

Progress of Study on Mesogen-Jacketed Liquid Crystalline Polymers at Peking University

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Structure and Property of Mesogen-Jacketed Liquid Crystalline Polymers

Mesogen-Jacketed Liquid Crystalline Polymers, MJLCPs, are polymers with mesogenic side groups directly attached to main-chains without using flexible connecting spacers and are able to form liquid crystalline structures. An earlier example of MJLCPs is poly-[2,5-bis(methoxyphenylcarbonyloxy)styrene] that has a polyethylene backbone and mesogenic *p,p'*-bis(methoxybenzoyloxy)phenyl as side groups (Figure 1). It has a high T_g of 160 °C and forms very stable liquid crystalline phase. That the mesophase gives the banded textures and its chain in THF solution has a persistence length as high as 12 nm both indicate a significant chain rigidity of this MJLCP.

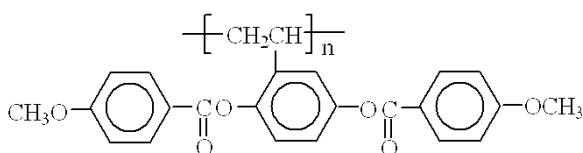


Figure 1. Poly[2,5-bis(4'-methoxyphenylcarbonyloxy)styrene]

Molecular weight is important for formation (and structure) of liquid crystalline phase of MJLCPs. Normally, a molecular weight above a critical value is needed. For instance, poly(2,5-bis(4-methoxyphenyl)oxycarbonyl)styrene, PMPCS, forms mesophase only when molecular weight is higher than ten thousands. Interestingly, with further increasing molecular weight the mesophase of PMPCS will change from a nematic columnar to a hexatic columnar nematic. Further structure-property studies of MJLCPs suggested that the side groups are not necessary mesogenic so long as they are large enough and be attached directly to the backbone. It was found that not only all the polymers of the dicycloalkyl esters of vinylterephthalic acid such as poly[dicyclopentyl vinylterephthalate] and poly[dicyclohexyl vinylterephthalate] are liquid crystalline, even those polymers of certain dialkyl esters of vinylterephthalic acid are liquid crystalline. These include the polymers with the alkyl groups of 3-10 carbon atoms. For instance, the careful studies of poly(di-2-propyl vinylterephthalate) and poly(di-4-heptyl vinylterephthalate) revealed that they formed hexagonal columnar phases. Since MJLCPs tend to form columnar phase the previous studies offered also the opportunity to manipulate the diameter of the molecular columns and thus the supramolecular structures.

Block Copolymers

Many if not all of the styrenic monomers of MJLCPs are readily polymerizable using such "living" polymerizations as the nitroxide-mediated and the atom transfer radical polymerizations. This gives us a unique handy tool for synthesizing block copolymers, especially when a rod block of different length is desired (Figure 2).

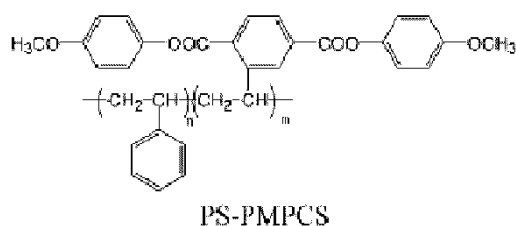


Figure 2. A Rod-Coil Diblock Copolymer

The block copolymers self-assembly in solution and in bulk as any other block copolymers do. However, since the nature and the length of the blocks are relatively easy to be adjusted in this case, more opportunities and flexibility one may have in designing and preparing supramolecular structures. An interesting observation has been for the block copolymer poly(styrene-*b*-MPCS) in solution when micellar structure with PMPCS blocks form the core and PS blocks form the shell. Since the core radius remained as a constant, close to the contour length of the PMPCS block, the diameter of the core and the thickness of the shell can be manipulated by the lengths of the two blocks.

Another and more recent result is the first observation of a tetragonally perforated layer structure which is formed of poly(styrene-*b*-MPCS) in bulk when the fraction of styrene exceeds certain value depending on molecular weight.

Naturally one can synthesize also multiblock copolymers using the same concept and reactions. The rod-coil-rod copolymers have been synthesized to test the possibility of making thermoplastic elastomer using MJLCP as the physical crosslinking components. Although the preliminary results are not encouraging when the rubber property is concerned, it is astonishing that the structure and the property are much maintained at above T_g of the rods by the liquid crystalline phase of PMPCS blocks.

Studies of Functional MJLCPs

It is conceivable that the bulky and rigid side groups in MJLCPs will help stabilizing helical conformations once formed of the polymers and thus offer a chance of making optically active materials. In one try of this effort, we successfully polymerized free-radically a monomer, (+)-2,5-bis[4A-((S)-2-methylbutyloxy) phenyl] styrene, which is itself chiral so that the helix-sense selection was induced during polymerization. The resulted polymer is chiral, but most interestingly the optical activity remains after the initial stereogenic center in the side group of the monomer is chemically removed.

The approach of MJLCP can also be applied to synthesize electro-optic materials. Preliminary studies include synthesis of the series of MJLCPs as showing in Figure 3 using electron transporting oxadiazole moieties as side groups. Some representative data are given in Table 1 where PCT is the polymer with R t-Butyl.

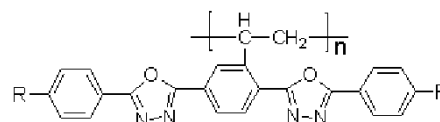


Figure 3. MJLCPs useful as electron transporting materials

Table 1. Device Performance for PCT and PVK as Host Materials

Host	V_0/V	$L_{max}/cd/m^2$	$\eta_{ext max}/\%$	$\eta_{Lmax}/lm/W$	$\eta_{Imax}/cd/A$
PVK (PBD)	10.5	1999	0.24	0.073	0.68
PCT (TPD)	9.7	3702	0.28	0.12	0.83

* Device Structures: ITO/PEDOT(50 nm)/PCT:TPD:IrMDPP or PVK:PBD:IrMDPP(10 wt%, 50 nm)/BCP(10 nm)/Alq3(30 nm)/Mg:Ag (10: 1, 150 nm)/Ag(10 nm)

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