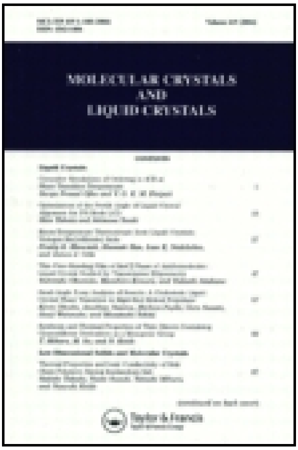


Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

Structure of Polymer Liquid Crystals and Electro-Optical Properties

Seiji Ujiie [a], Naoyuki Koide [a] & Kazuyoshi Iimura [a]

[a] Department of Chemistry, Faculty of Science, Science University of Tokyo, Kagurazaka, Shinjuku-ku, Tokyo, 162, JAPAN

Version of record first published: 13 Dec 2006.

To cite this article: Seiji Ujiie , Naoyuki Koide & Kazuyoshi Iimura (1987): Structure of Polymer Liquid Crystals and Electro-Optical Properties, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 153:1, 191-198

To link to this article: http://dx.doi.org/10.1080/00268948708074535

Mol. Cryst. Liq. Cryst., 1987, Vol. 153, pp. 191-198
Photocopying permitted by license only

Printed in the United States of America

STRUCTURE OF POLYMER LIQUID CRYSTALS AND ELECTRO-OPTICAL PROPERTIES

SEIJI UJIIE, NAOYUKI KOIDE
AND KAZUYOSHI IIMURA
Department of Chemistry, Faculty of Science,
Science University of Tokyo, Kagurazaka,
Shinjuku-ku, Tokyo 162, JAPAN

Abstract Electro-optical properties of the comb-like and the main chain type liquid crystalline polymers were investigated in terms of the molecular weight and the polymer structures. The comb-like polymer has acrylic or methacrylic skeletal chain with 4-cyanobiphenylbenzoate as a mesogenic pendant group. The response time on application of DC field was longer for the methacrylic polymer owing to its less mobility of the skeletal chain. The main chain type polymer with α-cyanostilbene as a mesogenic moiety exhibited a relatively short response time as low as 200ms. This is likely originated from a large dielectric anisotropy of the mesogenic moiety.

INTRODUCTION

Since electro-optical property of low mass nematic liquid crystals was first described by Heilmeir et al.[1], their applications have been extensively investigated and have led to fruitful success. Recently, various kinds of thermotropic liquid crystalline polymers have been synthesized, and their electro-optical properties were also reported by many research groups[2-5].

Although the liquid crystalline polymer is not necessarily suitable for a high speed display device, the basic study on the relations between the structure of liquid crystalline polymers and electro-optical properties is important to bring about possibility for new applications.

In this report we describe the electro-optical properties of the comb-like polymers with mesogenic group attached to acrylic or methacrylic polymer backbone through different lengths of alkyl spacer, and of the main chain type polyester and polycarbonate with mesogenic group alternatively linked with flexible alkyl or oxyethylene spacer. The influence of polymer structure and molecular weight on the electro-optical properties are discussed.

EXPERIMENTAL

Substances

The structure of liquid crystalline polymers investigated are shown in Figure 1, and their thermal properties are listed in Table 1.

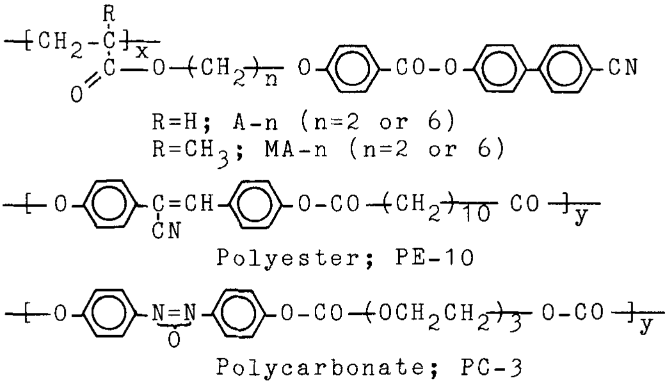
Acryl or methacryl monomer was prepared by reacting 4-(ω-acryloyloxyalkoxy)-benzoyl chloride or 4-(ω-methacryloyloxyalkoxy)-benzoyl chloride with 4-hydroxy-4'-cyanobiphenyl, respectively, and polymerized using AIBN or BPO6).

Polyester was obtained by reacting 4,4'-dihydroxy- α-cyanostilbene with α, ω-dodecane-dioyl chloride6).

Polycarbonate was obtained by reacting 4,4'-dihydroxyazoxybenzene with triethyleneglycol- α,ω -

dichloroformate7).

The samples with different molecular weight were obtained by changing polymerization conditions for the comb-like polymers, and by fractional precipitation using the mixed solvent


R=H; A-n (n=2 or 6)
R=CH$_3$; MA-n (n=2 or 6)

Polyester; PE-10

Polycarbonate; PC-3

FIGURE 1. Structures of polymers.

