

SYNTHESIS OF A NOVEL "MESOGEN-JACKETED LIQUID CRYSTAL POLYMER" BASED ON VINYLTEREPHTHALIC ACID*

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Abstract Poly{2, 5-bis[(p-methoxyphenyl)oxycarbonyl]styrene} was successfully synthesized. This new polymer has a structure characteristic of mesogen-jacketed liquid crystalline polymers (MJLCPs) and does form a liquid crystal phase above its glass transition. It thus became the starting member of a new series of MJLCPs. The synthesis of the polymer as well as the liquid crystalline properties of the polymer and its monomer was discussed. A brief comparison of the new monomer and polymer with some previously reported counterparts was also included.

Keywords Mesogen-jacketed liquid crystal polymer; Vinylterephthalic acid; Poly{2, 5-bis[(p-methoxyphenyl)oxycarbonyl] styrene}

INTRODUCTION

The concept of "Mesogen-jacketed liquid crystal polymer" (MJLCP) was first proposed by Zhou *et al.* to describe the side chain liquid crystal polymers in which the mesogenic units were attached laterally to the main chain without or with only short spacers^[1,2]. Because of the spatial requirement of the bulky and rigid mesogenic units, the main chain of the polymer has to take the extended and stiffened conformation and the "jacket" is formed with the mesogenic units around the backbone. This idea was supported by Hardouin and his co-workers through their neutron scattering experimental data^[3]. Some other experimental results also showed that the mesogen-jacketed liquid crystal polymers have special characteristics which distinguished them from the normal side chain liquid crystal polymers^[4,5]. For example, the MJLCPs can form banded texture by shear flow in their liquid crystal

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state and have larger persistent length in solution^[6,7]. However, only two series of typical MJLCPs, based respectively on 2-vinyl-1,4-dihydroxybenzene and 2-vinyl-1,4-phenylenediamine, have been synthesized by now. New polymers are desired in order to have a better understanding of the structure-property relations of the MJLCPs. Besides, even for the two series of MJLCPs mentioned above, the study on their properties and structures is still limited due to the difficulties involved in the synthesis of the two types of pre-monomers. Here we report the synthesis of a new MJLCP from vinyl terephthalic acid which is new and easier to synthesize than 2-vinyl-1,4-dihydroxybenzene and 2-vinyl-1,4-phenylenediamine.

EXPERIMENTAL

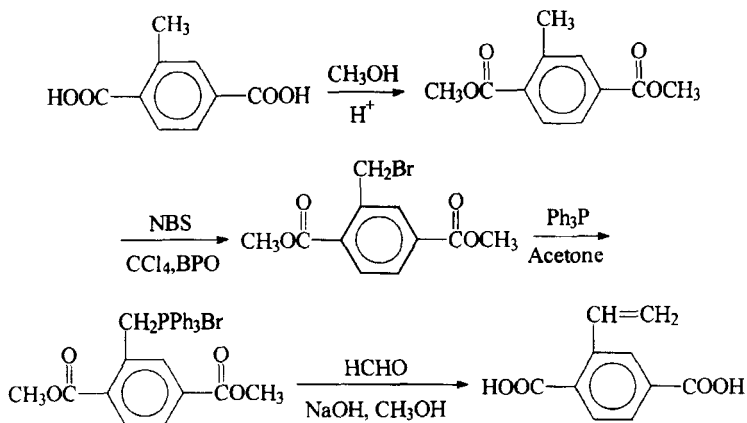
The instruments and materials

¹H-NMR spectra, Elemental analysis and Mass spectrum were obtained from Bruker ARX400 NMR spectrometer, Carlo Erba 1106 instrument and VG-ZAB-HS mass spectrometer respectively. Differential scanning calorimetry (DSC) curves were recorded on a Shimadzu DSC-50 instrument or PE 7 series. The liquid crystal properties were also characterized by a Leitz Laborlux 12 Pol polarizing optical microscope (POM) with a Leitz 350 hot stage.

The 2-methylterephthalic acid was synthesized according to the literature^[8]. The p-methoxyphenol was synthesized by the method of Klarmann et al.^[9]. All other reagents and the solvents were chemical pure or analytical reagents as received.

