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Synthesis and Properties of Polyacetylene Liquid Crystals Containing Perfluorinated Alkyl Chain

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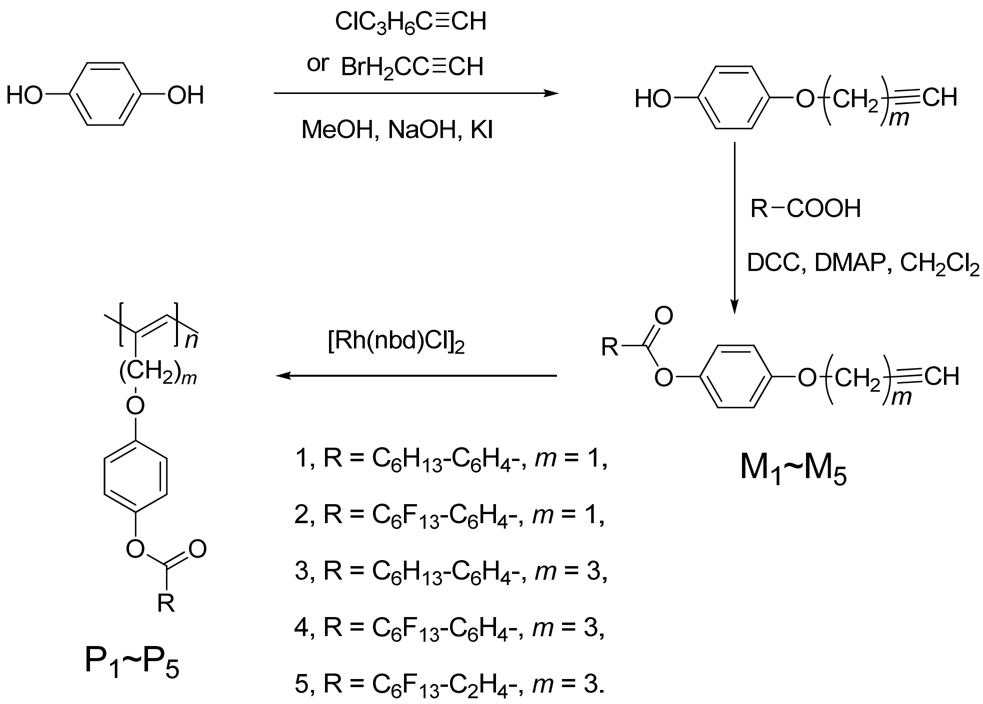
Abstracts: Liquid crystal monomers and polymers containing fluorinated alkyl chain have been prepared. The polymerization initiated by $[Rh(nbd)Cl]_2$ has afforded the products in moderate to high yields. The molecular weight of polymers has been measured with gel permeation chromatography (GPC), the results show that the transition metal catalyst in THF/Et_3N solvent system gives the best results for the polymerization. Monomers and polymers are characterized by IR and ^{1}HNMR, and the liquid crystalline properties are evaluated by using POM, DSC and TGA. The results show that the monomers with fluorinated chain and polymers show SmA phase. The fluorinated polymers possess higher clearing points and broader mesophases than the alkyl chain polymers.

Keywords: conjugated polymers; polyacetylenes; liquid crystals; liquid-crystalline polymers; SmA phase; fluorophobic effect; microsegregation

Introduction

Polyacetylene is an important kind of conjugated polymers with novel structures and special properties, and it has been extensively studied for its potential industrial applications [1,2]. Recently, liquid crystalline polyacetylenes have been investigated by many research groups [3-5]. However, the results show that it is difficult to display satisfactory phase behavior at low temperature because of the rigid backbone. Unsubstituted polyacetylene is unstable at room temperature, its low thermal stability and poor solubility in organic solvents prevent its practical applications.

Achiral liquid crystals with perfluorinated or semi-perfluorinated alkyl chain can display ferroelectric liquid crystalline properties, which have great potential applications in flat panel display industry [6]. Fluorophilic effect between perfluorinated chains of liquid crystals can increase the melting points and clearing points, enhance their thermal stability, and promote the ordered layer self organization. Fluorinated liquid-crystalline polymers are a relatively new class of macromolecules [7-12]. Perfluorinated alkyl chain is more rigid and less flexible than alkyl chain, therefore it can enhance the thermal stability of polyacetylene (the main chain) and induce the polymer to show liquid crystalline behavior. We have synthesized discotic liquid crystalline polyacetylenes [5] and fluorinated rod-like liquid crystals [6]. On the basis of these work, we design and synthesize liquid crystalline polyacetylenes with fluorinated alkyl chains, and study the physical properties of the monomers and polymers. The synthetic route for the monomers and polyacetylenes, see Scheme **1**.



