6648 *J. Phys. Chem. B* **1999,** *103,* 6648−6652

ARTICLES

Optical Properties of a Liquid-Crystalline Random Copolyester

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Received: December 17, 1998; In Final Form: April 27, 1999

We have investigated the optical properties of Vectra A910, a commercially produced liquid-crystalline copolyester consisting of 4-hydroxybenzoic acid and 6-hydroxy-2-naphthoic acid subunits. The polymer is highly fluorescent in the near UV with an emission maximum at 428 nm (2.90 eV) and an excitation maximum at 376 nm (2.66 eV). The time-resolved fluorescent decays at room temperature were found to fit stretched exponential decays. Furthermore, the fluorescence kinetics were found to be highly dependent upon the emission wavelength. These results are consistent with the disorder from the random nature of the copolymer.

Introduction

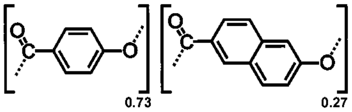
Polymers have long been recognized as having great potential as photonic materials. The development of polymer light-emitting diodes (LEDs) has stimulated a great deal of activity in the area of luminescent polymers.[1] Polymers have also been experimentally and theoretically studied for use as both second- and third-order nonlinear optical materials.[2−5] To produce the anisotropy required for second-order nonlinear applications, polymers are often poled, i.e., oriented with electric fields at temperatures higher than their glass transition temperature.[3] However, poled polymers do not always have a high degree of orientation. Furthermore, poled polymers are often not stable at high temperature, or even gradually decay at room temperature. Because of their excellent temperature stability and high degree of orientation, liquid-crystalline polymers (LCPs) are intriguing candidates for photonic applications.

The goal of this paper is to present studies of the photophysical properties of Vectra A910. We have found that Vectra A910 has a strong fluorescence in the near UV. The time-resolved photoluminescence kinetics are well described by stretched exponential decays, indicating significant disorder in the material. Although Vectra A910 is a random copolyester, it does not have a center of symmetry and exhibits a very strong second-order nonlinear optical response. To the best of our knowledge, these are the first fluorescence measurements of a main-chain random copolyester.

Background

Vectra is a liquid-crystal polymer (LCP) developed and commercially produced by Hoechst-Celanese, Summit, NJ (Hoechst-Celanese Corporation, Robert L. Mitchell Technical Center, Summit, NJ 07901). Vectra A is a member of a class of random copolyester LCPs composed solely of 4-hydroxybenzoic acid (HBA) and 6-hydroxy-2-naphthoic acid (HNA).

SCHEME 1



Unlike other LCPs investigated for optical applications, Vectra does not possess additional substituent or side groups. Vectra is also a thermotropic LCP, which possesses an inherent mesophase without the use of solvents.

This paper specifically focuses on the optical properties with a monomeric composition ratio of 73/27 HBA/HNA, as shown in Scheme 1. All further references to this compound will be referred to as copoly(HBA/HNA).

Traditionally, 2,6-disubstituted naphthalene groups are incorporated into main-chain polymers to introduce a transverse offset directly into the polymer backbone, which creates an additional crankshaft motion. Specifically, this has the effect of reducing the linearity and persistence length[6] of the HBA homopolymer, therefore creating the mesophase. Therefore, monomeric ratios can be varied to synthesize a copolymer with different solid crystal and isotropic liquid melting points, which will define the temperature range of the mesophase or liquid crystal state. Commercially, an optimum LCP has a low and broad temperature range for the liquid crystal phase to increase the ease and flexibility of melt material processing.[7]

X-ray crystallographic studies[8,9] reveal that aperiodic diffraction lines along the extended copolymer chain correspond to a completely random monomeric sequence. However, even with the existence of a random sequence, longitudinal registration does occur between molecules.[10] This registration leads directly to highly ordered domains, as compared to completely disordered and amorphous regions, within the LCP film. These domains, which are randomly distributed throughout the polymer film, were observed via X-ray,[11] dark-field transverse electron microscopy,[12] and polarized FTIR.[13] In extruded samples, these domains are roughly 40−90 nm long by 15−20 nm wide in the direction of extrusion.[12]

