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Synthesis of a New Side-Chain Type Liquid Crystal Polymer Poly[dicyclohexyl vinylterephthalate]

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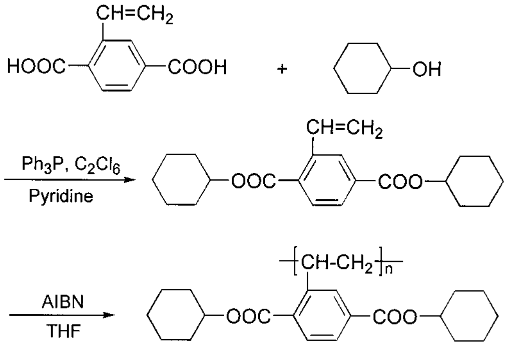
Scheme 1. Synthesis and Chemical Structure of the Monomer and the Polymer



Introduction. The properties and the chemical structure dependence of side-chain liquid crystal polymers have been extensively studied in recent years because of their potential applications in nonlinear optics, information storage, and display devices.[1,2] A side-chain liquid crystal polymer often comprises three basic components: a polymer backbone, a mesogenic unit, and a flexible spacer that bridges the mesogenic unit and the polymer backbone. Its properties may be affected by varying the chemical structures of these components. Empirical rules have been developed for systematically producing side-chain liquid crystalline polymers.[3,4] According to Finkelmann et al.,[5] if mesogenic groups are directly attached to the polymer main chain, thermal motions of the polymer segments and mesogenic groups are directly coupled. When the temperature is above the T_g, the polymer tends to adopt statistical chain conformations that hinder the anisotropic orientation of the mesogenic groups. Therefore, flexible spacers should be inserted between the backbone and mesogenic units to decouple their interactions. In such conditions, the mesogenic side chains can be anisotropically ordered in the liquid crystal state even though the polymer main chains tend to adopt the statistical random coil conformations. This idea of Finkelmann has been proven by many experiments and becomes a useful guide for molecular design of side-chain liquid crystalline polymers. On the other hand, the mesogen-jacketed liquid crystalline polymers (MJLCPs) form a different class of liquid crystalline polymers, not described by Finkelmann model.[6] In MJLCPs, the rodlike mesogenic units are connected at their gravity center (or a nearby position) to the main chain through no or only very short spacers. It has been proven that in this case the introduction of the flexible spacers to decouple the interactions of the main chain and the mesogenic side groups is not necessary for the polymer to form a liquid crystalline phase.[6−8] However, the rigid mesogenic units are believed to be essential for these two classes of the side-chain type polymers to form a liquid crystal phase, although in some cases the mesogenic group itself cannot form a stable liquid crystal phase,[9] and in few others the low molar mass liquid crystals can be flexible molecules.[10] Here we report the synthesis of a new polymer poly[di(cyclohexyl) vinylterephthalate] in which neither flexible spacers nor conventional rigid mesogenic units are included. We found that this polymer is amorphous below T_g but forms a liquid crystal phase above T_g. To our knowledge, it is the first liquid crystalline polymer that consists of nonrigid mesogenic side groups laterally attached to the main chain through no decoupling spacers.

Synthesis. The synthetic route of the monomer and polymer is shown in Scheme 1.

Vinylterephthalic acid (0.77 g, 4.0 mmol) and triphenylphosphine (2.2 g, 8.4 mmol) were dissolved in about 10 mLof dried pyridine to obtain solution A. Dried cyclohexanol (0.84 g, 8.4 mmol) and hexachloroethane (2.1 g, 8.8 mmol) were dissolved in 10 mL of dried pyridine to obtain solution B. Solution B was then dropped into solution A slowly. 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 three times. The organic layer was dried over anhydrous sodium sulfate and chloroform was removed by vacuum distillation. The residue was purified using column chromatography on silica gel with chloroform as eluant to obtain a colorless sticky liquid, 0.91 g (yield 64%). The structure of the monomer was proven by mass spectroscopy (VG-ZAB-HS instrument), ^{1}H NMR spectrometry (Bruker ARX 400), and IR (Vector 22 FT-IR) as follows: mass spectrum 356(parent), 274(base), 257,-193,192,175; ^{1}H NMR 1.30−1.96, m, 20H, 2× (5-CH_2−); 5.01−5.05, m, 2H, 2× (−OCH−); 5.39−5.77, 2d, 2H(═CH_2); 7.36−7.50, q, 1H (−CH═); 7.88−8.24, m, 3H (phenyl); IR(cm^{-1}) 1244 (C−O−C), 1717 (C═O), 2860 (CH_2, ν_{as}), 2936 (CH_2, ν_s).