Scheme **1** Synthesis of liquid crystalline monomers and polyacetylenes

Table 1 Polymerizations of the monomer (**M1-M5**)[a]

Entry	Monomer	Solvent[b]	Yield (%)	*Mw*[c]	*Mw/Mn*[c]
1	**M4**	THF/Et_3N	77.5	5,073	1.3
2	**M4**	Toluene/Et_3N	64.2	5,344	1.4
3	**M4**	DCM/Et_3N	75.2	6,059	1.3
4	**M4**	DMF/Et_3N	66.9	4,158	4.0
5	**M4**	$CHCl_3$/Et_3N	72.4	5,286	1.2
6	**M1**	THF/Et_3N	88.7	33,168	1.4
7	**M2**	THF/Et_3N	66.7	5,156	1.4
8	**M3**	THF/Et_3N	91.0	25,987	1.3
9	**M5**	THF/Et_3N	63.0	7,581	1.5

[a] Carried out under nitrogen at room temperature for 24h, $[Rh(nbd)Cl]_2$ catalyst, [M]:[cat] = 50:1

[b] For the mixture of THF/DCM/Toluene/DMF with Et_3N, volume ratio = 3:1.

[c] Estimated by GPC in THF on the basis of a polystyrene calibration.

Results and Discussion

Synthesis

The monomers have been prepared through conventional etherification and esterification reactions, and they have been purified by column chromatography. The polymerization of **M4** has been initiated by $[Rh(nbd)Cl]_2$ as the catalyst in different solvents for the optimization of reaction conditions. The molecular weight and distribution of **P4** in Table 1 shows obvious difference (Entry 1 to 4). Entry 4 in Table

1 shows that polymerization in DMF/Et_3N solvent system gives the macromolecule in much wider molecular weight distribution, while THF/Et_3N solvent system gives the polymer in high yield and narrow molecular weight distribution. So THF/Et_3N solvent system is chosen for the polymerization of other acetylene derivatives. The alkyl chain polymers **M1** and **M3** are prepared in higher yields, show higher molecular weights and better solubility in organic solvents than that of the fluorinated polymers.

Structural Characterization

The structures of monomers and polymers are confirmed by IR and ^1H NMR spectra. Figure 1 shows the IR spectra of monomer **M3** and its polymer **P3**. The monomer **M3** gives a strong sharp peak at 3271 cm^{-1} and a weak peak at 672 cm^{-1} due to C≡C stretching and ≡C-H bending vibrations, respectively. A small weak peak is shown at 2116 cm^{-1} for C≡C stretching. All the peaks of terminal alkynyl group, however, disappear in the spectrum of **P3**, indicating the acetylene triple bond of the monomer consumed in the polymerization.

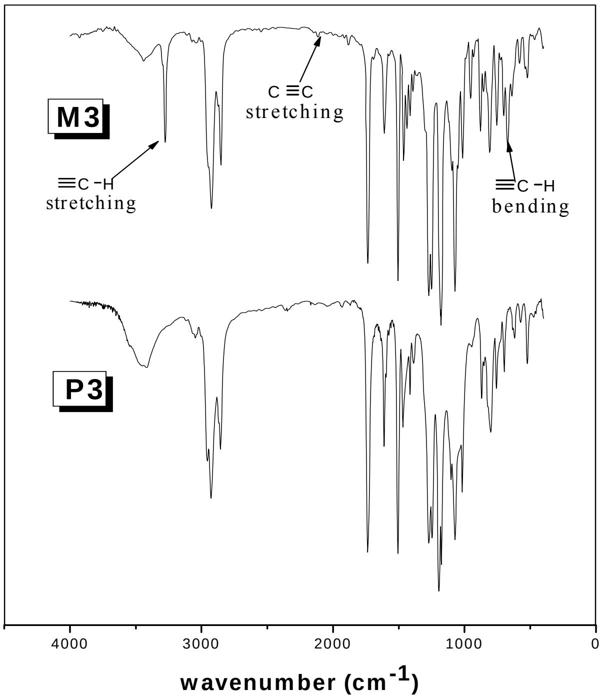


Figure 1 IR spectra of **M3** and its polymer **P3**

Figure 2, the ^1H NMR (400 MHz) spectrum of **P3**, shows no signal characteristic of the acetylene proton. However, the spectrum of monomer **M3** shows the three peaks of acetylenic at 1.98 ppm. Instead, a new peak is observed at 6.06 in ^1H NMR spectrum of **P3**.