An important aspect of copoly(HBA/HNA) is the three

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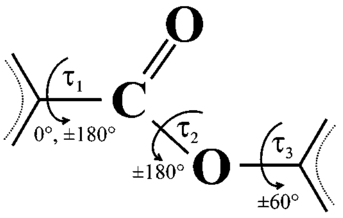
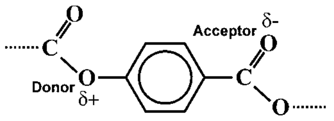
SCHEME 2



SCHEME 3



torsional bond angles within the ester linkage, Scheme 2. The torsional angles determine the degree of conjugation between adjacent aromatic, benzyl or naphthyl, rings. Hofmann et al.[10] employed molecular modeling to confirm the X-ray data. They found that in the extended chain ($\tau_2 = \pm 180°$) adjacent aromatic planes will possess an angular displacement of ±60° in the solid or crystalline state. This is primarily due to the steric stress between the carbonyl oxygen and the aromatic hydrogen placed on torsion τ_3. This torsion has the net effect of creating a helix through the length of the extended molecule. Gas-phase ab initio[14] calculations indicate that the energy maximum for this nonplanar torsion is on the order of 2 kcal/mol.

Another general aspect of copoly(HBA/HNA) is the presence of an oriented unidirectional permanent polarization or electric dipole moment within a single molecule. The ester oxygen acts as a donor of charge into its neighboring aromatic π-orbitals. The carbonyl oxygen will then accept this charge, as shown in Scheme 3. This donor−acceptor pair creates a strong permanent electric dipole with an approximate net direction along the nematic director. As opposed to related LCPs, such as poly(ethyleneterephthalate) (PET) or the polymer comprised of 50% HNA, 25% terephthalate, and 25% *p*-aminophenol (Vectra B), the unique tandem polymerization of the copoly(HBA/HNA) orients the polymer, producing a large dipole moment. The noncentrosymmetric character of the polymer chain was demonstrated by the observation of bulk second harmonic generation by Wanatabe et al.[5] The other LCPs mentioned above do not have a significant second-order nonlinear optical response.

Experimental Section

The extruded polymer films of copoly(HBA/HNA) with a molar composition of 73/27 were supplied by the Hoechst-Celanese Corporation. The extruded samples of 10, 20, 50, and 75 μm thickness used in these experiments are the Hoechst-Celanese standard commercial-grade Vectra A910.[15] X-ray and mechanical measurements of this material have been previously reported in the literature.[13,16−22] The steady-state photoluminescence measurements were done using a Spex FluoroMax Spectrofluorometer. The FT-IR measurements were done using a Matheson FT-IR Model RS-2. The FT-Raman measurements were done using a Nicolet Magna 760 with a FT-Raman module.

The time-resolved fluorescence measurements were done using a Hamamatsu Streak Camera Model C5680. Spectra were obtained from 420 nm (2.95 eV) to approximately 700 nm (1.77 eV). A 420 nm (2.95 eV) a long wavelength pass filter was used to filter the laser light. The experimental time resolution was about 80 ps, limited by jitter in the triggering electronics. This time resolution is sufficient to precisely measure the kinetics of the copoly(HBA/HNA) fluorescence reported in this paper. Typically less than 1 mW of 400 nm (3.10 eV) light was used to excite the sample.