Synthesis of the vinyl terephthalic acid

The route of the synthesis of the vinyl terephthalic acid was shown below:



Synthesis of dimethyl methylterephthalate In a 100 mL round-bottomed flask placed

a mixture of 9.0 g methylterephthalic acid (50 mmol) and 60 mL absolute methanol. 1 mL concentrated sulfuric acid was added. A reflux condenser was attached and the mixture was boiled gently for 8 h. Distilled off the excess methanol by rotary evaporator. The residue was dissolved in benzene and washed in turn with saturated salt water for two times, sodium carbonate solution for 3 times, and saturated salt water to neutrality. After the solution was dried over anhydrous sodium sulfate, the benzene was evaporated. The residue was recrystallized in petroleum to get the crystal which melted at $76 \sim 77^{\circ}\text{C}$ (literature: $76^{\circ}\text{C}^{[8]}$). Yield 80%.

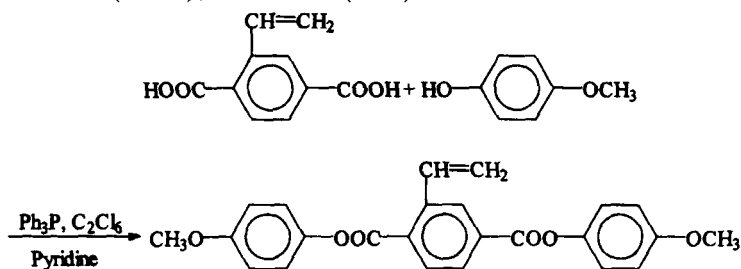
Synthesis of 2, 5-dimethoxycarbonylbenzyl phosphonium bromide In a 100 mL round-bottomed flask placed 10.0 g dimethyl methylterephthalate (48 mmol), 8.6 g N-bromosuccinimide (48 mmol), 0.5 g BPO (benzoyl peroxide) and 60 mL anhydrous carbon tetrachloride. A reflux condenser with dry tube was attached. The mixture was heated gently to reflux till the yellowish N-bromosuccinimide was transformed into the light succinimide which became suspended in the reaction mixture. Allowed the system to cool and filtered the mixture under suction. The carbon tetrachloride was evaporated by rotary evaporator and 13.0 g triphenylphosphine (50 mmol) and 40 mL acetone were added into the flask. The mixture was refluxed for 4~5 h and stood to cool. Then the mixture was filtered and the solid was washed with acetone for several times. After being dried, 16.0 g white crystals were obtained, yield 60%.

Synthesis of vinylterephthalic acid 2, 5-Dimethoxycarbonyl-benzyl phosphonium bromide 16 g and 50 mL methanol were put in a flask. Three grams of sodium hydroxide in methanol was dropped slowly into the flask while a stream of formaldehyde gas was introduced. Then 3g sodium hydroxide in water was added and the mixture was stirred at 50°C for several hours. Methanol was evaporated and the residue was filtered to remove the byproduct triphenylphosphine oxide. The filtrate was acidified by dilute sulfuric acid to $\text{pH}=2$. The solid product was filtered under suction and recrystallized in alcohol and water. A white product was got (3.1 g, yield 60%). Melting point: $302 \sim 304^{\circ}\text{C}$ (decomposing). $^1\text{H-NMR}$ (δ): 5.40~5.81, 2d, 2H($=\text{CH}_2$); 7.35 ~ 7.42, q, 1H($-\text{CH}=\text{}$); 7.85~8.16, m, 3H (phenyl); 13.14, s, 2H ($-\text{COOH}$).

Synthesis of the Monomer

Vinylterephthalic acid (4.0 mmol, 0.77 g) and triphenylphosphine (2.2 g, 8.4 mmol) were dissolved in 10 mL dried pyridine to obtain solution (A). p-Methoxyphenol (1.04g, 8.4 mmol) and hexachloroethane (2.1 g, 8.8 mmol) were dissolved in 10 mL dried pyridine to obtain solution (B). Then the solution (B) was dropped into the solution (A) slowly. The mixture was stirred at 60°C for 5 h. After cooling, the

mixture was poured into methanol/water solution. The precipitate was filtered and purified using column chromatography on silica gel with chloroform as eluant. The product was further purified by recrystallization in benzene/petroleum ether to get colorless crystal (1.1 g, yield 66%), m.p. 109~110°C. IR (cm^{-1}): 1720 ($\text{C}=\text{O}$). Mass spectrum: 404 (parent), 281 (base), 158, 130, 102. $^1\text{H-NMR}$ (δ): 3.83, 3.84, 2s, 6H, 2x($-\text{OCH}_3$); 5.47~5.86, 2d, 2H ($=\text{CH}_2$); 6.95~7.18, m, 8H (phenyl); 7.51~7.54, q, 1H ($-\text{CH}=\text{}$); 8.18~8.44, m, 3H (phenyl). Elemental analysis: Found (Calcd.): C%: 71.30(71.28), H%: 4.79 (4.98).



