

A NEW STRATEGY FOR THE DESIGN OF LIQUID CRYSTALLINE POLYMERS WITH FLEXIBLE AND APOLAR BUILDING BLOCKS*

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Abstract The synthesis and characterization of a new series of liquid crystalline polymers, poly(dicycloalkyl vinylterephthalate)s, are reported. The basic building blocks of these polymers are not mesogenic by themselves. However, very stable mesophases can be generated by self-assembly of the polymer molecules. This approach suggests a novel design strategy of liquid crystalline polymers with flexible and apolar building blocks.

Keywords Liquid crystalline polymers, Dicycloalkyl vinylterephthalates, Poly(dicycloalkyl vinylterephthalate)s, Self-assembly

INTRODUCTION

Liquid crystalline polymers (LCPs) are of great interest in areas such as high performance fibers, engineering plastics, composite materials, electro-optic display and information storage devices. Most of the LCPs have mesogenic units as building blocks. Typical mesogenic units mostly found in LCPs have significant rigidity and the shape of a rod. They are often made up by linking together two or more 1,4-phenylene rings by direct covalent bonding or through proper linking groups that can assure the linearity of the mesogenic unit. In some LCPs aromatic moieties other than 1,4-phenylene (*e.g.*, 2,6-naphthalene) are also used. Only in rare cases^[1, 2] the aliphatic rings including 1,4-cyclohexane and 1,3-dioxane are used to replace part of the phenylene rings in the mesogenic units. This indicates that not only the linear shape but also the rigidity and polarizability of mesogenic units are important for the formation of liquid crystals.

According to the location of the mesogenic units in the polymer molecules the polymers are classified as the main-chain type or the side-chain type LCPs. While the main chain LCPs were synthesized by condensation polymerizations, the side chain LCPs were mostly synthesized by addition polymerizations although other types of polymerization reactions were also used. The two types of LCPs also differ in properties. Most significantly, because the rigid mesogenic units are in the backbones in main chain LCPs, these polymers can be very rigid. On the other hand, the side chain LCPs can be rather flexible because the rigid moieties are only found in the side chains and have been attached to the backbone through decoupling flexible spacers^[3]. However, if the mesogenic units are attached as side groups to the polymer backbones laterally and directly or through only very short spacers the polymers may also show significant chain rigidity. Thus, a third type of LCPs is formed. They could be included in the category of side chain LCPs because they are synthesized by polymerization reactions, which have been used for other side chain type LCPs. On the other hand, however, they might also be included in the

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category of main chain LCPs because they have extended and stiffer backbones. The term “mesogen-jacketed liquid crystalline polymers” (MJLCPs) has been suggested by Zhou^[4] to distinguish the third type from other LCPs. The MJLCPs are relatively new and have been successfully synthesized only in a few research groups including that of Finkleman^[2], Keller and Hardouin^[5], Gray^[6], Percec^[7], Pugh^[8], Ober^[9], Zhou^[10], and a few others.

We have recently reported the synthesis of a new polymer, poly(dicyclohexyl vinylterephthalate)^[11]. As many other MJLCPs synthesized by us, this polymer was synthesized by chain polymerization of a vinyl monomer with AIBN as the initiator. It has a polyethylene backbone but substituted with a dicyclohexyl terephthalate group on every second backbone carbon atom. Interestingly, although dicyclohexyl terephthalate can hardly be regarded as a mesogenic rod and is rather flexible because it contains only one phenylene ring in the center and two flexible cyclohexyl rings at the two ends. This polymer does form a very stable liquid crystalline phase at temperatures above T_g . What has interested us even more is the finding of liquid crystallinity of poly(dicyclopentyl vinylterephthalate), another new polymer recently synthesized by us^[12]. To our knowledge, because of the extremely high degree of flexibility and the absence of linearity of the cyclopentyl ring, no effort has ever been made to incorporate this ring in any polymer so as to realize any liquid crystallinity. These recent results have led us to the idea that by using the unique molecular architecture of MJLCPs no traditional rigid rod-like mesogenic units are actually needed for realization of liquid crystallinity of polymers. In order to verify this notion and to achieve a better understanding of the relationship between molecular structure and liquid crystallinity of polymers, we have attempted to synthesize other poly(dicycloalkyl vinylterephthalate)s and poly(dialkyl vinylterephthalate)s. In this paper, the synthesis and the liquid crystalline properties of a series of poly(dicycloalkyl vinylterephthalate)s (Scheme 1 shows their structure) with the same backbone but various cycloalkane rings of different sizes are reported. Because there are no rigid rod-like mesogenic units present in the molecules we consider^[13] that the liquid crystalline structure is formed by self-assembly of the whole polymer molecules rather than by the ordered packing of “mesogenic units” as suggested for conventional side chain type LCPs.

