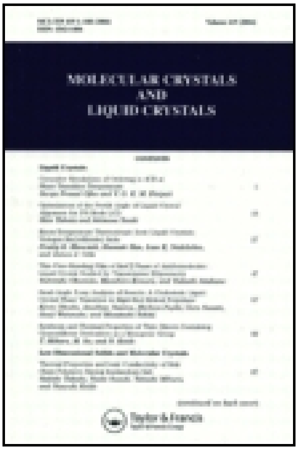

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Synthesis and Optical Properties of Monodisperse Side-Chain Electro-Optic Polymers

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Monodisperse side-chain electro-optic polymers were synthesized by Williamson synthesis using monodisperse polystyrene and disperse red-1 (DR-1) azo dye. Narrower dispersed EO polymer showed weaker absorptional tail suggesting that waveguides fabricated from these polymers have less optical losses in 650~850nm wavelength region. In host-guest system, however, monodisperse polystyrene doped with DR-1 showed no significant difference in absorption from DR-1 doped polystyrene with broader dispersity.

Keywords: electro-optic polymer; monodisperse polystyrene; azo-dye

INTRODUCTION

Electrooptic (EO) polymers are attractive materials for applications in the optical signal processing devices[1]. However, these materials absorb light slightly in the range of 650~850nm wavelength used for information processing systems due to the CT absorptional tail of the chromophore in the polymers. This absorption becomes significant optical losses for waveguides fabricated from these polymers with optical path more than 1 cm. At 830nm, it has been reported that side-chain polymers having disperse red-1 (DR-1) or trifluoromethyl-sulfonyl-amino-tolane attached to PMMA had weak absorptions compared to that of p-nitro-amino-tolan attached PMMA about an order of magnitude[2]. In this study, instead of favorable chromophores from the point of absorptional tail, we have noticed main-chain in polymer, and monodisperse polymer was used as backbone, since monodispersity of polymer backbone seems to construct homogeneous environment around chromophores and be effective to reduce the absorption of the chromophore in the longer wavelength region. As polymer matrix, monodisperse polystyrene was chosen because of its availability and excellent transparency[3]. As a chromophore, a standard azo dye, DR-1, was used. Monodisperse polystyrenes were chloromethylated, subsequently reacted with a sodium salt of DR-1 to obtain the corresponding side-chain polymers. Their optical properties were measured by UV-Vis spectroscopy in thin films fabricated by spin-coating from the polymer.

SYNTHESIS OF SIDE-CHAIN EO POLYMER

Polystyrene with narrow or broad molecular weight distribution was chloromethylated using standard method as follows[4][5]. Polystyrene (1.0 g) was dissolved in chloromethylethylether (60 ml), and 40 ml of chloromethylethylether solution of $ZnCl_2$ (0.3g) was added dropwise with stirring and heating this mixture to 50C°. After stirring for 5hr, a mixture of MeOH and 1,4 -dioxane (1:1, 7ml) was added and then the reaction mixture was poured into a mixture of MeOH and water (7:3, 100 ml). The resulting precipitate was filtered off, washed with MeOH, dissolved in THF and reprecipitated into MeOH. The resulting polymer was dried under vacuum.

Side-chain EO polymer was prepared according to the procedure reported by Noël et al.[6][7]. 4-Nitro-4'-(N-ethyl-N-(2-hydroxyethyl)amino)azo benzene (DR-1) was dissolved in THF (5ml), and 5ml of aqueous NaOH (2.5g) was added with vigorous stirring. Tetrabutylammonium hydrogensulfate (0.1g) in 2.5ml of water was then added to the reaction mixture. After stirring for about 15min, chloromethylated polystyrene (0.3mg) dissolved in 10ml of THF was added dropwise. The reaction mixture was stirred for 48hr at room temperature under air and then poured into cold water (300ml). The resulting precipitate was filtered off and repeatedly washed with water until the filtrate was at neutral pH. The precipitate was then dissolved in THF and reprecipitated into cyclohexane. The resulting polymer was dried under vacuum. Figure 1 shows the chemical structure of the polymer.

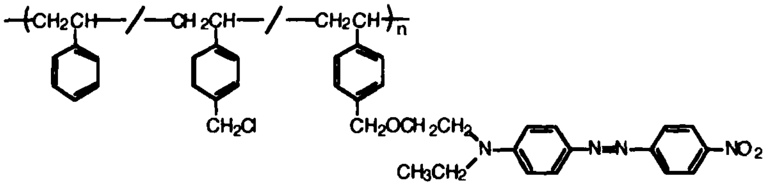

FIGURE 1 Side-chain EO polymer synthesized in this study

OPTICAL PROPERTIES

Characteristic features of the polymers are shown in Table. Polymers synthesized at DR-1 feed ratio of 20 mol% to styrene repeating unit have contents of 3~5 mol% of DR-1. These chromophore contents are less than that of reported result for other synthesis root[8]. This may be due to the fact that synthetic parameters are not optimized. In the case of DR-1 feed ratio of 30mol% to styrene repeating unit, the content of 11mol% was obtained.