TABLE 1. Thermal properties of polymers

Sample	Mn	[η](dl/g)	Transition temp.1)(° C)
A-2	6200	-	g (95.0)N(303.0)I
	11300	-	g(100.0)N(315.0)I
A-6	14100	-	g (60.0)S(332.0)I
MA-2	9000	-	g(113.0)N(296.0)I
	21500	-	g(145.0)N(312.0)I
MA-6	10300	-	g (60.0)S(328.0)I
PE-10	20000	0.37	K(134.0)N(198.0)I
PC-3	7200	0.13	K(10.4)S(47.0)N(130.1)I
	13500	0.20	K(13.0)S(57.0)N(147.4)I
	23000	0.27	K(16.5)S(66.0)N(150.4)I

1) g,glassy state;K,solid phase;N,nematic phase; S,smectic phase;I,isotropic phase. Numerals in parentheses indicate the transition temperatures.

system of THF(good solvent) and methanol(poor solvent) for the main chain type polymer, PC-3.

Measurement of Electro-optical Effect

The sample was sandwitched between conductive glass plates coated with In_2O_3/SnO_2. The cell maintained at constant temperature on the Mettler Hot Stage FP52 with the control unit FP5. The response time(rise time;τ_r and decay time;τ_d) was determined by recording the change in transmitted birefringent light intensity through the sample cell kept at the mesomorphic temperature.

On application of a DC voltage above the threshold a dynamic scattering texture appeared and the transmission of light was inhibited. On removal of the DC voltage the transmittance of birefringent light was recovered quite slowly. The rise time on application of a DC electric field of 60V is defined as the time required for the transmission of the sample between cross polars to drop from 90% to 10% of its initial light intensity. The decay time was obtained from the reverse process of the transmittance. Transmitted light intensity was monitored with a photo-diode, and was recorded.

RESULTS AND DISCUSSION

As shown in Figure 2, τ_rs observed at a reduced temperature(T/Ti=0.82 for the comb-like polymers and 0.94 for the main chain type polymers) are decreased with increasing applied voltage and reached to a constant value. Inverse of τ_r

was found to be linear against V^2 in a similar manner as observed for low mass liquid crystals.

Decay times(τ_d) on removal of the electric field were several ten times of τ_r for the comb-like polymers(A and MA), however, those of main chain type of polymers(PC and PE) were several hundreds times of τ_r. The large τ_d amounting to several tens or hundreds seconds is likely originated from higher viscosity of the polymer melt.

Figure 3 shows the temperature dependence of τ_r for the comb-like polymers in the mesomorphic temperature region. At a temperature near the isotropization point shorter response times as low as 200ms have been observed.

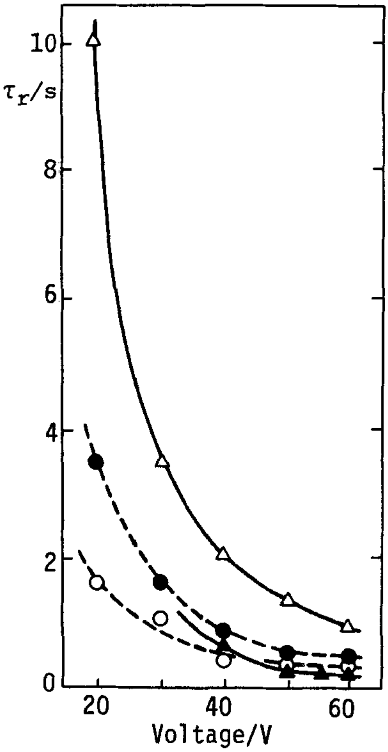


FIGURE 2. Relation between rise time(τ_r) and applied voltage: ○, A-2(Mn=11300); ●, MA-2(Mn=9000); ▲, PE-10(Mn=20000); △, PC-3 (Mn=7200).

Comparing with the polymers having the same backbone structure and spacer length, τ_r becomes longer for the higher molecular weight polymers. The smectic polymers(MA-6, A-6) exhibit longer τ_r in comparison with τ_r of the nematic polymers(MA-2,A-2), and a steep increase in τ_r with lowering temperature is observed for the smectic polymer. These data would be resulted from a higher orientational order in the smectic phase.

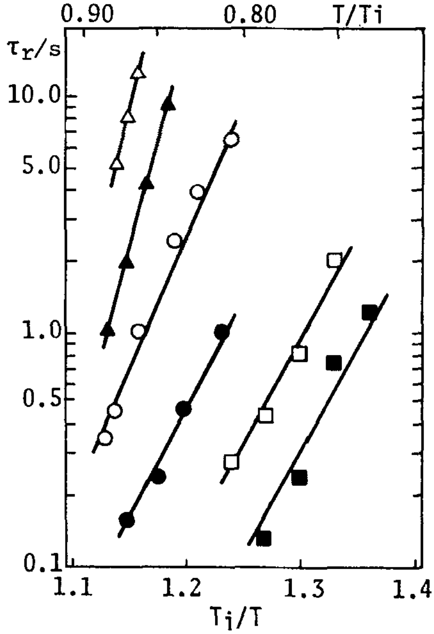


FIGURE 3. Temperature dependence of τ_r for the comb-like polymers; ■ , A-2(Mn=6200); □ ,A-2(Mn=11300); ▲ ,A-6(Mn=14100) ; ● ,MA-2(Mn=9000); ○ ,MA-2(Mn=21500); △ ,MA-6(Mn=10300): T , measuring temperature; Ti , isotropization temperature.