EXPERIMENTAL

Materials

Vinylterephthalic acid was synthesized using the previously reported method^[10]. Tetrahydrofuran (THF, Acros 99%) and pyridine (Acros 99%) were heated under reflux over calcium hydride for at least 8 h and distilled before use. 2,2'-Azobisisobutyronitrile (AIBN, Acros 99%) was purified by recrystallization from ethanol. Cyclobutanol (99%), cyclopentanol (99%), cyclohexanol (99%), cycloheptanol (99%), cyclooctanol (99%), cyclododecanol (99%), triphenylphosphine (99%) and hexachloroethane (99%) were purchased from Acros Company and used as obtained. All other reagents and solvents were commercial products.

Measurements

¹H-NMR spectra of the polymers were obtained on a Bruker ARX 400 spectrometer using CDCl₃ as solvent. Mass spectra were recorded on a VG-ZAB-HS mass spectrometer. Relative molecular weights were measured on a Waters 150C gel permeation chromatograph equipped with three Waters Styragel columns (10³, 10⁴, 10⁵ Å) using THF as eluent at room temperature. The column system was calibrated by a set of monodispersed standard polystyrenes. DSC curves were obtained using a TA DSC 2010 differential scanning calorimeter. Thermogravimetric analyses (TGA) were performed on a TA SDT 2960 instrument. Polarized optical microscopy (POM) observation was performed on a Leitz Laborlux 12 Pol microscopy with a Leitz 350 hot stage. Powder X-ray diffraction studies were carried out with a Rigaku Dmax-2400 diffractometer.

Computer Modeling

The theoretical fully extended length of side group, dicycloalkyl terephthalate, was calculated on a Power Macintosh 7100/66AV computer using MacSpartan Plus software (Method: Geometry Optimization; level: AM1).

Syntheses of Monomers

The monomers were prepared as in the following example of dicyclopentyl vinylterephthalate (M-5). Vinylterephthalic acid (0.77 g, 4.0 mmol) and triphenylphosphine (2.2 g, 8.4 mmol) were dissolved in 10 mL dried pyridine to obtain solution A. Dried cyclopentanol (0.72 g, 8.4 mmol) and hexachloroethane (2.1 g, 8.88 mmol) were dissolved in 10 mL dried pyridine to obtain solution B. Then solution B was slowly dropped into solution A, and the mixture was stirred at 60°C for 5 h. After cooling to room temperature, the mixture was poured into dilute HCl and extracted with chloroform for 3 times. The organic layer was dried over anhydrous sodium sulfate. The chloroform was removed by vacuum distillation. The residue was purified using column chromatography on silica gel with chloroform as eluent to get a colorless liquid product with a yield of 60%. $^1\text{H-NMR}$ (δ) 1.66–1.98 (m, $-\text{CH}_2-$, 16H), 5.40–5.76 (m, $\text{CH}_2=$ and $-\text{OCH}$, 4H), 7.36–7.43 (m, $-\text{CH}=$, 1H) and 7.84–8.19 (m, phenyl ring, 3H). Mass spectrum (m/e) 328 (parent), 260, 243, 175, 130, 102 and 85 (base).

Dicyclobutyl vinylterephthalate (M-4)

$^1\text{H-NMR}$ (δ) 1.69–2.49 (m, $-\text{CH}_2-$, 12H), 5.18–5.27 (m, $-\text{OCH}$, 2H), 5.41–5.78 (m, $\text{CH}_2=$, 2H), 7.39–7.47 (q, $-\text{CH}=$, 1H) and 7.90–8.22 (m, phenyl ring, 3H). Mass spectrum (m/e) 300 (parent), 229 (base), 175, 130 and 102.

Dicyclohexyl vinylterephthalate (M-6)

$^1\text{H-NMR}$ (δ) 1.34–1.96 (m, $-\text{CH}_2-$, 20H), 5.01–5.05 (m, $-\text{OCH}$, 2H), 5.30–5.77 (m, $\text{CH}_2=$, 2H), 7.36–7.50 (q, $-\text{CH}=$, 1H) and 7.88–8.24 (m, phenyl ring, 3H). Mass spectrum (m/e) 356 (parent), 274 (base), 257, 193 and 175.