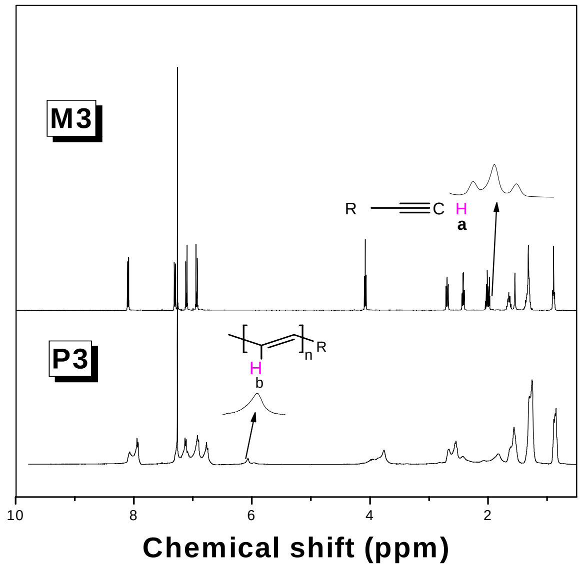


Figure 2 ^{1}H NMR spectra of **M3** and **P3** in $CDCl_3$

Table 2 Mesophase, phase transition temperature and enthalpy change of monomers^a and polymers^b

Monomers and polymers	*T*, °C [*ΔH*, kJ/mol]	
	The First Cooling	**The Second Heating**
M1	I 45(22.65)Cr	Cr 62(24.34) I
M2	I 101(2.73) SmA 80(30.89) Cr	Cr 91(32.93) SmA 102(2.53) I
M3	I 23(0.5) Cr_1 -10(7.7) Cr_2	Cr 44(23.88) I
M4	I 96(3.99) SmA 89(28.55) Cr	Cr 97(33.42) I
M5	I 45(4.21) SmA 21(22.02) Cr	Cr 43(26.4) SmA 46(3.82) I
P1	I 52(0.03) g	g 71(0.02) I
P2	I 184(0.16) SmA 89(2.56) g	g 136(3.09) SmA 184(0.14) I
P3	I 91(0.83) SmA	g 50(0.39) SmA 131(0.36) I
P4	I 228(0.6) SmA 94(1.1) g	g 111(1.7) SmA 242(0.9) I
P5	I 174(0.95) SmA 45(1.25) g	g 62(2.34) SmA 174(0.68) I

[a] Data taken from the DSC thermograms recorded under nitrogen in the second cooling and third heating scans; DSC date measured with heating and cooling rate of 10°C/min under N_2 atmosphere. abbreviations: Cr, crystal; SmA, smectic A phase; I, isotropic liquid; g, glassy state.

[b] Abbreviation: mru = monomer repeat unit.

Thermal Stability and Mesomorphism

The thermal stability of polymers has been investigated with thermogravimetry analysis (TGA) under air atmosphere with heating rate of 20°C/min. It is demonstrated that the polymers are thermal stable and begin to lose weight at 220°C.

The phase transition behavior of the monomers and polymers has been studied with DSC and POM, the results are summarized in Table 2. The optical textures of the mesophases are shown in Figure **1**.

The data in Table **2** show that the fluorinated momomers **M2** and **M4** possess higher melt points and clearing points than that of their alkyl chain analogues **M1** and **M3**. **M5** has only one benzene ring and it still exhibits SmA phase. This result can be explained with the fluorophobic effect of the fluorinated alkyl chain [6]. The strong microsegregation between Rf chain and other part of molecule makes the liquid crystalline molecules self organize to ordered layer structure and show SmA phase. The monomers **M1** and **M3** with alkyl chain do not show liquid crystalline properties.

The polymers display high clearing points and wide mosophase temperature ranges than that of their monomers. The rigidity of the polyacetylene backbone may cause the difference. Moreover, **P3** also show SmA phase because of the rigidity of conjugated alkenes main chain, while its monomer **M3** does not possess liquid crystalline properties. **P1** has no liquid crystalline property, may be due to the spacer between mesogen and the rigid polyacetylene main chain is too short for the mesogen to form ordered liquid crystal packing.

