Self-assembled Nanoscaled Fibers Prepared by Polymerizable Rod-Coil Oligomer in Thermosetting Blends

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Introduction

The modification of thermoset resins with rubbers [(1)], thermoplastics [(2)] and liquid crystalline thermosets [(3)] has been a significant challenge in the past several decades, however, these methods could also have some drawbacks in either thermal, processing or internal stress properties. Except the hybrid of carbon nanotubes [(4)] and blending of thermotropic liquid crystal polymers [(5)] with thermosetting systems, to our knowledge, no report was published on the formation of self assembled fibers reinforcing thermosetting systems.

Self-assembly is a rapid pathway from small molecules to supramolecular nanometer-sized objects that cannot be synthesized by conventional chemical reactions [(6)]. The process involves the formation of discrete ensembles of molecules, supermolecules, and nanoparticles into extended ordered arrays, such as crystals, liquid crystals, and colloids. Block copolymers, especially rod-coil block copolymers represent a unique class, where various hierarchical self-assemblies at different compositions have been observed experimentally [(7)]. An unprecedented self-organization was suggested for coil-coil-rod ABC triblock molecules [(8)], which can self-assemble into mushroom-shaped nanostructures, and further organized into noncentrosymmetric polar monolayer structures. Jenekhe reported on the self-assembly behavior of rod-coil diblock copolymers consisting of poly(phenylquinoline) as the rod block and PS as the coil block [(9)]. Novel aggregates in the forms of hollow spheres, lamellar, hollow cylinders, and vesicles in a selective solvent for the rod segment were observed. These results provide potential applications for new functional materials.

Although block copolymer are often self assembled into nanofibers from well controlled solutions, actually, due to technical difficulties arising from the tendency of the growing thermosetting network to

expel any kind of inclusions or molecules initially dispersed or solubilized in the precursor mixture, micrometer-sized soft inclusions have so far been arrested in the fully cured state [10]. By using block copolymers with one block miscible with the epoxy matrix, Marc A. Hillmyer et al [11] had reported nanostructured-toughening epoxy. As the amount of epoxy added to the block copolymer is increased, the blend microstructure evolves from lamellar, to gyroid, to cylinders, to body-centered cubic packed spheres and ultimately disordered micelles [12].

In the present work, we report in the first time that a new method was used to create in situ self-assembled nanoscaled fibers in epoxy resin blends by an epoxy function terminated ABA rod-coil triblock oligomer with a poly(ethylene oxide) midblock and two aromatic azomethine liquid-crystalline endblocks. In the curing proceeding of the blends with epoxy resin, supramolecular nanorods of the triblock oligomer were transformed to polymer nanoscaled fibers while the epoxy functional end groups co-reacting with epoxy resin. Furthermore, uniform crosslinked nanorod structures could also be obtained in the neat ABA triblock oligomer cured with imidazole at the liquid crystalline state.

Experimental Part

Materials and sample preparation

Epoxy precursor diglycidyl ether of bisphenol A (DGEBA) with182-192 g/eq, DER331, was provided by Dow Chem. Co. 2-undecylimidazole (trade name C11Z) was used as initiator of the polymerization of epoxy and was provided by Shikoku Chem Co. Japan. All the other chemicals were purified before use.

Triblock oligomer (Figure 1) with PEO block molecular weight of about 400 (LC400) and 600 (LC600) are synthesized as following. 4-(4-Hydroxybenzylideneimino)aniline was synthesized by mixing equimolar amounts of benzidine and 4-hydroxybenzaldehyde in DMF, Mp, 240°C. Dichlorides $Cl(-CH2-CH2-O)_{n-1}$- CH2-CH2-Cl were synthesized by mixing the corresponding glycol HO(-CH2-CH2-O)n-H and dry pyridine with thionyl chloride. Bis-benzaldehyde of PEG ethers was synthesized by mixing the dichloride, K_2CO_3 and 4-hydroxybenzaldehyde in dried DMSO. Bis-azomethine of PEG ethers were synthsized by mixing equimolar amounts of 4-(4-Hydroxybenzylideneimino)aniline and bis-benzaldehyde of PEG ethers, the resultants were epoxy functionalized with large excess of epichlorohydrin.