Dicycloheptyl vinylterephthalate (M-7)

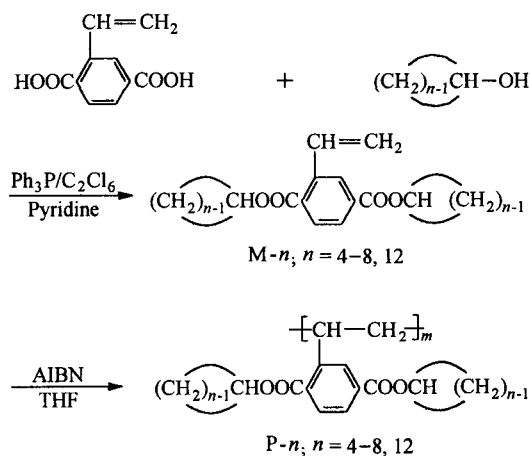
$^1\text{H-NMR}$ (δ) 1.59–2.03 (m, $-\text{CH}_2-$, 24H), 5.18–5.23 (m, $-\text{OCH}$, 2H), 5.40–5.77 (m, $\text{CH}_2=$, 2H), 7.39–7.46 (q, $-\text{CH}=$, 1H) and 7.86–8.22 (m, phenyl ring, 3H). Mass spectrum (m/e) 384 (parent), 288 (base), 257, 193 and 175.

Dicyclooctyl vinylterephthalate (M-8)

$^1\text{H-NMR}$ (δ) 1.59–1.98 (m, $-\text{CH}_2-$, 28H), 5.19–5.23 (m, $-\text{OCH}$, 2H), 5.40–5.76 (m, $\text{CH}_2=$, 2H), 7.38–7.45 (q, $-\text{CH}=$, 1H) and 7.85–8.21 (m, phenyl ring, 3H).

Dicyclododecyl vinylterephthalate (M-12)

$^1\text{H-NMR}$ (δ) 1.37–1.88 (m, $-\text{CH}_2-$, 44H), 5.25–5.29 (m, $-\text{OCH}$, 2H), 5.40–5.77 (m, $\text{CH}_2=$, 2H), 7.39–7.47 (q, $-\text{CH}=$, 1H) and 7.89–8.22 (m, phenyl ring, 3H).



Scheme 1 Synthetic route of monomers M-n and polymers P-n

Polymerization

The polymers were obtained through solution polymerization. The reaction was carried out in THF solution at 60°C for three days, using 0.3% equivalent moles AIBN as initiator. The polymers were precipitated in and washed with methanol.

RESULTS AND DISCUSSION

The monomers were prepared from cycloalkanol and vinylterephthalic acid through phosphorylation reaction as shown in Scheme 1. As previously reported for M-5 and M-6^[11, 12], all products are colorless isotropic liquids at room temperature. They were easily polymerized to moderately high molecular weight polymers by way of convenient radical polymerization. After polymerization, the characteristic resonance peaks of vinyl groups in the ¹H-NMR spectrum (not shown) of monomers disappeared and those of $-\text{CH}-\text{CH}_2-$, polymer backbone, were observed instead, indicating the formation of the polymers. The results of polymerization are summarized in Table 1.

Table 1. Properties of the polymers

Polymers	$M_n (\times 10^{-4})$	M_w/M_n	T_g^a (°C)	T_d^b (°C)	T^c (°C)	T_i (°C)
P-4	1.6	2.2	89	337	~144	255
P-5	1.0	1.6	89	282	~150	267
P-6	1.0	1.8	102	293	~155	~295 ^d
P-7	2.1	3.9	95	283	~155	~290 ^d
P-8	0.84	2.5	92	265	~155	~283 ^d
P-12	0.95	3.7	91	262	~160	~298 ^d

^a The data were taken from second heating; ^b The temperature at which the weight loss reached 1 %; ^c The temperature at which a noticeable birefringence was identified; ^d Isotropization was accompanied by decomposition

The polymers (P-*n*) were characterized by using TGA, DSC, POM and XRD. Initial POM observation and XRD measurement show that the polymers are noncrystalline at room temperature.

The results from TGA analysis show that these polymers are fairly stable. As seen in Fig. 1 and Table 1, the onset of the weight loss of polymers in nitrogen occurs at temperatures higher than 260 °C. The thermal decomposition seems to be ring-size dependent with only slight deviation from the trend. The polymer having the smallest aliphatic rings (P-4 containing cyclobutane rings) has the highest decomposition temperature of 337 °C, and that having the largest rings (P-12 with cyclododecane rings) has the lowest decomposition temperature of 262 °C. In addition, the weight loss in the first decomposition stage at temperatures below 400 °C is also ring-size dependent. The larger the aliphatic ring, the higher is the percentage weight loss. This ring-size-dependent decomposition suggests that a larger ring may have weakened the ester bond to a greater extent. However, if we compare the thermal stability of this series of polymers with poly(diphenyl vinylterephthalate)^[10] we find that the polymer of the phenyl esters is more stable than the present polymers of the aliphatic ring esters. This may be rationalized by considering the partial conjugation of the ester group with the two phenylene rings present in poly(diphenyl vinylterephthalate) and the lack of the same conjugation in the present polymers.