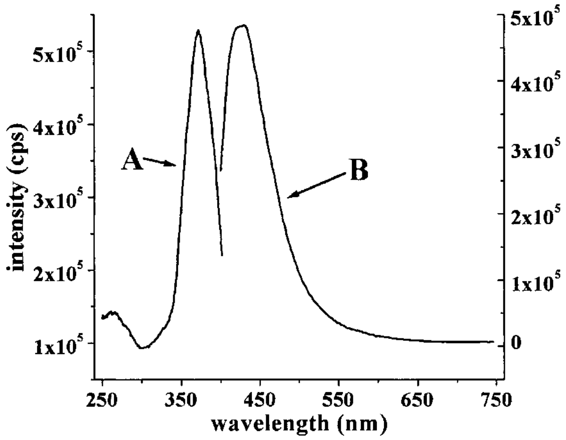


Figure 1. Fluorescence excitation (A) and emission (B) spectra for a 20 μm copoly(HBA/HNA) film at ambient conditions. Excitation was monitored at 420 nm (2.95 eV), and emission was excited at 380 nm (3.26 eV).

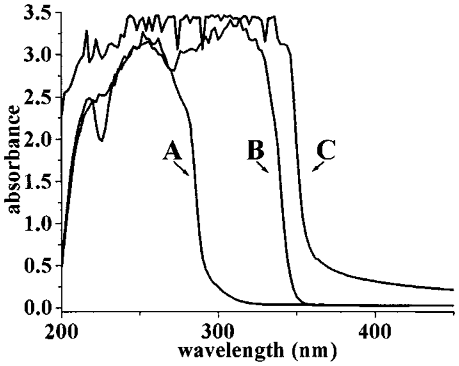


Figure 2. Absorption spectra of HBA in 1 mM ethanol (A), HNA in 1 mM ethanol (B), and 10 μm copoly(HBA/HNA) film (C) at ambient conditions.

The nonlinear optical experiments were performed with a femtosecond Ti:sapphire laser operating at 800 nm (1.55 eV). The incident laser light was reflected at a 45° angle from the polymer surface. The polymer was rotated with respect to the polarization of incident fundamental light by a rotary stage. The reflected second harmonic light was detected through a monochromator and single-photon-counting electronics. Quartz and β-barium borate (BBO) crystals were used as reference materials.

Results and Discussion

Steady-State Spectroscopy. The steady-state fluorescence excitation and emission spectra taken at room temperature are shown in Figure 1. The fluorescence spectrum exhibits a maximum at 428 nm (2.90 eV) with a long tail into the visible. The absorption maxima of the HBA and HNA monomers are 256 (4.84 eV) and 315 nm (3.94 eV), respectively, as shown in Figure 2. The fluorescence maximum of the polymer is considerably red shifted from the known results for both monomers of HBA and HNA. This red shifting of the polymer fluorescence is consistent with some degree of conjugation along the polymer chain. The weak conjugation of the polymer also leads to a strong absorption edge in the polymer around 375−400 nm. This is also demonstrated in the photoluminescence excitation spectra, Figure 1. Further evidence for some degree

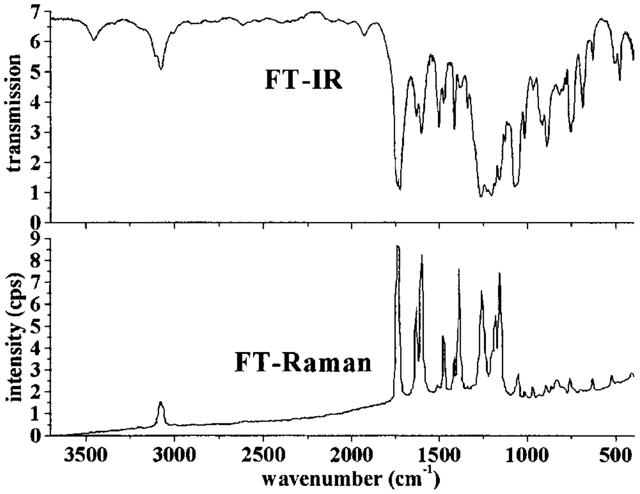


Figure 3. FT-IR and FT-Raman spectra for copoly(HBA/HNA) at ambient conditions.