Crystalline samples of triblock oligomer LC400 was prepared by slow cooling down of melted samples at a rate about 0.1°C/min on a silica wafer to room temperature. For polymerization of ABA triblock oligomer, LC400 was dissolved in chloroform with 4 percent of 2-undecylimidazole and after then solvent was removed, the sample was cured in a liquid crystalline phase at 140°C under nitrogen atmosphere for 5 hours. Triblock oligomer (LC400 or LC600) with DGEBA was prepared by dissolved

oligomer of 5%, 10%, and 20% (weight) to epoxy precursor at elevated temperature, 4 percent of imidazole C11Z was next dissolved in the blend to yield an optically homogeneous one.

Measurement

^{1}H NMR spectra were recorded on a Bruker spectrometer (500 MHz, DMX 500). XRD experiments were performed at Philips X'pert MPD Pro X-ray diffraction. The polarized light microscopy (PLM) experiments were performed using an Olympus BX51P microscope, also equipped with the Instec HCS410 hot stage. AFM was performed using a Nanoscope IV scanning microscope controller, Veeco Metrology Group, atomic force microscopy. The experiments were preformed in the tapping mode in dry air (RH ~ 20%). Transmission electronic microscopy (TEM) was performed using a JEM-1200EX TEM; samples were cast on copper grids. The morphology of the isothermally cured blends was observed under a scanning electron microscope (SEM) (Tescan TS 5163 MM). The samples were fractured in liquid nitrogen. All samples were coated with gold and mounted on copper mounts.