Having considered the possible thermal decomposition, all the DSC experiments were run to well below the T_d . The DSC trace of the second heating scan of P-*n* is shown in Fig. 2. P-4 undergoes a glass transition at 89 °C. When this polymer was observed under POM, the powder sample was slightly birefringent presumably because of the presence of a low degree of mesomorphic order formed during preparation of the sample. When it was heated to above T_g , no immediate development of birefringence was observed. The birefringence developed at a noticeable rate only when the temperature was raised to about 144 °C. The anisotropic-isotropic transition was observed at 255 °C. However, neither the ordering exotherm for mesophase formation nor the disordering endotherm for mesophase disappearance was detected by DSC under the experimental conditions.

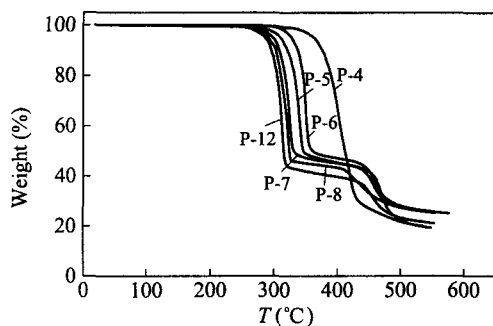


Fig. 1 TGA thermograms of P-*n*
Heating rate: 20 K/min; Atmosphere: N₂

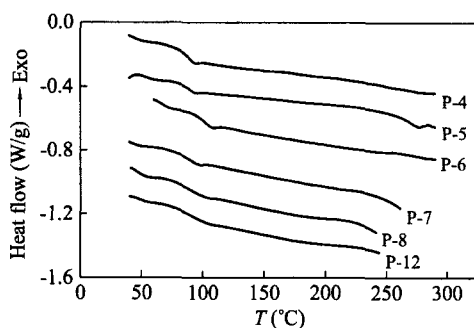


Fig. 2 DSC thermograms of P-*n* observed from the second heating
Heating rate: 20 K/min; Atmosphere: N₂

P-5 exhibits an endothermic peak centered at 276°C with a ΔH of 0.36 kJ/mol besides a glass transition at 89°C. Thermal POM demonstrates that P-5 begins to soften at 140°C and becomes birefringent at 150°C. The birefringence becomes weaker at 240°C and disappears completely at 267°C. Because the TGA test has shown that the polymer has 1% or 5% weight loss at 282°C or 304°C, respectively, the endothermic peak at 276°C is attributed to the phase transition from liquid crystal to isotropic liquid but not to thermal decomposition.

The thermal behaviors of P-6, P-7, P-8 and P-12 are almost the same as those of P-4 except that their T_g are a little higher than that of P-4 and P-5. The birefringence appears when the temperature is significantly higher than T_g and disappears when thermal decomposition starts.

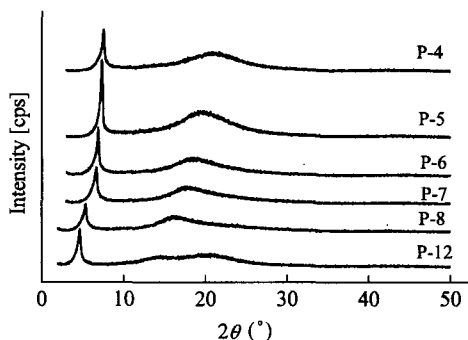


Fig. 3 Powder X-ray diffraction patterns for P-*n*

Figure 3 shows the WAXD powder patterns of P-*n* having been annealed in and quenched from the liquid crystalline state. All the polymers gave smectic type X-ray diffraction patterns, showing a diffused halo at larger angles and a relatively sharp peak at lower angles. The d -spacing corresponding to the sharp peak is listed in Table 2. The d -spacing of each polymer is a little shorter than the fully extended length of its side group and increases with the increasing of the size of side group. However, the assignment of this mesophase as smectic is questionable. First, no characteristic textures of smectic phase were observed on POM; secondly, the mesophase of some other mesogen jacketed liquid crystalline polymers that gave similar XRD patterns have been assigned as nematic by Xu^[14] and Ober^[9] and their coworkers. According to these researchers, the polymer main chain can be seen as a thick rod because of the mesogen-jacketed structure. Therefore the sharp diffraction at lower angles can be attributed to the spacing between the rods rather than the thickness of smectic layers. Recently, X-ray studies on the mesophase of poly[di(4-heptyl) vinylterephthalate], which is similar with P-*n* in architecture, have been reported by us^[13]. Our experimental results have shown that poly[di(4-heptyl) vinylterephthalate] forms a thermotropic hexagonal columnar phase with $a = b = 1.84$ nm by cooperative assembly of main chains and side

