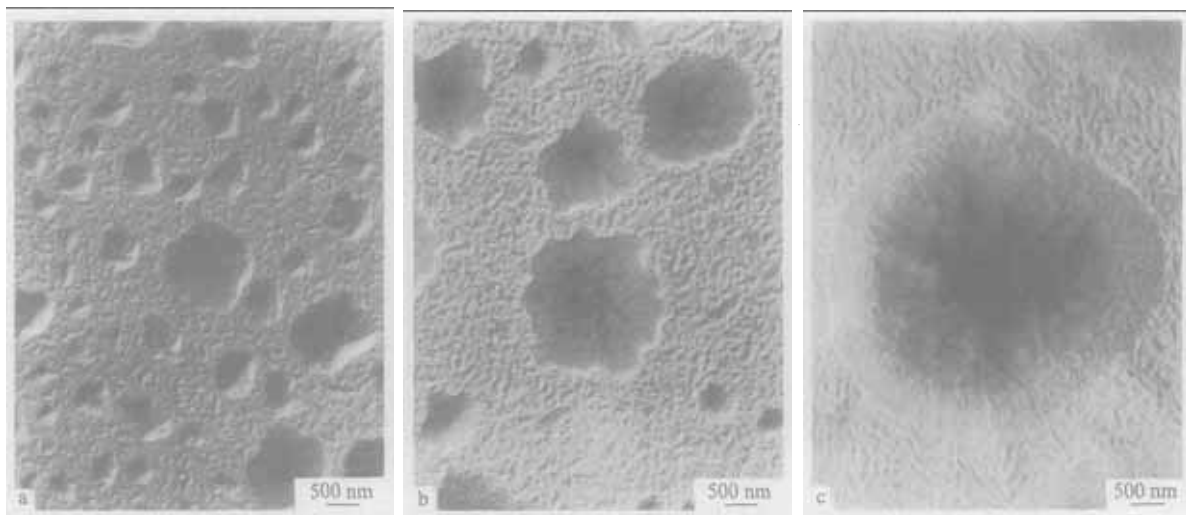


Fig. 5 TEM micrographs of the coTPP-7/11 thin films annealed at 153°C for 15 h
a) coTPP-7/11(1/9); b) coTPP-7/11(3/7); c) coTPP-7/11(6/4)

CONCLUSION

The study of structure and morphology of coTPPs-7/11 thin films show that mono-domains can form in the Φ phase if the TPP-7 monomer composition is lower than 70%. The molecular mobility is large enough to allow large-scale molecular motion to form these domains. On the basis of the TEM results, the coTPP-7/11(5/5) exhibits a continuous change from the isotropic in-plane, in-plane uniaxial, to the tilted orientation before the final homeotropic alignment. The mono-domain formation is similar to a nucleation process, while a continuous domain growth resembles a self-assembly process. The evolution of mono-domains along all directions at a

nearly equal rate reflects the hexagonal symmetry. A composition-dependence can also be observed in the formation of mono-domains, which is associated with the number of methylene units in the copolymers.

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REFERENCES

- 1 Cheng, S.Z.D., Yoon, Y., Zhang, A., Savitski, E.P., Park, J.Y., Percec, V. and Chu, P., *Macromol. Rapid Commun.*, 1995, 16: 533
- 2 Yoon, Y., Zhang, A., Ho, R.M., Cheng, S.Z.D., Percec, V. and Chu, P., *Macromolecules*, 1996, 29: 294
- 3 Yoon, Y., Ho, R.M., Moon, B., Kim, D., McCreight, K.W., Li, F., Harris, F.W., Cheng, S.Z.D., Percec, V. and Chu, P., *Macromolecules*, 1996, 29: 3421
- 4 Yoon, Y., Ho, R.M., Savitski, E.P., Li, F., Cheng, S.Z.D., Percec, V. and Chu, P., "Liquid-Crystalline Polymer Systems Technological Advances", in: "ACS Symposium Series 632", American Chemical Society, Washington, DC, 1996, p.358
- 5 Yoon, Y., Ho, R.M., Li, F., Moon, B.S., Park, J.Y., Harris, F.W., Cheng, S.Z.D., Percec, V. and Chu, P., *J. Therm. Anal.*, 1996, 47: 957
- 6 Yoon, Y., Ho, R.M., Li, F., Leland, M., Park, J.Y., Cheng, S.Z.D., Percec, V. and Chu, P., *Prog. Polym. Sci.*, 1997, 22: 765
- 7 Cheng, J., Yoon, Y., Ho, R.M., Leland, M., Guo, M., Cheng, S.Z.D., Percec, V. and Chu, P., *Macromolecules*, 1997, 30: 4688
- 8 Zheng, R.Q., Chen, E.Q., Cheng, S.Z.D., Xie, F.C., Yan, D.H., He, T.B., Percec, V., Chu, P. and Ungar, G., *Macromolecules*, 1999, 32: 3574
- 9 Zheng, R.Q., Chen, E.Q., Cheng, S.Z.D., Xie, F.C., Yan, D.H., He, T.B., Percec, V., Chu, P. and Ungar, G., *Macromolecules*, 1999, 32: 6981
- 10 Zheng, R.Q., Chen, E.Q., Cheng, S.Z.D., Xie, F.C., Yan, D.H., He, T.B., Percec, V., Chu, P. and Ungar, G., *Macromolecules*, 2000, 33: 5159
- 11 Ho, R.M., Yoon, Y., Leland, M., Cheng, S.Z.D., Yang, D., Percec, V. and Chu, P., *Macromolecules*, 1996, 29: 4528
- 12 Ho, R.M., Yoon, Y., Leland, M., Cheng, S.Z.D., Percec, V. and Chu, P., *Macromolecules*, 1997, 30: 3349
- 13 Percec, V., Chu, P., Ungar, G., Cheng, S.Z.D. and Yoon, C.Y., *J. Mater. Chem.*, 1994, 4: 719
- 14 Ungar, G., *Progr. Colloid. Polym. Sci.*, 1992, 87: 53
- 15 Ungar, G., *Polymer*, 1993, 34: 2050
- 16 Gane, P.A.C., Leadbetter, A.J.L. and WRIGHTEN, P.G., *Mol. Cryst. Liq. Cryst.*, 1981, 66: 247
- 17 Destrade, C., Foucher, P., Gasparoux, H. and Tinh, N.H., *Mol. Cryst. Liq. Cryst.*, 1984, 106: 121
- 18 Rabek, J.F., "Experiments in Polymer Chemistry", John Wiley & Sons, New York, 1980
- 19 Chao, C.Y., Hui, S.W., MacLennan, J.E., Chou, C.F. and Ho, J.T., *Phys. Rev. Lett.*, 1997, 78: 2581