TABLE 1: FT-IR/Raman Energy Assignments for Vectra A910

mode	maximum/ center	range	type
ring-hydrogen bend	885.2 max	854.3−946.9	doublet
C−O−C stretch	1074.2 max	1027.9−1097.3	singlet
O=C−O−C stretch	1230.4 center	1137.8−1322.9	broadened
ring breathing	1560.2 center	1454.1−1666.2	two mirrored doublets
C=O stretch	1727.9 max	1666.2−1816.6	singlet
ring-hydrogen stretch	3081.7 max	2970.0−3189.7	singlet
overtone	3455.8 max	3371.0−3533.0	singlet

of conjugation in the polymer is the absorption tail that extends into the visible region, Figure 2.

We have used FT-IR and FT-Raman spectroscopies to characterize the vibrational spectra of copoly(HBA/HNA), Figure 3. FT-Raman was necessary because residual fluorescence made it impossible to obtain Raman spectra of copoly(HBA/HNA) using visible light. Careful inspection of the FT-Raman data shows that a shoulder is present in the data to approximately 1000 cm^{-1}. We attribute this feature to residual fluorescence of copoly(HBA/HNA). The peaks are tabulated and identified in Table 1. The peak assignments were done by analogy to other polymeric compounds.[23]

Upon irradiation with 800 nm (1.55 eV) light from a femtosecond laser, a blue spot is visible on the polymer surface. Spectral resolution of this light with a monochromator reveals that it is second harmonic light (400 nm, 3.10 eV), with no light detected at frequencies away from the bandwidth of the laser. The blue emission occurs at twice the laser frequency as the laser wavelength is scanned from 820 to 780 nm. For the above reasons, we discount the possibility that the light is due to fluorescence from excited states produced by multiphoton excitation.

A plot of the second-harmonic response versus rotational angle of a 50 μm thick copoly(HBA/HNA) sample is shown in Figure 4, along with a fit to a $\sin^2 \theta$ curve. The variation of the second-harmonic generation (SHG) as the copoly(HBA/HNA) is rotated demonstrates the anisotropic nature of the nonlinear optical response. The intensity of the frequency-doubled light reaches a maximum when the film's polymer chains are oriented along the polarization direction of the incoming light, and a minimum when the chains are perpendicular to the incoming polarization. Similar results for the SHG anisotropy were obtained by Watanabe and collaborators.[5]

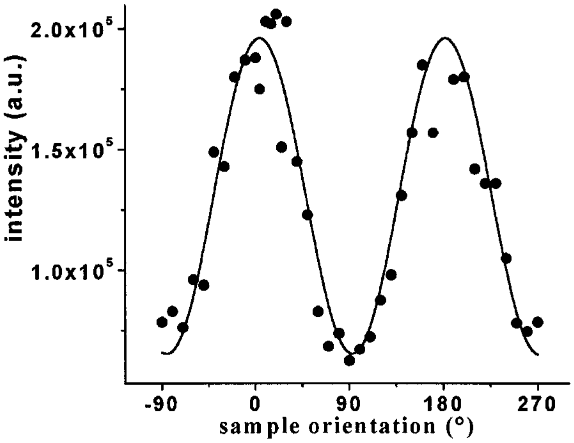


Figure 4. Linearly polarized second-harmonic response versus chain orientation for 50 μm copoly(HBA/HNA) film at ambient conditions.

To further quantify the second-harmonic response of copoly(HBA/HNA), we have compared our second-harmonic signals to a quartz standard. We estimate that the $\chi^{(2)}_{zzz}$, where z is along the direction of the polymer chain, is 1.3×10^{-10} m/V. Asada et al.[24,25] and Wanatabe et al.[5] report a value of 5×10^{-12} m/V, with the incident wavelength at 1064 nm. This difference is attributed to the two-photon resonance of the polymer at 400 nm (3.10 eV).