groups. Because the chemical structure of P-*n* is similar to that of poly[di(4-heptyl)vinylterephthalate], they may also form a hexagonal columnar phase. Nevertheless, more studies are needed before one can identify definitely the type of the mesophase of these new polymers.

Table 2. XRD data of powder samples quenched from liquid crystalline state

Sample	2θ (°)	d -spacing (nm)	l^* (nm)
P-4	6.56	1.35	1.52
P-5	6.36	1.39	1.57
P-6	5.90	1.50	1.77
P-7	5.64	1.57	1.79
P-8	5.40	1.64	1.85
P-12	4.66	1.89	2.18

* Calculated full length of side group of P-*n*

It is interesting to consider why these polymers form so stable a liquid crystal phase. For low molar mass compounds, the primary factors for the formation of a liquid crystal phase are the overall molecular shape, the anisotropic polarizability and the rigidity of the compound. A common type of molecular species that forms thermotropic liquid crystals possesses an axial core fitted with flexible chains at each end^[15]. Generally, the central core consists of two or more 1,4-phenylene rings with conjugated interconnecting linkages. When a large number of these molecules are linked together they form polymeric liquid crystals. However in our new polymers, no such conventional mesogenic units are incorporated. The basic building blocks are di(cycloalkyl) terephthalate (as side group) and the polymer backbone. The side groups are formed by only one phenylene ring and two flexible cycloalkyl rings. Di(cycloalkyl) terephthalates do not form any liquid crystal phase probably because they do not have a rod-like shape with significant length-to-width ratio and polarizability. On the other hand, the polymer backbone is nothing more than a substituted polyethylene chain and is also non-mesogenic. Thus, we cannot find the answer for the liquid crystallinity of the polymers from either the viewpoint of the polymer backbone or the side groups. The answer must then lie in the restricted molecular geometry and the reduced molecular flexibility of these mesogen-jacketed type polymer molecules as a whole. In poly(dicycloalkyl vinylterephthalate) there is a side group di(cycloalkyl vinylterephthalate) laterally attached to each repeating $-\text{CHCH}_2-$ unit of the polymer backbone. Thus, the population of the side groups around the main chain is very high and accordingly the free volume for the bulky side groups is small. The inversion between the axial and the equatorial conformers of cycloalkyl ring is dramatically hindered by the steric interaction. To increase the packing efficiency and to reduce the repulsive force among the side groups as much as possible, the equatorial conformers will be strongly favored and the side groups tend to extend fully and align orderly. Therefore, the originally flexible and potentially linear shaped di(cycloalkyl) terephthalate groups are converted to the rigid and linear shaped mesogenic units, resulting in the formation of a liquid crystal phase. In other words, the spatial interaction of the side groups plays very important role in the mesophase formation of the title polymers.

CONCLUSIONS

The results discussed above suggest that dynamic variations in molecular structure, such as conformational and geometrical changes, have to be taken into account in the way a mesophase is formed and stabilized while designing liquid crystalline polymers. As we have shown, the flexible building blocks like polyethylene backbone and 2,5-bis[(cycloalkyloxy)carbonyl]phenyl can be used to construct liquid crystalline polymers in an appropriate way. Therefore, we have shown a strategy of designing liquid crystalline polymer by taking advantage of the cooperative interaction of backbone and side groups. Our new strategy is to make use of the spatial interaction among the main chain segments and the side groups so as to convert the originally flexible moieties into rigid mesogenic units and make the liquid crystal phase highly stabilized. This strategy is quite different from what has been applied to other liquid crystal polymers, in which the structure of mesogenic units is often so modified as to increase their rigidity, polarity, polarizability and the length to diameter ratio of the mesogenic rods, but the

important role that the spatial interactions of side units play in forming the mesophase is unfortunately neglected. Because the structure and properties of both backbone and pendent group can be easily tailored, the preparation of liquid crystalline polymers with novel functions is possible according to this strategy.

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