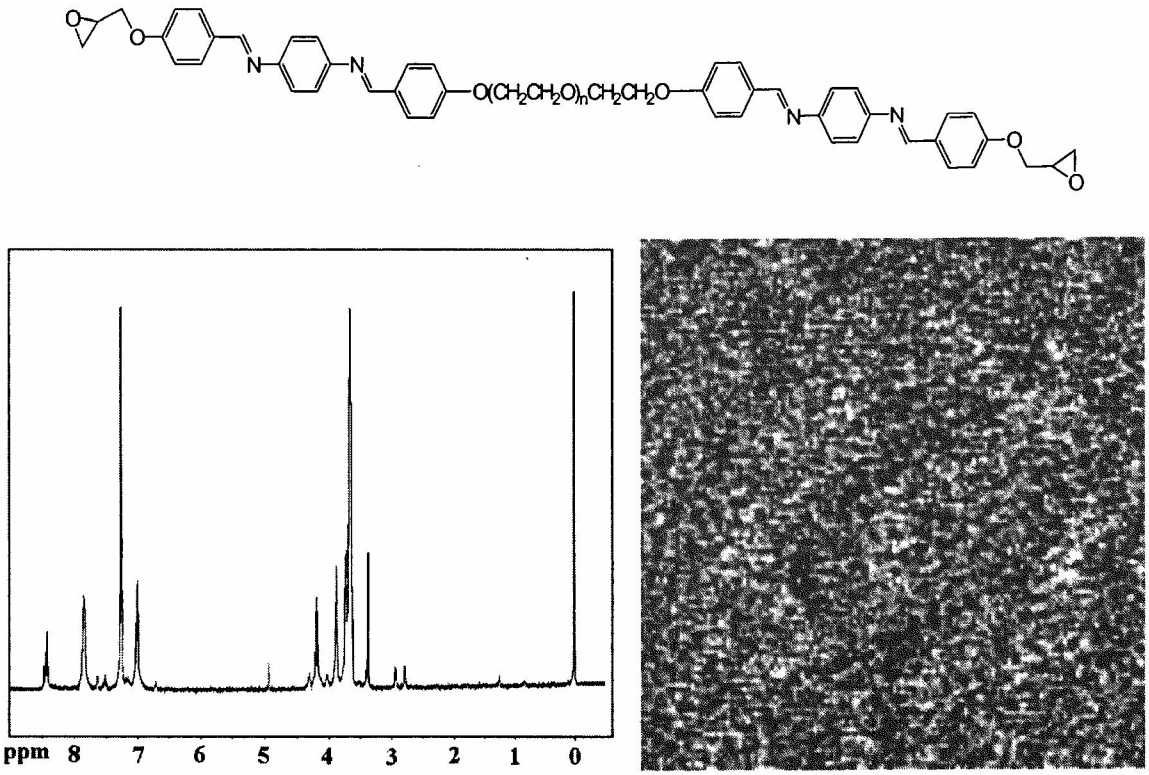


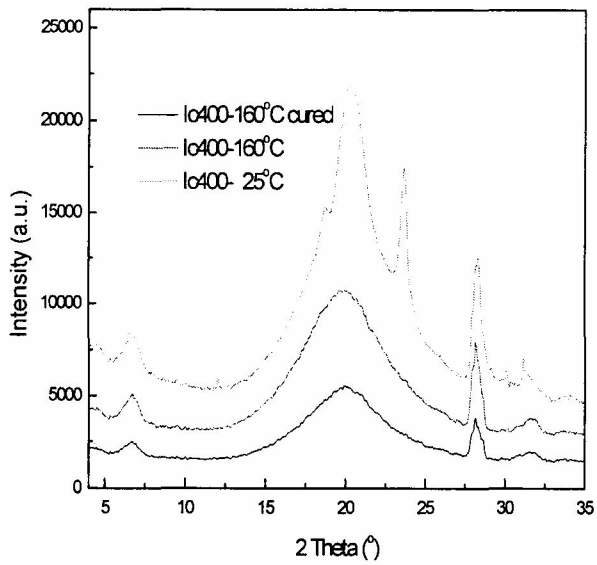
Figure 1. ^{1}H NMR spectrum of LC-400 triblock oligomer and its Tapping-mode AFM phase image (phase contrast) at room temperature. Image size: 500nm; *z*-scale (contrast): 8 nm; scan rate: 1 Hz.

Results and discussion

As oligomeric block copolymers containing thermosetting mesogens have not been studied as extensively as calamitic liquid crystalline block copolymers, here we synthesized a thermosetting ABA rod-coil-rod triblock oligomer, aromatic azomethine - block-poly(ethylene oxide)-block- aromatic azomethine with epoxy end group, by first coupling 4-(4-Hydroxybenzylideneimino)aniline with the resultant of 4-hydroxybenzaldehyde and dichloride-terminated PEO oligomer, which were prepared by the reaction of the corresponding oligoethylene glycols with an excess of thionylchloride in the presence of pyridine; then being epoxy functionalized with large excess of epichlorohydrin. The purity obtained product was checked by thin-layer chromatography (TLC) and was confirmed to be in full agreement with the structure presented by 1H NMR (Figure 1).

Rod-coil-rod molecule LC400 melts into the nematic liquid crystalline phase at 123°C, and then transforms into an isotropic liquid at 153°C, which was detected by Polarizing Optical Microscopy (POM) and DSC. The peak melting temperature (Tm) of the azomethine liquid crystalline block was lowed down with the increase of PEO block molecular weight, as in LC600, with PEO block molecular weight of about 600, the transform temperature range 116-145 °C. X-ray diffraction patterns showed only a broad halo during the heating of LC400 up to melt point, indicative of a change from crystalline state to liquid crystalline state in Figure 2.

Crystalline samples of triblock oligomer LC400 was prepared by slow cooling down of melted samples on a silica wafer to room temperature. As shown in Figure 1, the Tapping-mode AFM images indicate that LC400 self-assembles into nanorod structure with longitude about 10 nm.



