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Synthesis and Polymerization of 2,5-Bis(4'-alkoxyphenyl)styrene for Mesogen-Jacketed Liquid Crystal Polymers

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SUMMARY: A series of novel reactive liquid crystals, 2,5-bis(4'-alkoxyphenyl)styrene, was designed and synthesized to prepare stereoregular mesogen-jacketed liquid crystal polymers (MJLCPs). These monomers are different from their analogous studied previously in that they do not contain polar linkages such as ester or/and amide group and therefore are expected to polymerize easily both by radical and ionic polymerization. The preliminary studies show that the resulting polymers have higher glass transition temperature (Tg) and much better thermal stability than their analogous.

Introduction

Liquid crystal polymers (LCPs) have received long-standing attention for applications in engineering plastics and optic, electrooptic, or nonlinear optic devices$^{1)}$. Most of the LCPs have mesogenic units as building blocks. Depending on their architecture, LCPs can be divided into two categories$^{2-5)}$, namely main chain liquid crystal polymers (MC-LCPs) and side chain liquid crystal polymers (SC-LCPs). The former has the mesogens incorporated into the polymer backbones, the later has the mesogens attached to the main chain of macromolecules as side groups. According to Finkelmann$^{6)}$, flexible links are needed to decouple the movements of the main chain and of the mesogenic side groups for SC-LCPs to achieve the liquid crystallinity. Thereafter, the statistical movements and conformational changes of the main chain backbones will have little effects on the self-organization of the mesogens. As a result, SC-LCPs resemble in many of their properties the analogous small liquid crystal molecules and are expected to show rapid response to outer electro-magnetic fields. On the other hand, because of the molecular constitution and the inherent rigidity of rod-like mesogens, MC-LCPs are rigid or semi-rigid and are applicable as high strength and high modulus materials with high heat deflection temperatures.

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A couple of years ago, Zhou and coworkers initiated a research program on another class of LCPs[7, 8)], mesogen-jacketed liquid crystal polymers (MJLCPs). This kind of novel liquid crystalline materials are constructed by laterally attaching the mesogenic units to the main chain via no or only short spacers. Compared to the most intensively studied SC-LCPs, the main chain of MJLCPs are forced to extend and to take rigid conformation because of high population of both bulky and rigid side groups around the backbone. Therefore, the properties of rigid or semi-rigid polymers as represented by main chain type liquid crystal polymers are exhibited. Additionally, the advantages of MJLCPs, compared to MC-LCPs, are they may be synthesized by chain polymerization as for many conventional side chain type liquid crystal polymers.

Since then, we have prepared and characterized a wide array of MJLCPs. Figure 1 shows the chemical structures of some representative monomers for MJLCPs. Most of them were prepared based on vinylhydroquinone[4)], 2-hydroxy-5-aminostyrene[9)], 2,5-diaminostyrene[10)] and vinylterephthalic acid[11)] respectively and the mesogenic groups were usually made up of three benzene rings linked together by ester or/and amido groups. Recently, we found that by using the unique architecture of MJLCPs no traditional rigid rod-like mesogenic units were actually needed for realization of liquid crystallinity of polymers[12-14)]. Thereafter, a new design strategy of LCPs with flexible and apolar building blocks was suggested[15)].

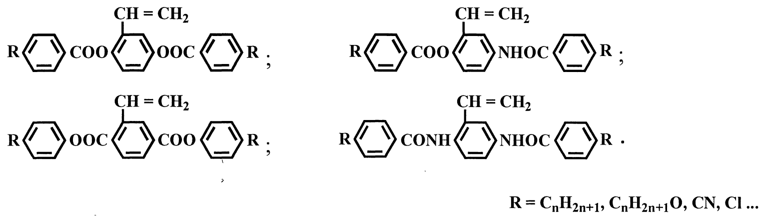
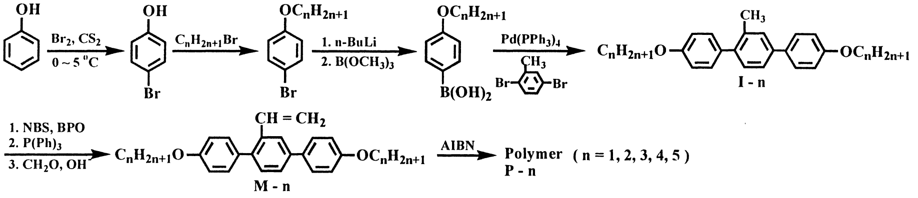


Figure 1. Monomer structures of some representative MJLCPs.