The polymerization of the monomer was carried out in THF solution at 60 °C using 0.3% mol equiv AIBN as initiator. The polymer was precipitated in and washed with methanol. The molecular weight of the polymer was determined by a Waters 201 GPC instrument with polystyrene as standard. Found: $M_n = 2.7 \times 10^4$, $M_w/M_n = 2.4$.

Results and Discussion. The monomer was an oily liquid at room temperature, and no mesophase was detected by means of polarizing optical microscope (POM). Its differential scanning calorimetry (DSC) curve showed also only one melting endotherm at −30 °C.

The monomer was easily polymerized to a moderately high molecular weight polymer by way of convenient radical polymerization. The WAXD of powder samples showed that the polymer was amorphous at room temperature. The lack of any crystallinity of this and other homologous MJLCPs[6] indicates that the bulky side groups hinder the crystallization of these polymers as what the phenyl group does for atactic polystyrene. Since the TGA analysis (at a heating rate of 20 °C/min in nitrogen atmosphere) had showed a 1% weight loss

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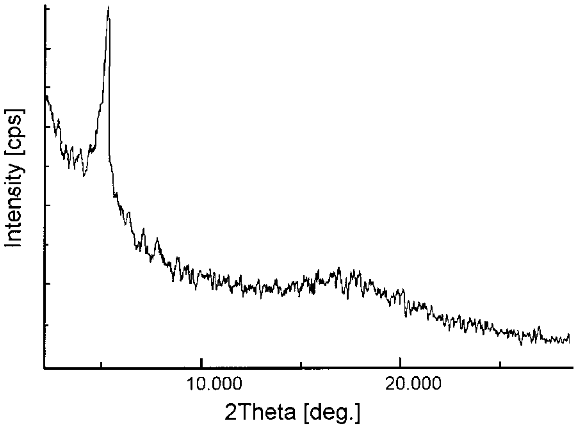

Figure 1. Powder X-ray diffraction pattern of the polymer after treated at 210 °C for 30 min in argon.

at 293 °C, our DSC experiments were run so as not to exceed this temperature. The DSC heating curve showed no endothermic peak but only one glass transition at 99 °C which is 20 °C degrees lower than the T_g of its homologous polymer poly[bis(*p*-methoxyphenyl) vinylterephthalate).[11] These two polymers have the same carbon−carbon main-chain but different side groups. It is bis(*p*-methoxyphenyl) terephthalate for the one with higher T_g but di(cyclohexyl) terephthalate for the polymer of this report. Because, for the carbon−carbon chain polymers, the polymer with higher steric hindrance parameter would have higher T_g and less chain segment mobility,[12] we see that the chain of poly[bis(*p*-methoxyphenyl) vinylterephthalate) is more sterically hindered by the side groups than the chain of the title polymer which has less rigid side groups.