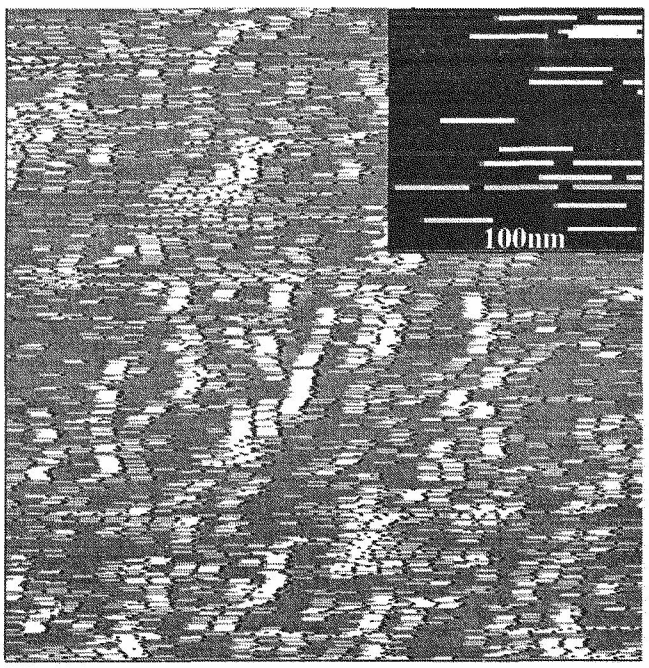
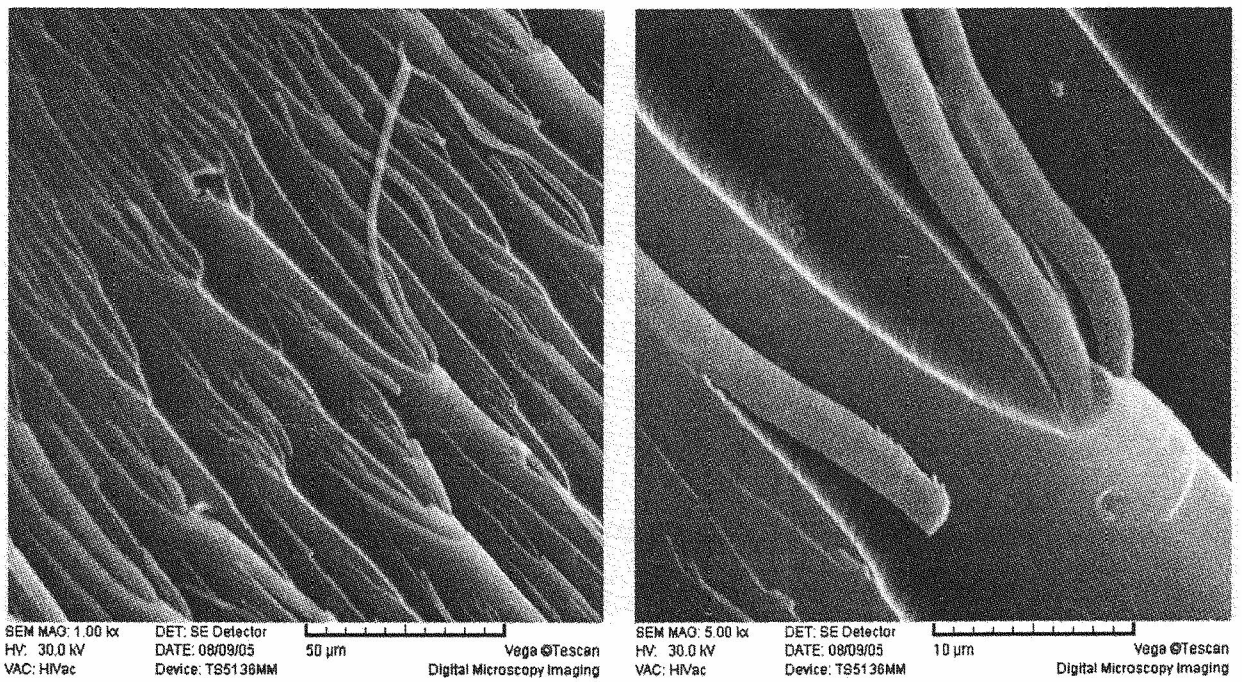


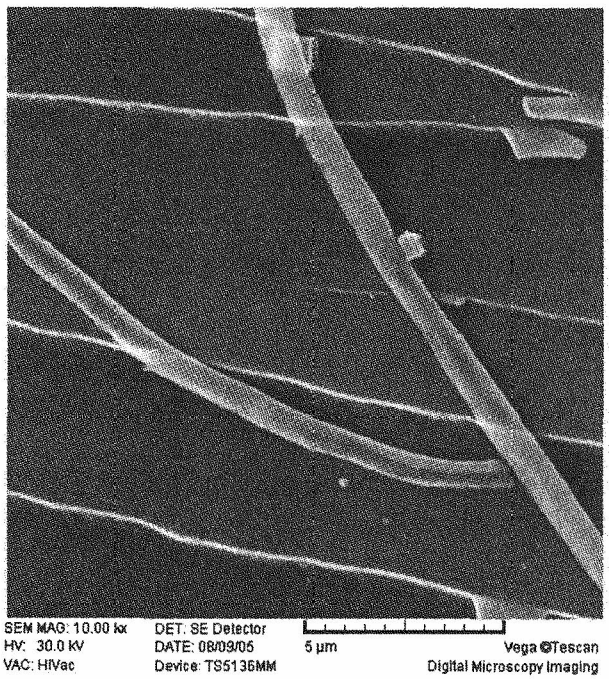
Figure 2. X-ray diffraction patterns of LC-400 at different states, and Tapping-mode AFM images of a LC400 sample cured with C11Z (4%) at 140°C. Image size: 1μm; *z*-scale (contrast): 150 nm; scan rate: 1 Hz, phase contrast.