Unfortunately, all previously reported MJLCPs were synthesized by free radical polymerization and hardly by anionic or cationic living polymerization since the polar linkage groups of mesogens, like -COO- and -CONH-, tend to react with the active species severely. This restricts their application in synthesis of macromolecules with complex and controlled architectures.

Our synthetic focus of the present work has been on the design and synthesis of stereoregular MJLCPs, which are expected to be much different from those reported previously in many aspects. This paper reports on synthesis and polymerization of 2,5-bis(4'-alkoxyphenyl)-styrene, where para-terphenyl subsituted by alkoxy groups at both ends is used as mesogenic side group. Because of the absence of the polar linkage groups as employed in previous reported MJLCPs, 2,5-bis(4'-alkoxyphenyl)styrene would be polymerized easily by both free radical polymerization and ionic polymerization.



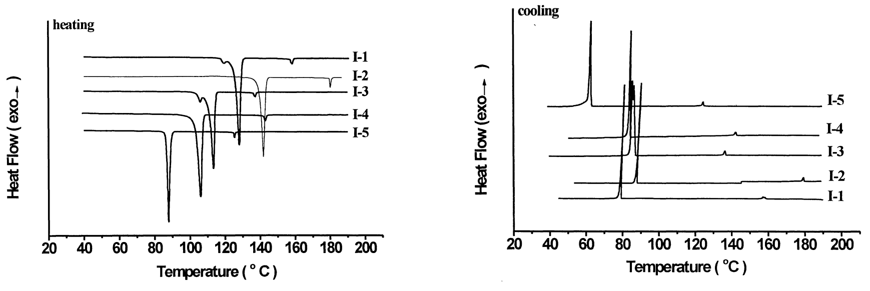
Scheme 1. Synthetic route.

Synthesis

In order to meet our requirements, a multi-steps synthetic route was designed as outlined in the Scheme 1. p-Bromophenol was prepared from phenol. 4-Methoxybromobenzene and 4-ethoxybenzene were obtained by etherification of p-bromophenol with dimethyl sulfate and diethyl sulfate respectively. Other 4-alkoxy-bromobenzenes were synthesized by etherification of p-bromophenol with corresponding alkyl bromides. The obtained 4-alkoxy-bromobenzenes were treated with n-BuLi in dry THF at –78 °C under argon, followed by reaction with trimethylborate, and finally hydrolysis with hydrochloric acid to form p-alkoxyphenylboronic acid. The next step was the tetrakis(triphenylphosphine)palladium-catalysed Suzuki cross-coupling reaction of p-alkoxyphenylboronic acid with 2,5-dibromotoluene. The resulting product was purified by column chromatography (silica gel, dichloromethane/pertroleum ether) followed by recrystallization from the mixture of petroleum ether and dichloromethane. Target monomers were prepared using aqueous Wittig reaction as the key step. The structures of the intermediates and monomers were confirmed by conventional techniques including proton NMR, mass spectrometry, FTIR and elemental analysis.

Thermal behaviour of I-n

All intermediates and monomers are white crystals at room temperature. Their melting and liquid crystal phase transitions were characterized by DSC and polarized optical microscope. Figure 1(a) shows the DSC thermograms of the key intermediates on heating scans. Each curve of compounds I-2, I-4 and I-5 contained two endothermic peaks. When observed under polarized optical microscope, the first peak at lower temperature was due to melting transition, and the second peak at higher temperature corresponded to the transition from anisotropic phase to isotropic phase. The DSC curves of I-1 and I-3 show another small endothermic peak at the temperature below melting point. They may have been caused by crystal-crystal transitions.



(a) (b)

Figure 1. DSC thermograms of the compounds I-n obtained on (a) heating and (b) cooling.

On cooling, all samples display two ordered transitions (Figure 1(b)). Supercooling of the crystallization temperature occurred with all compounds investigated, but this was not significant for the transition of the isotropic state to mesophase.

The results of DSC studies are listed in Table 1. The enthalpy values corresponding to the second transition are less than 1.7 kJ/mol, which are in the same order of phase changes from nematic state to isotropic state. Therefore, the formation of nematic mesophases is suggested.

Table 1. Properties of the key intermediates I-n.

Compounds	Phase transitions(°C) and corresponding enthalpy changes(KJ/mol)	
	Heating	Cooling
I-1	K128.2(35.2)N158.6(1.15)I	I157.4(1.28)N81.6(33.1)K
I-2	K142.0(39.6)N180.6(1.75)I	I179.5(1.71)N90.9(29.5)K
I-3	K113.5(40.9)N137.5(0.93)I	I136.5(0.67)N85.8(28.6)K
I-4	K106.1(37.6)N143.1(1.43)I	I142.4(1.10)N85.3(30.1)K
I-5	K87.8(29.3)N125.5(0.95)I	I124.6(1.02)N63.2(24.9)K

Figure 3 is a representative polarized optical micrograph showing the schlieren texture of I-5. In this photograph there are a series of black brushes connected to point defects. The presence of two as well as four brushes is also shown. The texture observed by polarized optical microscope and the small enthalpy changes are characteristics of nematic mesophases.