The second-harmonic response of copoly(HBA/HNA) will depend in part on the second-harmonic response of its monomeric subunits, HBA and HNA. Das and co-workers[26] have measured the molecular hyperpolarizability of HBA and related molecules using hyper-Rayleigh scattering. They found that the acidic form of HBA has a β of 30.3×10^{30} esu in water. The molecular hyperpolarizability of HBA could not be previously measured, because the weak acid will partially dissociate in solution. They confirmed the moderate β for HBA with quantum chemical calculations. Previous[27] studies of donor/acceptor groups of aromatic rings have clearly demonstrated that increasing the donor/acceptor strength of the molecule significantly increases the molecular hyperpolarizability. The previously stated work of Asada[24,25] and Wanatabe[5] confirm the existence of dipolar interactions on the monomeric scale to support polymeric second-harmonic responses. Although measurements are not available, similar arguments should apply to the HNA monomer.

Time-Resolved Fluorescence. We have examined the time dependence of the copoly(HBA/HNA) fluorescence at room temperature. Typical results are displayed in Figure 5. The decays are clearly not single exponential; however, the time-resolved fluorescence can be described well by a single stretched exponential, where α is the stretching coefficient and τ is the lifetime.

$$I(t) = I(0) \exp(-(t/\tau)^{\alpha}) \tag{1}$$

The time-resolved fluorescence data was fit to eq 1 by plotting $\ln(\ln(I(0)/I(t)))$ versus $\ln(t)$. The slope of this line is α and the y-intercept is $-\alpha \ln(\tau)$. This analysis allows us to uniquely determine both α and τ. The quality of the fits was excellent as shown in Figure 6. The small deviation at short times is attributable to the undefined slope of eq 1 at $t = 0$. α and τ as a function of emission wavelength are plotted in Figure 7. We found that α was approximately independent of emission energy. The average value of α was 0.78 ± 0.02. In contrast, τ was found to increase with increasing emission wavelength. In

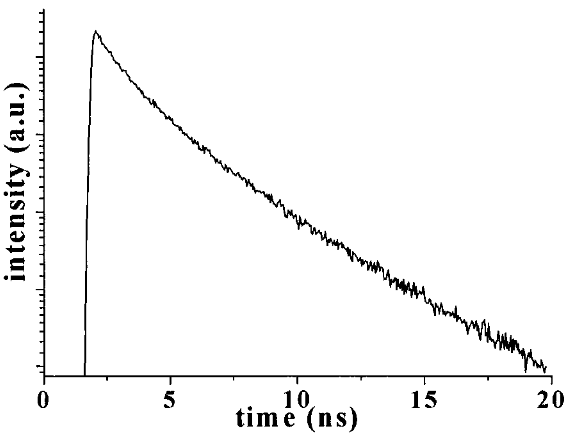


Figure 5. Time-dependent fluorescence response for a 75 μm copoly(HBA/HNA) film at ambient conditions. The excitation wavelength was 400 nm (3.10 eV), and the emission was monitored at a wavelength of 462 nm (2.68 eV). The incident polarization is parallel to the chain orientation.

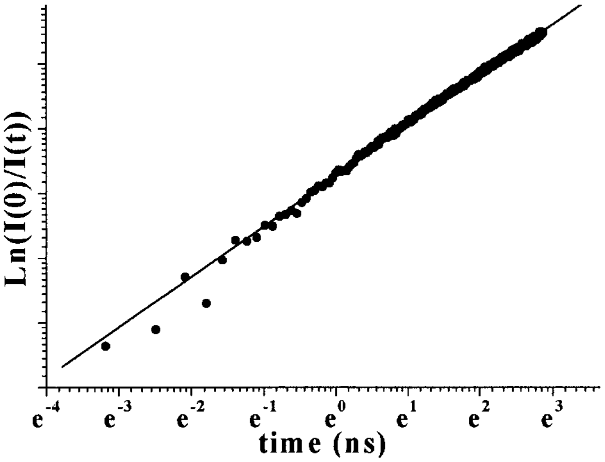


Figure 6. Time-dependent fluorescence emission from Figure 5 on a ln−ln versus ln scale. From the linear fit $\alpha = 0.78 \pm 0.002$ and $\tau = 2.57 \pm 0.02$ ns with an overall correlation coefficient of 0.9979.