The methacrylic polymers(MA-6, Mn=10300 and MA-2, Mn=9000) always exhibit a longer τ_r than the acrylic polymers(A-6,Mn=14100 and A-2,Mn=11300) with higher molecular weights. The difference in τ_r should be ascribed to the mobility of the polymer backbones. α -Methyl group in the methacrylic backbone hinders rotational motion of the skeletal chain. Measurement of threshold voltage(V_{th}) supports the above interpretation. V_{th}s of the acrylic polymer(A-2,Mn=11300) and the methacrylic polymer (MA-2,Mn=9000) at a reduced temperature of T/Ti= 0.82 were determined to be 11.0 and 15.0V, respectively. These data well reflects the polymer chain mobility.

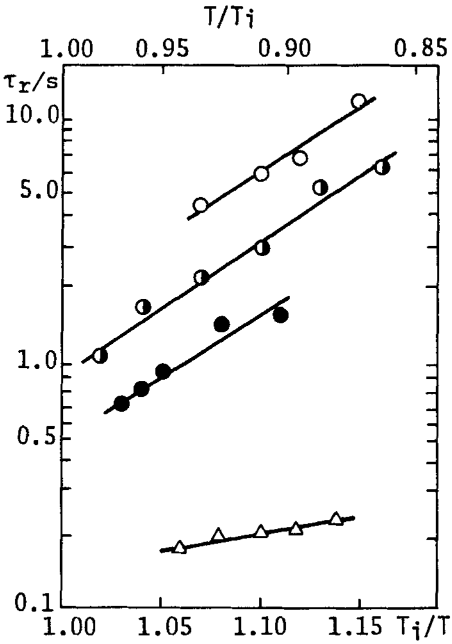


FIGURE 4. Temperature dependence of τ_r for the main chain type polymers: ● ,PC-3(Mn=7200); ◑ ,PC-3(Mn=13500); ○ , PC-3(Mn=23000); △ ,PE-10 (Mn=20000).

Figure 4 shows the temperature dependence of τ_r for the main chain type of polymers. Both Polyester(PE-10) and Polycarbonate(PC-3) exhibited nematic phase.

Values of τ_r for PC-3 change in the order of several seconds depending on its molecular weight. The higher molecular weight polymer shows longer τ_r, which becomes short

TABLE 2. Activation energy

Sample	Mn	Ea(KJ/mol)
PC-3	7200	44.0
	13500	44.0
	23000	48.0
PE-10	20000	33.0

with raising temperature.

In spite of the large molecular weight, τ_r of PE-10 is in the order of several one-tenth seconds and its temperature dependence is small. Apparent activation energy of orientation for PE-10 is smaller than that of PC-3 (Table 2).

This can be understood as the difference between their dielectric anisotropies($\Delta\varepsilon$). Mesogenic groups for both polymers have a negative dielectric anisotropy, and $\Delta\varepsilon$ for PE-10 and PC-3 are estimated as -5.5 and -0.2, respectively, from the data of the corresponding low mass liquid crystals[8]. τ_r is inversely proportional to $\Delta\varepsilon$. Accordingly, τ_r becomes shorter for the polymer with large $\Delta\varepsilon$, assuming that the melt viscosities of these polymers have the same order in magnitude.

ACKNOWLEDGMENT
The authors are grateful to Messrs. T.Michihata, K.Funaki and J.Amano for preparations and characterization of the polymer samples.

REFERENCES

1. G.H.Heilmeier, L.A.Zanoni and L.A.Barton, Proc.IEEE., 56, 1162(1968)
2. H.Finkelmann and H.Ringsdorf, Makromol.Chem., 179, 273(1978)
3. H.Ringsdorf and R.Zentel, Makromol.Chem., 183, 1245(1982)
4. H.Pranoto and W.Haase, Mol.Cryst.Liq.Cryst., 98, 299(1983)
5. H.J.Coles and R.Simon, Mol.Cryst.Liq.Cryst. Lett., 1, 75(1985), 3, 37 (1986)
6. K.Iimura, N.Koide and M.Takeda, to be published in "Current Topics in Polymer Science, Hanser pub.
7. R.Ohta, Y.Kanai, K.Funaki, J.Amano, S.Ujiie, N.Koide and K.Iimura, Koubunshi Ronbunshu, 43, 301(1986)
8. "New Technology with Liquid Crystals"(Japanese), edited by S.Matumoto and I.Tsunoda(Kogyou-Chosa-Kai, Tokyo, 1983)P72 and 85.