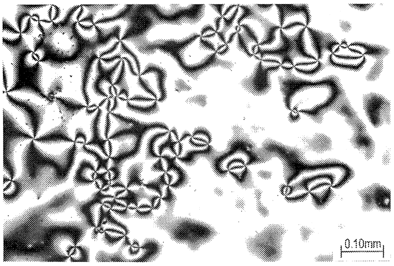


Figure 3. Polarized optical micrograph of the compound I-5 taken at 122 °C.

In figure 4, melting and clearing temperatures of I-1 to I-5 as a function of length of the end groups are plotted. Both melting and clearing points of the intermediates decrease regularly in a zig-zag fashion as the number of methylene groups increased. This is quite common in many low molecular weight liquid crystalline compounds

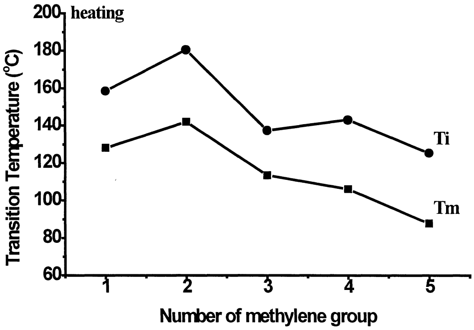


Figure 4. Dependence of the phase transitions of I-n on the number of the methylenic units in the n-alkoxy end groups.

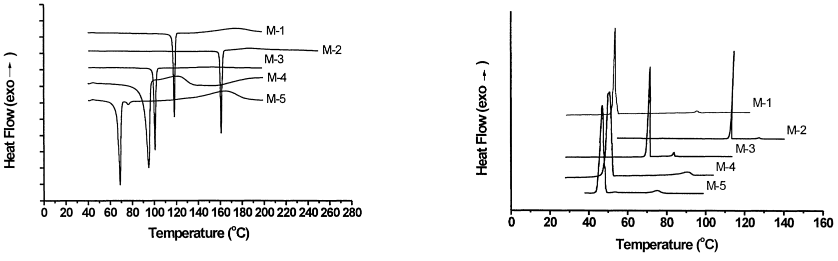
Thermal behaviour of M-n

The melting and liquid crystalline phase transitions of monomers are summarized in Table 2. Compared to their predecessors, the attachment of bulky vinyl groups as substituents led not only to a decrease in melting temperature, but also to distinctly reduced liquid crystalline temperature ranges, or to a reduced stability of the mesophases, presumably because of the increased separation of mesogens.

Table 2. Properties of the monomers M-n.

Monomers	Phase transitions (°C) and corresponding enthalpy changes (KJ/mol)		Thermal induced polymerization (°C)
	Heating	Cooling	
M-1	K118.4(30.4)I	I96.9(0.55)N54.0(16.3)K	173.2
M-2	K161.0(25.3)I	I127.6(0.60)N114.9(17.6)K	187.2
M-3	K100.8(30.9)I	I83.8(0.87)N71.8(26.7)K	152.6
M-4	K94.6(30.0)I	I90.8(0.73)N51.0(15.2)K	122.3
M-5	K69.2(27.6)N76.8(0.69)I	I75.3(1.09)N47.2(27.8)K	165.3

Figure 5(a) shows the DSC heating scans of the monomers. M-1, M-2, M-3 and M-4 contain one endothermic peak and one exothermic peak, which correspond to the melting transition and the thermal induced polymerization. The thermal behaviour of the monomer M-5 is quite different from the other four compounds. In addition to the previously observed endothermic melting peak at 69.1 °C and the exothermic polymerization peak at 163.2 °C, a small endothermic peak at 76.5 °C was observed, which corresponds to the clearing transition of the mesophase.



(a) (b)

Figure 5. DSC thermograms of the monomers M-n obtained on (a) heating and (b) cooling scans.

When the samples were cooled from the isotropic melt before the polymerization started, the two ordered transitions took place. This means that the monomers M-1, M-2, M-3, M-4 exhibit a monotropic mesophase and M-5 an enantiotropic one.

Figure 6 shows the microphotograph of the monomer M-5 taken at 74 °C with magnification of one hundred. It also shows the birefringent mesophase with nematic schlieren textures.