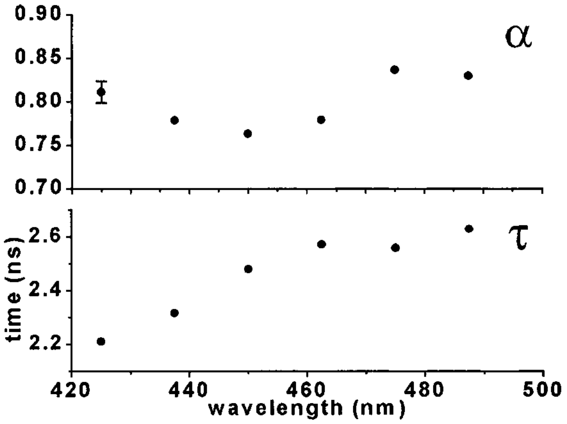


Figure 7. Wavelength dependence of α and τ for a 75 μm copoly(HBA/HNA) film at ambient conditions.

contrast to the SHG measurements, the fluorescence kinetics were not dependent upon chain orientation.

Stretched exponential behaviors were first used by Kohlrausch[28] to describe mechanical relaxation data in 1863. In recent years, stretched exponential decays have been observed in a great many physical,[29−31] chemical,[32−34] and specifically polymeric[35−38] systems. This extensive work, in a wide variety of systems, has demonstrated that stretched exponential kinetics are associated with disorder. The disorder is either energetic, i.e., a distribution in barrier heights, or topological, i.e., structural disorder. Stretched exponential dynamics indicate that the first moment of the distribution of lifetimes is infinite. Physically this means that there is small, but sufficient probability of the lifetime to be much longer than the experiment, so that the average is not well-defined. Because of the common occurrence of disorder on multiple time scales, stretched exponential decays are often observed in polymeric systems.

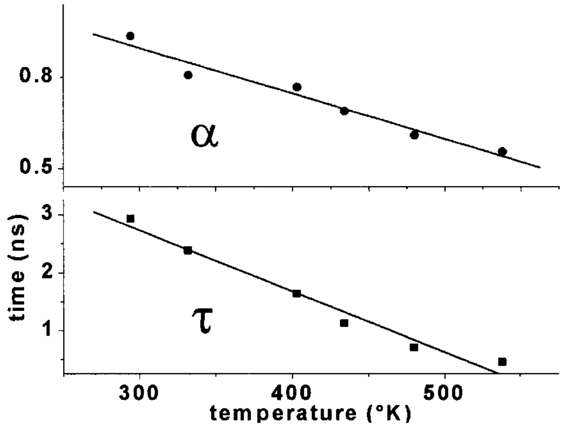


Figure 8. Temperature dependence of α and τ for a 75 μm copoly(HBA/HNA) film.

Time-resolved photoluminescent measurements of poly(phenylenevinylene) (PPV),[38,39] and related luminescent polymers, have shown similar stretched exponential behavior. Physically, the stretched exponential is due to a distribution of decay rates. This distribution of decay rates in the polymer chain is usually associated with a distribution in chain or conjugation lengths.[40,41] In the case of copoly(HBA/HNA), there is also a distribution of random monomers which make up the polymer. We hypothesize that the random nature of the copolyester units is the origin of the disorder that causes the stretched exponential decay.

We have also measured the time-resolved fluorescence of copoly(HBA/HNA) as a function of temperature. The decays maintain their stretched exponential character over the temperature range studied, 300−500 K. We plot both α and τ versus temperature for the 450 nm emission as shown in Figure 8. The stretching coefficient α is observed to decrease linearly with increasing temperature. This trend is opposite to what is commonly observed in disordered systems. The decreasing α is qualitatively consistent with increasing disorder and a broad distribution of lifetimes. We hypothesize that the decrease in α is due to torsional motion, which is thermally activated at temperatures above the polymer's glass transition. Torsional motion along the polymer chain is an example of dynamic disorder, and has been investigated in several test systems.[42] A more extensive study of the temperature dependence of the Vectra A910 fluorescence will be the subject of future paper.