Monomers and polymers have been studied with polarizing optical microscopy. Both **M2** and **M5** show focal conical fan-shaped texture of SmA phase. The polymer **P2** displays small domains of ordered liquid crystalline phase.

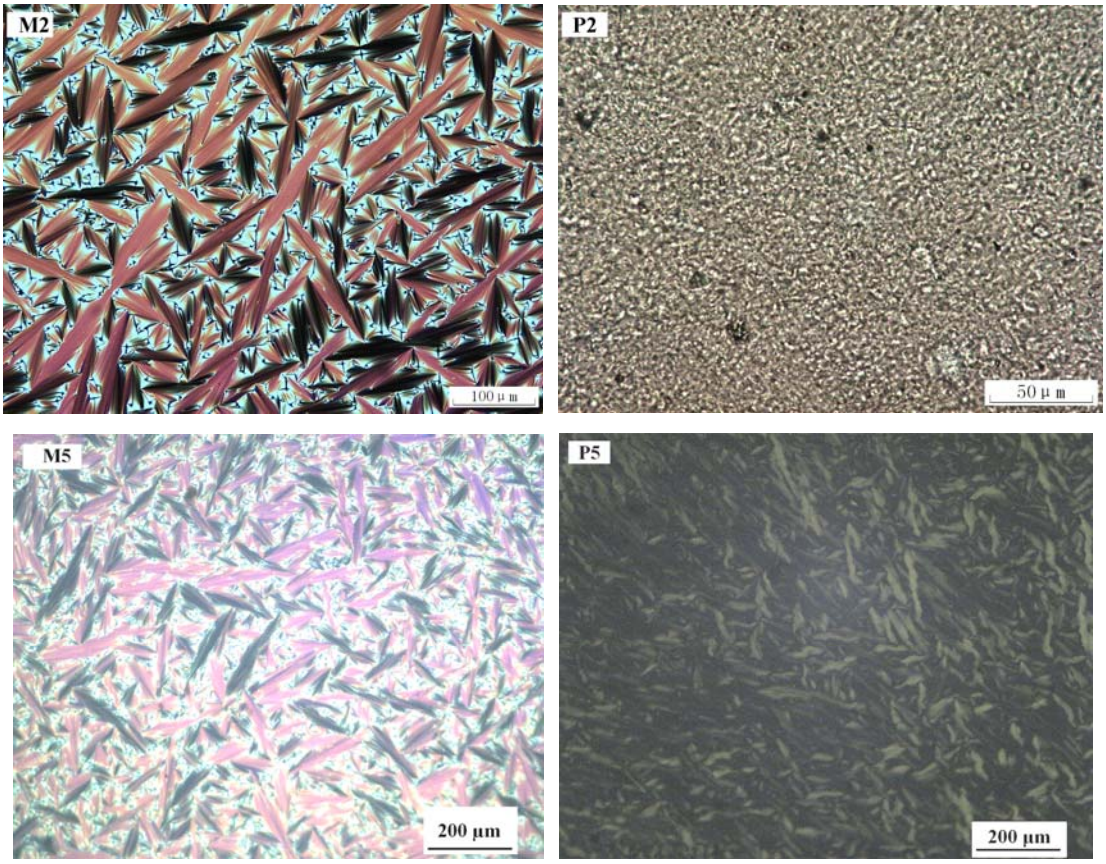


Figure 1 POM textures observed on the cooling from isotropic liquid
M2 at 101 °C; **P2** at 170 °C; **M5** at 50 °C; and **P5** at 150 °C.

Conclusion

We have designed and synthesized a series of acetylene liquid crystalline monomers and polymers with Rf chain and hydrocarbon chain, respectively. The influence of fluorinated alkyl chain on thermal and mesomorphic properties has been investigated and discussed.

The fluorinated monomers show SmA phase, To **M5** which has only one benzene ring, it still displays SmA phase due to the fluorophobic effect of Rf chain.

The GPC result proves that $[Rh(nbd)Cl]_2$ as the catalyst initiates successfully the polymerization of 1-alkynes in good yields and moderate Mw. All polymers are thermally stable and lose little of their weights when heated to $220^{o}C$. The polymers with Rf chain possess SmA phase with higher clearing points and broader mesophase ranges than that of the polymers with alkyl chain.

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