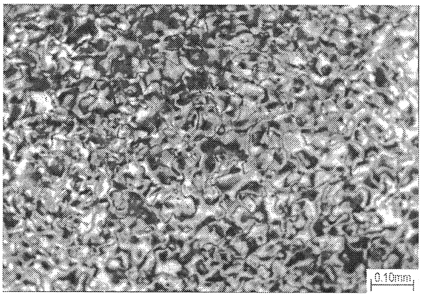


Figure 6. Polarized optical micrograph of the monomer M-5 taken at 74 °C.

Properties of polymers

All the monomers are easily polymerized to moderately high molecular weight polymers by the way of convenient radical polymerization. The results of polymerization and characterization of resulted polymers were summarized in Table 3. P-n is thermally stable. As can be seen from Table 3, the temperature of 5% weight loss of the polymers in N_2 is higher than 360 °C. P-1 undergoes a glass transition (Tg) at 229 °C. When observed under thermal polarized microscopy, the powder samples were only slightly birefringent presumably because of the presence of a low degree of mesomorphic order formed during preparation of the samples. When they were heated to above Tg, immediate development of birefrigence was observed. In addition, no visual disappearance of birefrigence was observed before the polymer decompose. This means that the mesophase formed by P-1 is very stable. The thermal behaviour of P-2, P-3, P-4 and P-5 is almost the same as this of P-1 except their glass transition temperatures decrease with the increase of the length of the end group.

Table 3. Properties of the resulting polymers P-n.

Polymers	Mn × 10^{-4}	Mw/Mn	Tg (°C)	Td (°C, 5% weight loss)	Liquid crystallinity
P-1	3.05	3.85	229.5	371.8	yes
P-2	0.60	3.10	182.0	371.0	yes
P-3	4.05	1.96	166.3	362.7	yes
P-4	1.34	1.90	159.6	385.6	yes
P-5	4.73	1.85	140.5	366.1	yes

Conclusions

To conclude, a series of novel MJLCPs was successfully prepared by free radical polymerization of newly synthesized monomers, 2,5-bis(4-alkoxyphenyl)styrene. The preliminary studies showed that all the polymers had a higher glass transition temperature and a much better thermal stability than their analogous. These polymers formed very stable liquid crystal phases above Tg. These monomers were different from their analogous studied previously in that they contained no polar linkages such as ester or/and amide group. It was expected that stereoregular MJLCPs could be produced from them. The controlled polymerization is under way.

Acknowledgement

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References

1. Blumstein, A., *Polymeric Liquid Crystals*, Plenum Press: New York, **1985.**
2. McArdle, C. B., *Side Chain Liquid Crystal Polymers*, Blackie and Sons: Glasgow, **1989.**
3. Donald, A. M., Windle, A. H., *Liquid Crystalline Polymers*, Cambridge University Press: Cambridge and New York, **1992.**
4. Zhou, Q. F., Wan, X. H., Zhang, D., Feng, X. D., *In Liquid Crystalline Polymer Systems—Technological Advances*, Isayev, A. I., Kyu, T., Cheng, S. Z. D. Eds., ACS Symposium Series 632: Washington, D.C., **1996.**
5. Percec, V., Pugh, C., in *Reference 2*, p30-105, and the references cited therein.
6. Finkelmann, H., Ringsdorf, H., Wendorff, H. J., *Makromol. Chem.,* **1978**, 179, 273.
7. Zhou, Q. F., Li, H. M., Feng, X. D., *Macromolecules,* **1987**, 20, 233.
8. Zhou, Q. F., Zhu, X. L., Wen, Z.Q., *Macromolecules*, **1989**, 22, 491.
9. Wan, X. H., Zhou, Q. F., Zhang, D., Zhang, Y., Feng, X. D., *Chemical Journal of Chinese Universities*, **1998**, 19, 1507.
10. Zhang, D., Zhou, Q. F., Ma, Y. G., Wan, X. H., Feng, X. D., *Polymer for Advanced*

Technology, **1997**, 8 (4), 227.

11. Zhang, D., Liu, Y., Wan, X., Zhou, Q. F., *Macromolecules,* **1999**, 32, 5183.
12. Zhang, D., Liu, Y., Wan, X., Zhou, Q. F., *Macromolecules,* **1999**, 32, 4494.
13. Tu, H., Zhang, D., Wan, X., Chen, X., Zhou, Q. F., *Macromol. Rapid. Commun.,* **1999,** 20, 555.
14. Tu, H. L., Wan, X. H., Liu, Y. X., Chen, X., Zhang, D., Zhou, Q. F., Shen, Z. H., Ge, J. S., Cheng, S. Z. D., *Macromolecules*, **2000**, 33, 6315.
15. Tu, H. L., Wan, X. H., Zhang, D., Zhou, Q. F., submitted to *Chemistry of Materials*.