Summary

We have investigated the photophysical properties of a thermotropic liquid-crystalline random copolyester, copoly(HBA/HNA). To the best of our knowledge, these are the first fluorescence measurements of a random main-chain copolyester. The copoly(HBA/HNA) was found to have a strong fluorescence in the UV, with a peak at 428 nm (2.90 eV). The room-temperature fluorescence lifetimes were found to be in the nanosecond regime, with decay kinetics being well described by a stretched exponential function. The stretching coefficient,

α, was found to be 0.78 ± 0.02 at room temperature. Furthermore, the fluorescence kinetics were found to be highly dependent upon the emission wavelength, increasing with decreasing emission energy. The stretched exponential decays are consistent with the disorder from the random nature of the copolymer. Although copoly(HBA/HNA) is a random copolymer, due to the orientation of the monomers it is noncentrosymmetric along the chain axis. The noncentrosymmetric nature of copoly(HBA/HNA) is experimentally demonstrated by the observation of a strong second-order nonlinear response from the polymer.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research. This work was also funded by a Rutgers University−Hoechst-Celanese Innovative Research Award. We would like to thank Dr. Jim Elliot for helpful discussions, Prof. S. Isied for the use of his spectrophotometer, and Bill Ceislick of Hamamatsu Corporation for the loan of the streak camera. We also thank Rich Carl of Nicolet Corporation for the FT-Raman measurements in this paper and, finally, Milan Popheristic for his help with the Ti: sapphire laser.

References and Notes

(1) Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay, K.; Friend, R. H.; Burn, P. L.; Holmes, A. B. *Nature* **1990**, *347*, 539.

(2) Bredas, J. L.; Silbey, R. *Conjugated Polymers*; Kluwer Academic Publishers: Boston, 1991.

(3) Prasad, P. N.; Williams, D. J. *Introduction to nonlinear optical effects in molecules and polymers*; John Wiley & Sons: New York, 1991.

(4) Craig, G. S. W.; Cohen, R. E.; Schrock, R. R.; Silbey, R. J.; Puccetti, G.; Ledoux, I.; Zyss, J. *J. Am. Chem. Soc.* **1993**, *115*, 860−7.

(5) Watanabe, T.; Miyata, S.; Furukawa, T.; Takezoe, H.; Nishi, T.; Sone, M.; Migita, A.; Watanabe, J. *Jpn. J. Appl. Phys.* **1996**, *35*, L505−7.

(6) Cox, M. K. *Liquid crystal polymers*; Pergamon Press: New York, 1987; Vol. 1, No. 2.

(7) Isayev, A. I.; Kyu, T.; Cheng, S. Z. D. *Liquid-Crystalline Polymer Systems, Technological Advances*; American Chemical Society: Washington, DC, 1996; Vol. 632.

(8) Blackwell, J.; Gutierrez, G. A.; Chivers, R. A. *Macromolecules* **1984**, *17*, 1219−1224.

(9) Viney, C.; Mitchell, G. R.; Windle, A. H. *Mol. Cryst. Liq. Cryst.* **1985**, *129*, 75−108.

(10) Hofmann, D.; Schneider, A. I.; Blackwell, J. *Polymer* **1994**, *35*, 5603−5610.

(11) Nicolson, T. M.; Mackley, M. R.; Windle, A. H. *Polymer* **1992**, *33*, 434−5.

(12) Spontak, R. J.; Windle, A. H. *J. Polym. Sci.: Part B: Polym. Phys.* **1992**, *30*, 60−9.

(13) Kaito, K.; Kyotani, M.; Nakayama, K. *J. Polym. Sci.: Part B: Polym. Phys.* **1993**, *31*, 1099−1108.

(14) Ruiten, J. v.; Meier, R. J.; Hahn, C.; Mosell, T.; Sariban, A.; Brickmann, J. *Macromolecules* **1993**, *26*, 1555−63.

(15) Calundann, G. W. Melt processable thermotropic wholly aromatic polyester. U.S. Patent 4,184,996, 1980.

