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A new approach to anisotropic conductive networks

A liquid-crystalline side-chain polymer containing a thienyl moiety at the extremity of its side chain

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Summary

A liquid-crystalline bifunctional monomer with two different reactive moieties was prepared by esterification of 4-(6-(acryloyloxy)hexyloxy)benzoic acid and 4-[11-(3-thienyl)undecyloxy]-4'-hydroxybiphenyl. A mesogenic side-chain polyacrylate containing a thienyl moiety at the extremity of its side chain was obtained by radical polymerization of the monomer. The subsequent reaction of the thienyl moiety with $FeCl_3$ leads to the formation of an anisotropic network with a poly(thiophene) unit.

Introduction

Anisotropic networks have been recognized to be useful for functional materials with optic, electric, magnetic, and elastic properties because of macroscopically stable molecular order (1-8). A wide variety of anisotropic networks have been prepared by cross-linking reaction of side-chain polymers (2, 3), by polymerization of mesogenic molecules with two identical functional groups such as acrylates and epoxides (4-6), or by self-assembly of multifunctional H-bonding molecules (7,8). On the other hand, the preparation of anisotropic conductive materials has been attempted by synthesizing liquid-crystalline polymers with conjugated backbones (9-12). Liquid crystals that possess electro-active moieties are a new class of materials. If conductive polymers with liquid-crystalline order could be preserved by cross-linking, conductive materials with stable anisotropic structure would be obtained.

We report here a new approach to a conductive network with mesomorphic order involving the preparation of a side-chain polyacrylate containing a polymerizable thienyl group and the subsequent reaction of this moiety. In this method, once anisotropic order is achieved by the processible mesogenic side-chain polymer, the molecular order of the polymer could be fixed by the cross-linking reaction.

Experimental

Preparation of polymers 2 and 5

Mesogenic monomer **1** was prepared by esterification of 4-(6-(acryloyloxy)-hexyloxy)benzoic acid (13) and 4-[11-(3-thienyl)undecyloxy]-4'-hydroxybiphenyl that was obtained by etherification from 4,4'-dihydroxybiphenyl and 1-bromo-11-(3-thienyl)undecane (14) with N,N'-cyclohexylcarbodiimide in methylene chloride. The crude product was purified on a silica gel column using methylene chloride/hexane 1:1 as eluent followed by recrystallization from methylene chloride and hexane. Yield 46 %. M.p. 77 °C. Polyacrylate **2** was prepared by radical polymerization of **1** with AIBN (1 mol%) at 60 °C in toluene. The resultant polymer was precipitated in ether.

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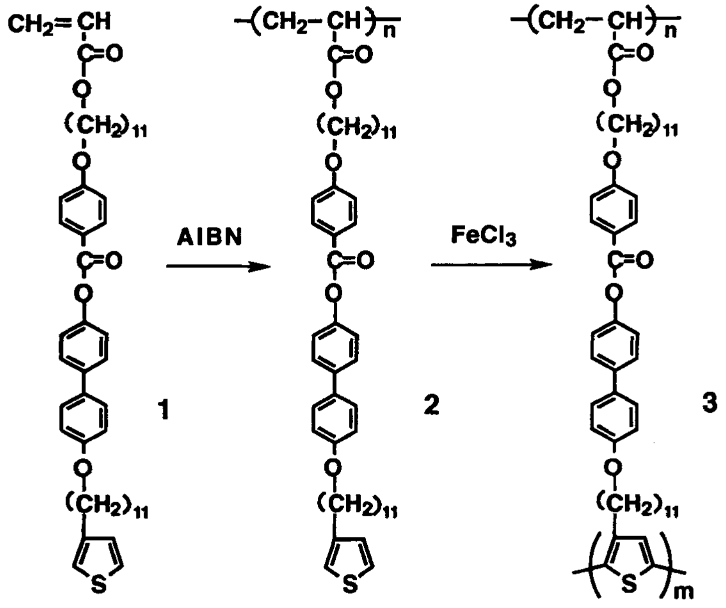
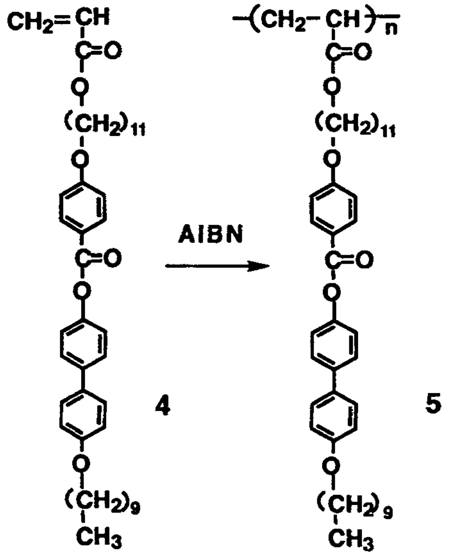
Yield 85 %. M_n= 8400, M_n/M_w = 1.46. Polymer **5** was also obtained from **4** by the same procedure. Yield 80 %.

Oxidation of polymer 2

A thin film of polymer **2** was cast on a quartz plate from chloroform solution. The film heated to 150 °C (a smectic C phase) was cooled rapidly to room temperature. Oxidation reaction for the film of **2** was performed in a mixture of ether (30 ml) and $FeCl_3$ (1.5 g) for 36 h. The resultant sample was washed with methanol for 24 h and dried in vacuum.





Characterization

Thermal properties were examined by use of differential scanning calorimeter (Mettler DSC 30) and polarizing microscope observation (Olympus BH2 and Mettler FP82HT). UV-vis spectra were measured by use of a Jasco Ubest-50 UV/Vis spectrometer.