Synthesis of the Polymer

The radical polymerization of the monomer was carried out in THF solution at 60°C using 0.5% equivalent moles AIBN as initiator.

RESULTS AND DISCUSSION

The structures of vinylterephthalic acid and the monomer have been confirmed by the conventional analysis including proton NMR, elemental analysis, and mass spectrometry. Fig. 1 is the NMR spectrum of the monomer.

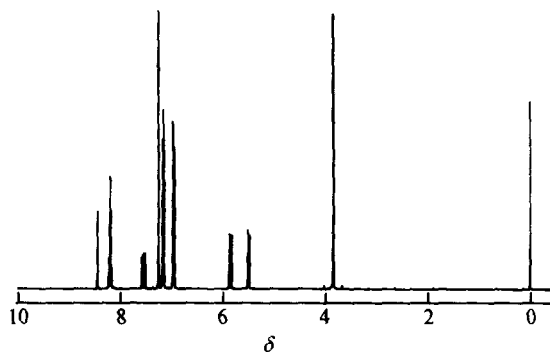


Fig. 1 The NMR spectrum of the monomer

The monomer melts at 109~110°C and forms a liquid crystalline state which

becomes isotropic at $144\sim 145^{\circ}\text{C}$. The optical textures suggest that the liquid crystal phase is nematic. Fig. 2 shows the mesophase textures of the liquid crystal state of the monomer. The phase transition of the monomer was further verified on DSC instrument under nitrogen flow with heating rate of $10^{\circ}\text{C}/\text{min}$. Fig. 3 is the DSC heating curve for the monomer, in which we see an endothermic peak centered at about 114°C (Somewhat higher than the $109\sim 110^{\circ}\text{C}$ obtained from the POM observations) and a wide exothermic peak around $150\sim 180^{\circ}\text{C}$. The first endothermic peak is the transition of the crystal to the nematic liquid crystal phase. The second wide exothermic peak is of the thermal polymerization of the monomer. The transition of the nematic liquid crystal phase to isotropic ($144\sim 145^{\circ}\text{C}$ from POM) can not be seen in this DSC figure because the expected peak was overlapped by the exothermic peak of the thermal polymerization of the monomer. It shows clearly that the monomer polymerize easily even though the two bulky substituent groups are attached to the ortho and meta position of the styrene.

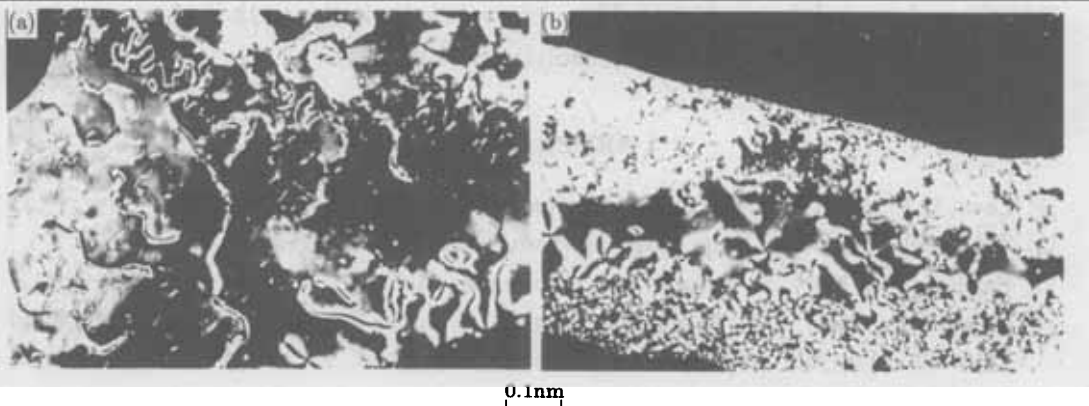


Fig. 2 Polarized microscopic textures of the monomer

- (a) inversion walls at 140°C , cooling from isotropic phase, magnification 100X;
 (b) schlieren texture at 138°C , cooling from isotropic phase, magnification 100X