When observed under a polarizing optical microscope, the polymer softened at about 140 °C and formed a liquid crystal phase which showed increased birefringence with time. The birefringence remained strong above this temperature until at about 300 °C when extinction slowly occurred. However, no typical textures of this birefringent phase could be used to identify the mesophase. Therefore, a Rigaku Dmax-2400 diffractometer (with a nickel-filtered CuKα, 40 kV voltage, 30mA electric current, a scanning rate of 5°}/min, and a scanning scope 1.5−40°) was used to take its X-ray diffraction. The polymer was heated at 210 °C (significantly higher than its T_g of 99 °C but still much lower than its T_d of 293 °C) for 30 min in argon atmosphere so that the liquid crystal phase was formed. It was then quenched to room temperature with ice water to obtain a glassy liquid crystalline phase. After this treatment the sample was used for the X-ray diffraction study. The diffraction pattern is shown in Figure 1. A diffused scattering halo at angles around $2\theta = 16.54°$ and a sharp diffraction peak at $2\theta = 5.32°$ can be seen in the curve. This result may be interpreted by the presence of a smectic-type structure. Thus the diffraction around 16.54° is attributed to the spatial correlation between di(cyclohexyl) terephthalate side groups, while the sharp diffraction at 5.32° (corresponding to a distance of 1.66 nm) is attributed to the layer thickness. Since the observed thickness is shorter than the fully extended length of 1.73 nm of the side groups, the side groups must be arranged in the layer so that the long axis tilts away from the layer normal. The tilt angle is calculated to be 20.3° since its cosine is 1.66/1.73. Considering the size of the tilt angle a smectic-C phase might be assigned to this phase. However, the phase could instead be assigned to nematic if the arguments of Xu et al.[13] and Ober et al.[14] were applied. Following these workers, because of the mesogen-jacketed structure, the polymer chain can be seen as a thick rod so that the sharp diffraction at lower angles may be attributed to the spacing between the rods rather than the thickness of the smectic layers. Because we lack the detailed information of the arrangement of the side groups and their orientation relative to polymer main chain, we are not in the position to declare with any certainty the type of the mesophase of this new polymer.

Since the TGA analysis has showed a 1% weight loss at 293 °C, the slow extinction of birefringence of this polymer observed on POM at higher temperatures must be caused by thermal decomposition, and the clearing point should be higher than 290 °C if no chemical decomposition had taken place. In other words, the mesophase of this new polymer is thermally very stable.

It is interesting to ask why this polymer forms so stable a liquid crystal phase. Generally, a rodlike mesogenic unit often consists of two or more 1,4-phenylene rings with conjugated interconnecting linkages and two terminal groups. The resulting mesogenic unit should have an anisotropic linear or planar shape with enhanced anisotropic polarizability and rigidity. However in our new polymer, the side groups are di(cyclohexyl) terephthalate, formed by only one phenylene ring but two cyclohexyl rings. The two cyclohexyl rings are in principle quite flexible and cannot conjugate with the phenylene ring to which they attach through ester groups. Furthermore, there is no electron-donor or electron-acceptor substituent used in the ends of the side groups, whereas these polar substituents are necessary for low molar mass liquid crystals even if no cyclohexane ring is used.[15] Thus, the degree of conjugation and the polarity and polarizability of the side group di(cyclohexyl) terephthalate are all low and not favorable for stabilizing a mesophase. This point may be demonstrated by comparison of the two monomers, di(cyclohexyl) vinylterephthalate and bis(4-methoxyphenyl) vinylterephthalate. The former has a very low melting point at −30 °C and forms no liquid crystal phase above melting; the latter melts at 109 °C and forms a stable liquid crystal phase after melting.[11] On the other hand, because the main chain of the polymer is nothing more than a substituted polyethylene chain, we cannot find the answer from the viewpoint of the polymer backbone either. The answer must then lie in the unique architecture of this mesogen-jacketed type liquid crystalline polymer. In each repeating $-CHCH_2-$ unit of poly(dicyclohexyl vinylterephthalate) there is a side group di(cyclohexyl) terephthalate which is attached, in the side-on mode, to polymer backbone without a spacer. Thus, the population of the side groups around the main chain will be very high and accordingly the free volume for the bulky side groups will be small. The inversion between the axial and equatorial chair conformers of cyclohexyl ring is thus dramatically hindered by the steric interactions. 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(cyclohexyl) terephthalate groups are converted to 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 mesophase formation of the title polymer.

In conclusion, we have successfully synthesized a new polymer poly[di(cyclohexyl) vinylterephthalate]. Although the polymer has no rigid-rod groups as mesogenic units, as is often found in other liquid crystal polymers, it is liquid crystalline and forms a very stable liquid crystal phase in a broad temperature range from above T_g to below the thermal decomposition temperature. The liquid crystallinity of this polymer cannot be simply interpreted from the viewpoint of either rigidity or polarizability of the side groups. The strong steric interactions among the side groups and between the side groups and the main-chain segments have to be taken into prime consideration. The unique molecular construction of the mesogen-jacketed liquid crystalline polymers makes it possible to build polymeric liquid crystals by using even the originally very flexible moiety as mesogenic side groups as was demonstrated by the title polymer.

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