For polymerized of ABA triblock oligomer, imidazole was used as initiator, which could provide a quick chain-growth polymerization of the epoxy function and keep the oligomer in LC state. As shown Figure 2, the Tapping-mode AFM images, combined with optical microscopic and XRD, showed subsequently organized discrete bundles about 30 nm longtitude in the liquid crystalline phase, indicative of the preservation of the ordered symmetry and the dimensions of the discrete objects after polymerization. Based on the above results, it can be concluded that polymerization proceeds with retention of the size and shape of the self-assembled nanorod bundles, giving rise to the formation of macromolecular nanorod objects with well-defined shape and size.

Further blending of triblock oligomer with epoxy precursor DGEBA and imidazole was performed to get chain-growth polymerized thermoset systems. The samples were cured at below m.p. of oligomer (80°C) or above m.p. of oligomer (140°C) respectively, to evaluate the effect of LC phase on morphology of the cured samples.



(a)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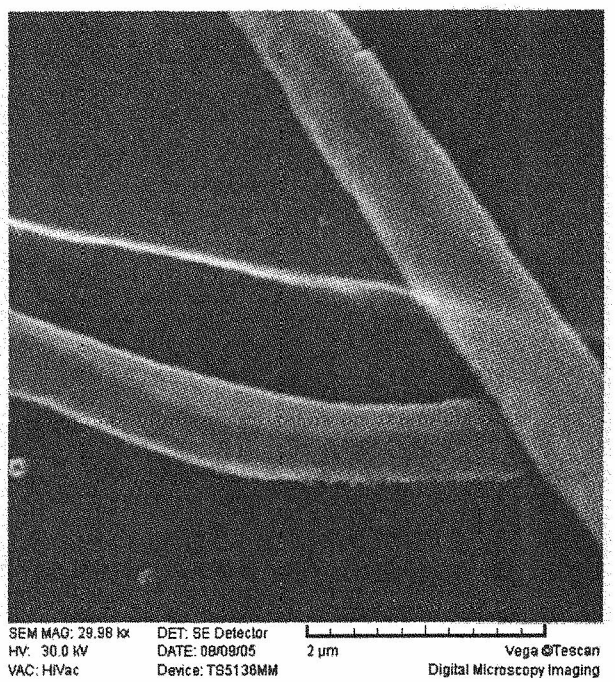
VAC: HiVac
DET: SE Detector
DATE: 08/09/05
Device: TS5136MM
5 µm
Vega ©Tescan
Digital Microscopy Imaging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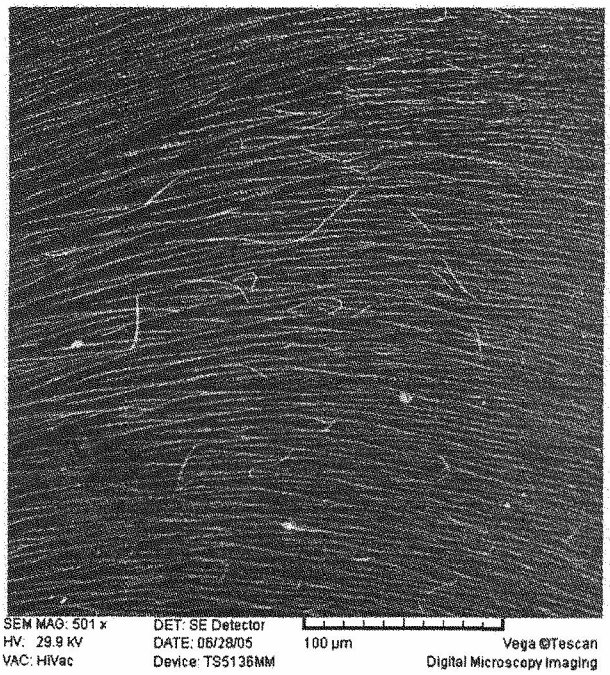
(b)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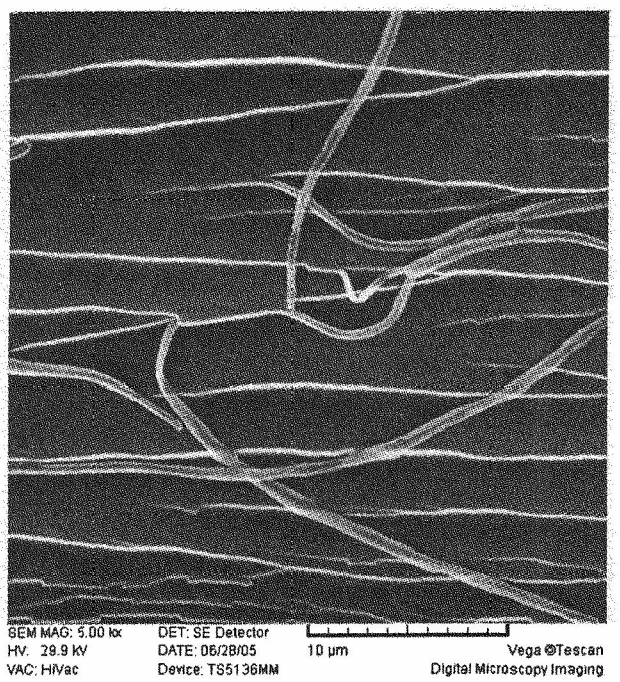
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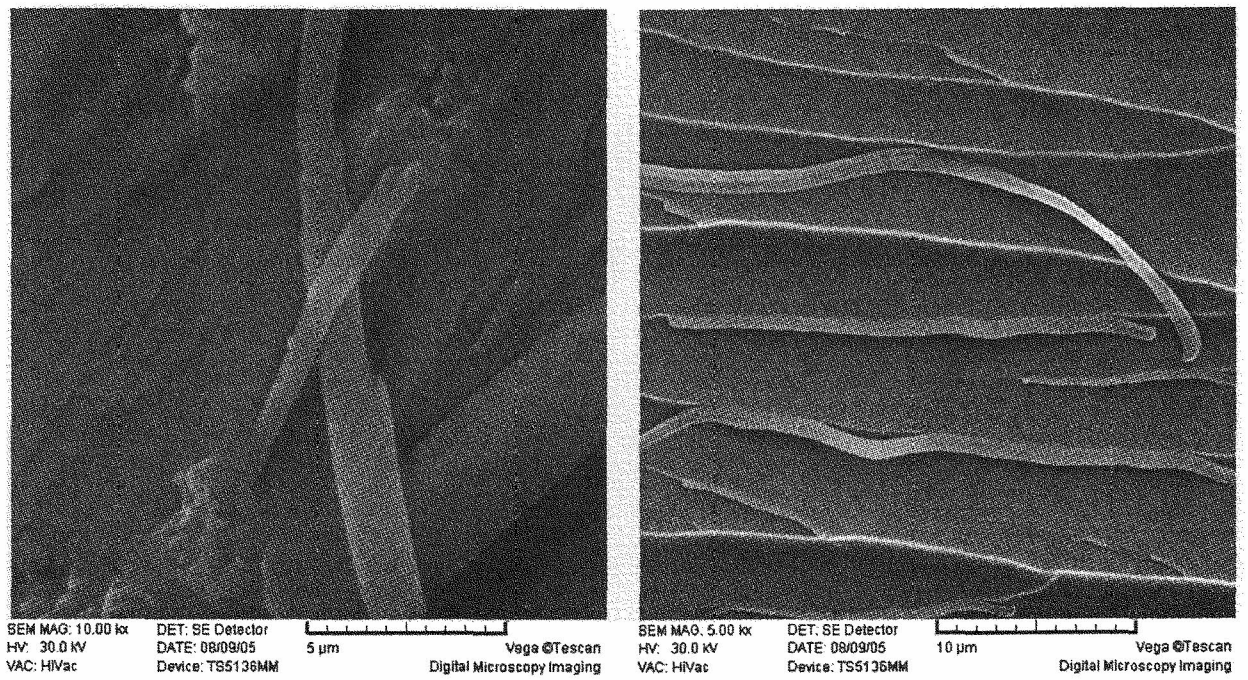
Digital Microscopy Imaging

(c)