Results and Discussion

Mesogenic bifunctional compound **1** with two different polymerizable moieties of acrylate and thienyl groups was designed to involve two step reactions of radical polymerization and oxidation reactions. The thiophene moiety substituted at the third position has been used for conductive polymers (11,15-17). The radical polymerization of **1** gave mesogenic side-chain polymer **2**. Polymer **5** with no thienyl group was also prepared from **4** for comparison. Table 1 gives transition temperatures of the monomers and the resulting side-chain polymers. The bifunctional mesogenic monomer **1** exhibits stable mesomorphic behavior. Smectic A and nematic phases are observed for **1**. The mesomorphic temperature range is 60 °C. Monomer **4** exhibits an ordered smectic and smectic C phases. Mesophases are stable up to about 200 °C for polymers **2** and **5**. The incorporation of the thienyl end group to the aromatic triad mesogen does not significantly decrease liquid crystallinity.

Table 1. Phase behavior of liquid-crystalline monomers and polymers.

Compound	K		S_X		S_C		S_A		N		I
1	•	77					•	113	•	137	•
2	•	139			•					194	•
4	•	102	•	106	•	150			•	157	•
5	•	129			•					204	•

K: crystalline, S_X: ordered smectic, S_C: smectic C, S_A: smectic A, N: nematic, I: isotropic.

The film thickness of polymer **2** cast on the quartz plate from chloroform solution was about 1 x 10^{-3} mm. After reaction with $FeCl_3$ in ether for 36 h, the film was washed with methanol. The color of the film turned from dark purple to yellow by washing. Figure 1 shows UV-visible absorption spectra of the film of polyacrylate **2** and the polyacrylate after the treatment of $FeCl_3$ and the subsequent washing. A new peak appears at 442 nm for the reacted film after the washing (Fig. 1b). Zinger et al. reported that for the UV-visible spectra of a substituted polythiophene obtained by chemical reaction after treatment with methanol, a peak was seen at 434 nm (16), which was considered to indicate a reduced state of a polythiophene. This result agrees well with the present observation. On polarizing microscope observation, birefringence is still seen after the reaction. Furthermore, no melting and isotropization transitions do not occur on heating, which suggests that a highly cross-linked structure of **3** is obtained. The same procedure was performed for polymer **4**, which has no thienyl group. After the treatment, no change of UV-vis spectra is observed and the sample exhibits melting and isotropization transitions on heating.

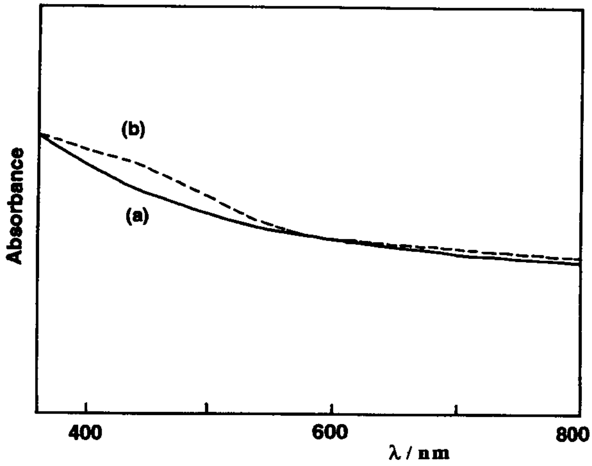


Fig. 1. UV-vis spectra of thin films of: (a) polymer **2** and (b) polymer **2** oxidized by $FeCl_3$ and subsequent washing with methanol.

These results indicate that the chemical reactions of the thienyl moieties in the mesomorphic order results in the cross-linking of the polymer by the polymerization of the thienyl moiety. This is a new approach to the combination of liquid-crystalline molecular order and electronic properties. Further studies on the control of molecular orientation and anisotropic conductivity are now underway.

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References and Notes

1. Kelly SM (1995) J Mater Chem 5: 2047.
2. Küpfer J, Finkelmann H (1991) Makromol Chem Rapid Commun 12: 717.
3. Brehmer M, Zentel R (1994) Mol Cryst Liq Cryst 243: 353.
4. Broer DJ, Hikemet RAM , Challa G (1989) Makromol Chem 190: 3201.
5. Broer DJ, Lub J, Mol GN (1995) Nature 378: 467.
6. Berkeley GG, Ober CK, Papathomas KI, Wang DW (1992) J Polym Sci Part A Polym Chem 30: 1831.
7. Kato T, Kihara H, Kumar U, Uryu T, Fréchet JMJ (1994) Angew Chem Int Ed Engl 33: 1644.
8. Kihara H, Kato T, Uryu T, Fréchet JMJ (1996) Chem Mater 8: 961.
9. Toyoshima R, Narita M, Akagi K, Shirakawa H (1995) Synth Met 69: 289.
10. Oh SY, Ezaki R, Akagi K, Shirakawa H (1993) J Polym Sci Part A Polym Chem 31: 2997.
11. Thobie-Gautier C, Bouligand Y, Gorgues A, Jubault M, Roncali J (1994) Adv Mater 6: 138.
12. Jin SH, Kim SH, Cho HN, Choi SK (1991) Macromolecules 24: 6050.
13. Portugall M, Ringsdorf H, Zentel R (1982) Makromol Chem 183: 2311.
14. Bauerle P, Wurthner F, Heid S (1990) Angew Chem Int Ed Engl 29: 419.
15. Kaeriyama K, Sato M, Tanaka S (1987) Synth Met 21: 41.
16. Zinger B, Greenwald Y, Rubinstein I (1991) Synth Met 41-43: 583.
17. Hallensleben ML, Howllwedel F, Stanke, D (1995) Macromol Chem Phys 196: 3535.