(16) Blackwell, J.; Gutierrez, G. *Polymer* **1982**, *23*, 671−5.

(17) Biswas, A.; Blackwell, J. *Macromolecules* **1988**, *21*, 3158−3164.

(18) Biswas, A.; Blackwell, J. *Macromolecules* **1988**, *21*, 3146−3152.

(19) Biswas, A.; Blackwell, J. *Macromolecules* **1988**, *21*, 3152−3158.

(20) Bedford, S. E.; Windle, A. H. *Polymer* **1990**, *31*, 616−20.

(21) Jansen, J. A. J.; Paridaans, F. N.; Heynderickx, I. E. J. *Polymer* **1994**, *35*, 2970−6.

(22) McCullagh, C. M.; Yu, Z.; Jamieson, A. M.; Blackwell, J.; McGervey, J. D. *Macromolecules* **1995**, *28*, 6100−7.

(23) Bower, D. I.; Maddams, W. F. *The vibrational spectroscopy of polymers*; Cambridge University Press: New York, 1989.

(24) Asada, T. *Mol. Cryst. Liq. Cryst.* **1994**, *254*, 125−35.

(25) Asada, T.; Tanaka, H. Nonlinear optical properties of the main-chain type liquid crystalline polymers. *SPIE* 1997.

(26) Ray, P. C.; Das, P. K.; Ramasesha, S. *J. Chem. Phys*. **1996**, *105*, 9633−9.

(27) Dulcic, A.; Sauteret, C. *J. Chem. Phys.* **1978**, *69*, 3453−7.

(28) Kolrausch, F. *Pogg. Ann. Phys*. **1863**, *119*, 352.

(29) Shlesinger, M. F. *Annu. Rev. Phys. Chem.* **1988**, *39*, 269−90.

(30) Shlesinger, M. F.; Klafter, J. *J. Phys. Chem.* **1989**, *93*, 7023−6.

(31) Klafter, J.; Shlesinger, M. F.; Zumofen, G. *Phys. Today* **1996**, 33−9.

(32) Klafter, J.; Shlesinger, M. F. *Proc. Natl. Acad. Sci*. **1986**, *83*, 848−51.

(33) Bendler, J. T.; Shlesinger, M. F. *J. Phys. Chem.* **1992**, *96*, 3970−3.

(34) Pavesi, L.; Ceschini, M. *Phys. Rev. B* **1993**, *48*, 17625−8.

(35) Kauffmann, H. F.; Mollay, B.; Weixelbaumer, W.-D.; Burbaumer, J.; Riegler, M.; Meisterhofer, E.; Aussenegg, F. R. *J. Chem. Phys.* **1986**, *85*, 3566−84.

(36) Muller-Horsche, E.; Haarer, D.; Scher, H. *Phys. Rev. B* **1987**, *35*, 1273−80.

(37) Tao, W. C.; Frank, C. W. *J. Phys. Chem.* **1989**, *93*, 776−84.

(38) Mollay, B.; Lemmar, U.; Kersting, R.; Mahrt, R. F.; Kurz, H.; Kauffmann, H. F.; Bassler, H. *Phys. Rev. B* **1994**, *50*, 10769−79.

(39) Kersting, R.; Mollay, B.; Rusch, M.; Wenisch, J.; Leising, G.; Kauffmann, H. F. *J. Chem. Phys*. **1997**, *106*, 2850−64.

(40) Kersting, R.; Lemmer, U.; Mahrt, R. F.; Leo, K.; Kurz, H.; Bassler, H.; Gobel, E. O. *Phys. Rev. Lett.* **1993**, *70*, 3820−3.

(41) Bassler, H.; Brandl, V.; Deussen, M.; Gobel, E. O.; Kersting, R.; Kurz, H.; Lemmer, U.; Mahrt, R. F.; Ochse, A. *Pure Appl. Chem.* **1995**, *67*, 377−95.

(42) Palszegi, T.; Sokolov, I. M.; Kauffmann, H. F. *Macromolecules* **1998**, *31*, 2521−6.