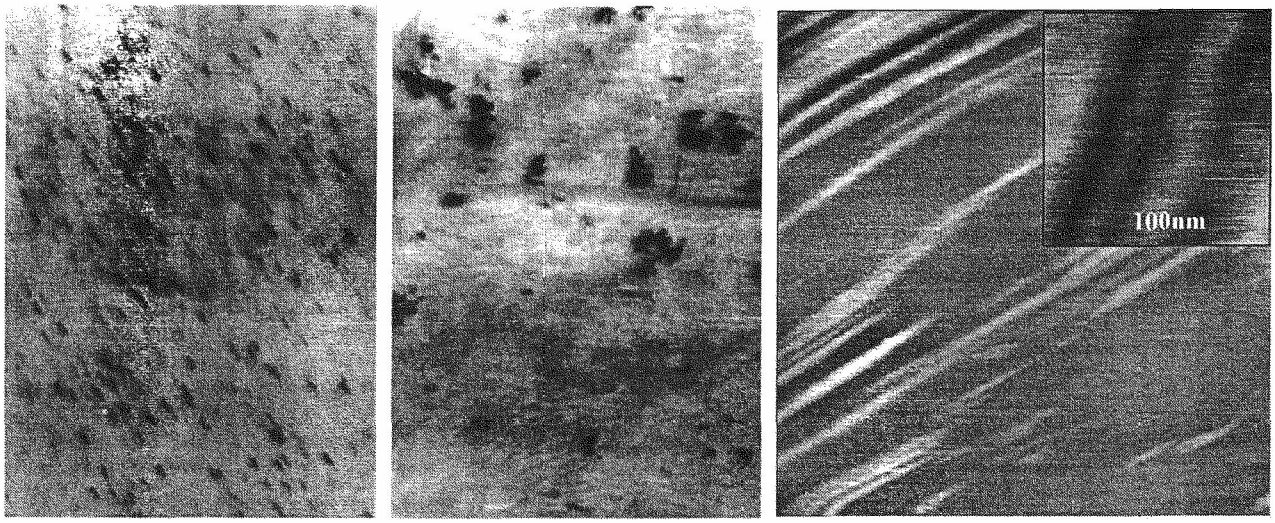
(d) (e)

Figure 3. Scanning electron microscopy and AFM images of nano-fiber formed in DGEBA/LC-400(5, 10, 20%), LC-600 (20%)/C11Z cured at 80°C and 140 °C for 5 hours. (a)LC400, 5%, 80 °C; (b) LC400, 5%, 140 °C; (c) LC400, 10%, 80 °C; (d) LC400, 20%, 80 °C; (e) LC600, 20%, 80 °C.

Remarkably, highly uniform nanoscaled fibers are observed by means of both SEM and AFM in the fully cured blend systems. For the samples fractured in liquid nitrogen, SEM images reveal that they are actually agglomerations of nanoscaled fibers lined in blend systems. As shown in Figure 3, fibers with diameter about 500nm and longer than 50 um are observed in all the blends.

The morphology of the nanoscaled fibers is almost unaffected when the curing temperatures were changed, i.e. in both crystalline and liquid crystalline phase. Moreover, nanoscaled fibers can be formed no matter what weight fraction of triblock oligomer was used in the blends. For example, uniform nanoscaled fibers were observed in SEM images of lc400 10% systems (Figure 3c), while nanoscaled fibers were also found in lc400 5% and 20% systems (Figure 3a and 3d).

The quantity and uniformity of the nanofibers seems to be affected only by the length of PEO blocks of the triblock oligomers. The higher the molecular weight of PEO blocks, the lower the volume fraction of nanofibers observed in the cured sample as shown in Figure 3(e) in the LC600 blends.

