

论文

## 含X-型二维液晶基元和顺式-4,4'-双(4-羟基苯基偶氮)二苯并-14-冠-4冠醚环液晶共聚酯的合成与表征

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收稿日期 2004-10-11 修回日期 2004-11-20 网络版发布日期 接受日期

**摘要** 以4,4'-( $\alpha$ , $\omega$ -辛二酰氧)二苯甲酰氯( $M_1$ )、2,5-二(对十二烷氧基苯甲酰氧基)对苯二酚( $M_2$ )和顺式-4,4'-双(4-羟基苯基偶氮)二苯并-14-冠-4( $M_3$ )为单体,通过溶液共缩聚反应,合成了一系列含X-型二维液晶基元和顺式-4,4'-双(4-羟基苯基偶氮)二苯并-14-冠-4冠醚环的主链型液晶共聚酯.单体1( $M_1$ )由对羟基苯甲酸和辛二酰氯,通过酯化和取代反应制备,单体2( $M_2$ )由2,5-二羟基苯醌和对十二烷氧基苯甲酰氯通过酯化和还原反应制备,单体3( $M_3$ )由顺式-二氨基二苯并-14-冠-4和苯酚通过重氮化和偶联反应制备.共聚酯的分子量不高,[ $\eta$ ]在0.35~0.25dL/g之间.单体的化学结构通过IR、UV、 $^1\text{H-NMR}$ 、MS和元素分析等方法确证.共聚酯的外观为黄色粉状固体,除CP9外,室温下不溶于 $\text{CHCl}_3$ 和THF溶剂.共聚酯的性质采用GPC、 $[\eta]$ 、DSC、TG、WAXD和POM等方法进行了研究.发现所有的共聚酯加热到各自的熔融温度以上都能形成液晶态,在液晶态可以观察到向列相的丝状织构或纹影织构.共聚酯的熔融温度( $T_m$ )和各向同性温度( $T_i$ )随共聚酯分子中顺式-4,4'-双(4-羟基苯基偶氮)二苯并-14-冠-4用量的改变呈规律性变化.WAXD研究进一步证实了共聚酯的液晶性.

**关键词** X-型二维液晶基元 顺式-4,4'-双(4-羟基苯基偶氮)二苯并-14-冠-4 液晶共聚酯 合成与表征

分类号

## SYNTHESIS AND CHARACTERIZATION OF LIQUID CRYSTALLINE COPOLYESTERS WITH X-SHAPED TWO-DIMENSIONAL MESOGENIC UNITS AND CROWNETHER CYCLE OF *cis*-4,4'-BIS(4-HYDROXY PHENYLAZO)DIBENZO-14-CROWN-4

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**Abstract** A novel series of main chain liquid crystalline copolyesters with X-shaped two-dimensional mesogenic units and crown ether cycles of *cis*-4,4'-bis(4-hydroxyphenylazo)dibenzo-14-crown-4 was synthesized via solution cocondensation polymerizations from 4,4'-( $\alpha$ , $\omega$ -octanedioylxy)dibenzoyl dichloride( $M_1$ ), 2,5-bis(*P*-dodecyloxybenzoyloxy)hydro-quinone( $M_2$ ) and *cis*-4,4'-bis(4-hydroxyphenylazo)dibenzo-14-crown-4( $M_3$ ) as the monomers. Monomer  $M_1$  was synthesized by esterification and substitution reaction of *P*-hydroxybenzoic acid and octanedioyl chloride. Monomer  $M_2$  was synthesized by esterification and reduction reaction of 2,5-dihydroxybenzoquinone and *P*-dodecyloxybenzoyl chloride. Monomer( $M_3$ ) was synthesized by diazotization and coupling reaction of *cis*-diaminedibenzo-14-crown-4 and phenol. The molecular weights of copolyesters are not high, and the  $[\eta]$  of the copolyesters ranges from 0.35~0.25 dL/g. The monomer structures were identified by using elementary analysis, IR, UV,  $^1\text{H-NMR}$  and MS etc. All the copolyester samples are yellowish powders and insoluble at room temperature in THF and  $\text{CHCl}_3$  except for sample CP9. The properties of copolyesters were investigated by using GPC,  $[\eta]$ , DSC, TG, WAXD and POM. It was found that all the copolyesters went into liquid-crystal phase when they were heated over their melting temperature( $T_m$ ). The thread texture and schlieren texture can be observed. Their melting temperature and isotropic temperature( $T_i$ ) change regularly with varying the *cis*-4,4'-bis(4-hydroxyphenylazo)dibenzo-14-crown-4 unit content in the copolyester. The WAXD study illustrated that the copolyesters are liquid crystalline with a nematic phase. A dispersive peak at  $2\theta$  near  $20^\circ$  appeared in their WAXD patterns, which is a typical

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character for quenched nematic liquid crystal copolyesters.

**Key words** [X-shaped two-dimensional unit](#) [cis-4,4'-bis\(4-hydroxyphenylazo\)dibenzo-14-crown-4](#)  
[Liquid crystalline copolyester](#) [Synthesis and characterization](#)

DOI:

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