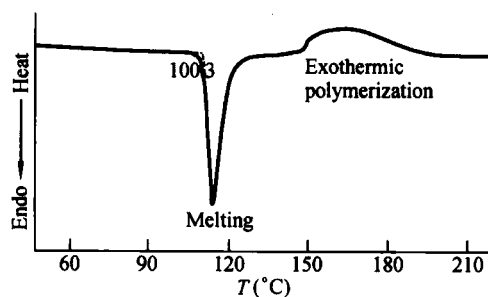


Fig. 3 DSC heating curve for the monomer

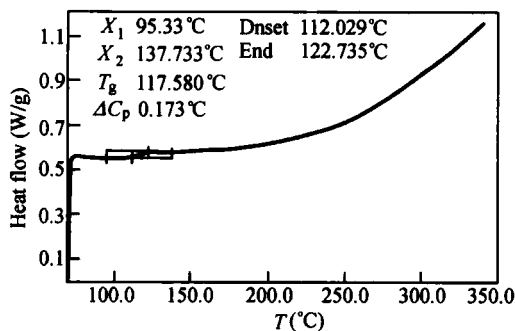


Fig. 4 DSC heating curve for the polymer

For comparison, we recall that the phase transition temperatures of the compound 2, 5-bis ((p-methoxybenzoyl)oxy)styrene are 184 and 195^[10]. Both the T_m and the T_i of our new monomer are much lower. The similar phenomenon has been observed and explained by many chemists^[11~13]. However, it is still interesting to note that the difference in the structure of these two monomers is only the order of $-\text{C}(=\text{O})-$ or $-\text{OC}(=\text{O})-$. A slight change in structure has resulted in a significant change in properties.

The polymer, which was obtained from the solution polymerization, has the molecular weight M_n of 2.0×10^4 and the M_w/M_n of 2.5 as determined by using GPC with polystyrene as standard in THF. On the polarizing optical microscope, we observed that the polymer was not crystalline but softened at around 160°C to form a liquid crystal phase. No clearing transition was observed below 320°C. Above this temperature the sample started to decompose making the T_i determination very difficult. The DSC heating curve for the polymer (see Fig. 4) showed also only a T_g (118°C) and not a T_i below 350°C. This observation is similar to that of our previous polymer poly[2, 5-bis((p-methoxy-benzoyl)oxy)styrene]^[6].

REFERENCES

- [1] Zhou, Q.F., Li, H.M., Feng, X.D., *Macromolecules*, **1987**, *20*, 233
- [2] Zhou, Q.F., Zhu, X.L., Wen, Z.Q., *Macromolecules*, **1989**, *22*, 491
- [3] Hardouin, F., Mery, S., Achard, M.F., Noirez, L., Keller, P., *J. Phys. II*, **1991**, *1*, 511
- [4] Zhou, Q.F., Wan, X.H., Zhang, D., Feng, X.D., "ACS Symposium Series 632: Liquid Crystalline Polymer Systems — Technological Advances", Edited by Isayev, A.I., Kyu, T., Cheng, S.Z.D., **1996**, p.344
- [5] Zhang, D., Zhou, Q.F., Ma, Y.G., Wan, X.H., Feng, X.D., *Polymer for Advanced Technology*, **1997**, *8* (4), 227
- [6] Xu, G., Wu, W., Shen, D., Hou, J., Zhang, S.F., Xu, M., Zhou, Q.F., *Polymer*, **1993**, *34* (9), 1818
- [7] Wan, X.H., Zhang, F., Wu, P., Zhang, D., Feng, X.D., Zhou, Q.F., *Macromol Symp.*, **1995**, *96*, 207
- [8] Bertley, W.H., *J. Chem. Soc.*, **1897**, *71*, 179
- [9] Klarmann, E., Catyas, Z.W., Shternov, V.A., *J. Am. Chem. Soc.*, **1932**, *54*, 303
- [10] Zhou, Q.F., Wan, X.H., Zhu, X.L., Zhang, F., Feng, X.D., *Mol. Cryst. Liq. Cryst.*, **1993**, *231*, 107
- [11] Dewar, M.J.S., Goldberg, R.S., *J. Org. Chem.*, **1970**, *35*, 2711
- [12] Dewar, M.J.S., Riddell, R.M., *J. Am. Chem. Soc.*, **1975**, *6658*
- [13] Uryu, T., Kato, T., *Macromolecules*, **1988**, *21*, 378