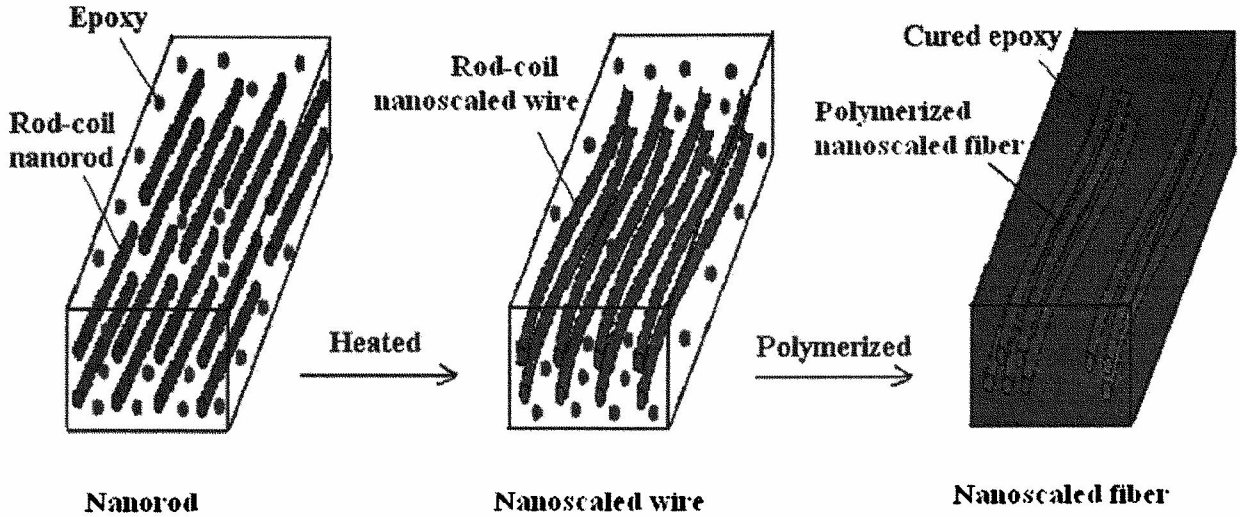


(a) (b) (c)

Figure 4. TEM (×100,000) of DGEBA/LC-400 (20%) at room temperature (25°C) (4a), heated to 80°C(4b), and Tapping mode AFM of DGEBA/LC-400 (20%)/C11Z cured at 80°C for 5 hours(4c). Image size: 1μm; *z*-scale (contrast): 150 nm; scan rate: 1 Hz

To investigate the supermolecular structure of rod-coil oligomer in thermoset resins, LC-400 was blended with DGEBA. As shown in Figure 4b, the nanorods of rod-coil oligomer dispersed in the epoxy solution at room temperature (25°C), i.e. the rod-coil oligomer preserved its supermolecular structure in the epoxy solution as in bulk state at room temperature (Figure 4a). Moreover, a significant difference of the supermolecular structure of the rod-coil oligomer LC-400 was observed at different temperature. As shown in Figure 4b, it displays the nanoscaled wire structure of LC-400 in the blend of DGEBA/LC-400 (20%) at above 73 °C, whereas, some clusters of LC-400 are observed by TEM.

Additionally, the blend of DGEBA/LC-400 (20%) was cured at 80°C in the presence of C11Z, LC-400 self assembled into nanoscaled fibers (Figure 4c), AFM shows the in situ formation of nanofibers in the curing process, in which the nanofibers are in fact bundles of aggregated regular oligomer nanowires dispersed in the epoxy matrix, they form nanoscopic block copolymer core/ epoxy shell-like fibers morphologies. And the whole self-assembly process is schemed as shown in scheme 1.



Scheme 1. Schematic representation of self-assembly of rod-coil oligomers in epoxy solution during the heating process and polymerization.

Obviously, as the miscibility of PEO and epoxy resin has been confirmed, it was speculated that the mixture is characterized by a negative Flory-Huggins interaction parameter χ[6, 12]. As the PEO block provide excellent solubility while the azimethine block are insoluble with epoxy resin, thus, it could be anticipated that the epoxy resin would swell the PEO domains in these block copolymers without dissolving the rod blocks and lead to an ordered composite. Gelation of the epoxy resin forces an expulsion out of the PEO from the matrix, at the same time, polymerization of the epoxy end-group of triblock oligomer results in anchoring at the epoxy matrix in the nanosize, therefore, the block copolymer/ epoxy with skin-core like nanoscaled fibers could result in an optically homogeneous materials.

Conclusion

Polymerizable liquid crystalline rod-coil-rod oligomers were self-assembled into a nanorod discrete structure in the liquid crystalline phase. Cross-linking of the oligomer in the 3-D ordered state proceeded with the retention of the ordered structure, leading to the formation of crosslinked objects with well-defined shape and size. When further blending the oligomer with epoxy precursor, nanoscaled fibers longitude in um size was observed in the cured samples at states of due to the formation of nanoscaled wire structure by the rod-coil oligomer, suggesting that the macromolecular objects are shape-persistent in epoxy precursor solutions as well as in cured blends. Therefore, the polymerization of reactive nanorod within the confined space and formation of nanoscaled fiber structure in epoxy precursor offers a novel strategy to create shape-persistent nano-objects which could be applied in toughening of thermosetting resin and developing of new functional materials.

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