TABLE 1 Characteristics of side-chain EO polymers

Starting Polystyrene		CCM[b]	DR-1 feed[c]	DR-1 cont.[d]
D[a]	Mn	(%)	(mol%)	(mol%)
1.01	99000	47	20	4.1
1.03	212500	73	20	5.4
1.03	212500	73	30	10.9
1.86	159600	77	20	3.2

a) Dispersity of starting polystyrenes. b) Conversion of chloromethylation determined by elemental analysis. c) Feed ratio of DR-1 to styrene repeating units. d) DR-1 content to styrene repeating units determined by elemental analysis.

Thin films were fabricated from these polymers by spin coating and Figure 2 show the UV-Vis absorption of these films. In these spectra which were

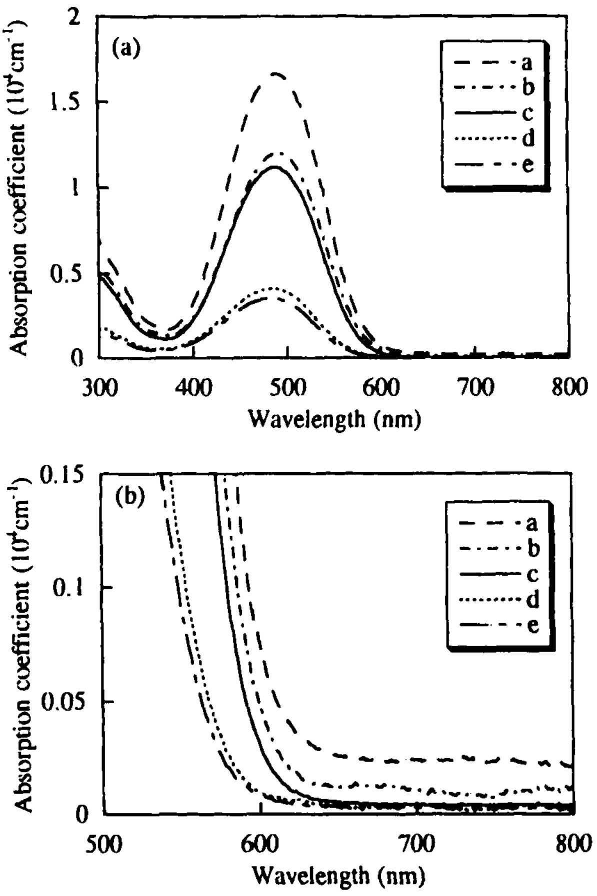

Figure 2 (a) UV-Vis absorption spectra of side-chain EO polymers and DR-1 doped polymers and (b) magnified spectra of (a) a~c:side-chain polymer. d,e:DR-1 doped polystyrene. a:D=1.86, 3.2mol% (DR-1 content), b:D=1.03, 5.4mol%, c:D=1.01, 4.1mol%, d:D=4.75, 1.74mol%, e:D=1.03, 1.74mol%.

normalized by film thickness, it is shown that absorption coefficients in the region of chromophore absorptional tail depend on the dispersities of each polymer backbones, i.e., the polymer with narrower dispersity has lower absorption coefficient.

This tendency was obtained for host-guest system, however, the unusual profile was shown for the thin film of polystyrene doped with DR-1 at a ratio of 5mol% , the same content obtained for the side-chain polymers. This implies that chromophores aggregated in this content, which indicates that chromophores covalently attached to polymer backbone are dispersed better into polymer matrix than those doped to polymer. To obtain usual UV-Vis spectra, it was necessary to reduce the chromophore content to 1.74mol% (5wt%). In this case, dispersity dependence did not appear in UV-Vis spectra, showing almost the same absorption coefficient in absorptional tail region as shown in Figure 3.

It seems that in the side-chain polymer, the effect of reducing chromophore absorption tail is due to its homogeneous environment around the chromophores which arises from the homogeneous length of matrix polymers. For understanding this effect, we consider a simple model[9], assuming that polymers form random coils and chromophores are attached to each polymer chain at a same ratio, separated at regular intervals to neighboring one. Considering an end-to-end vector $\underline{R}$ from one terminal group to another one in single polymer chain, its end-to-end distance $\langle \underline{R}^2 \rangle$ is related to bond-vector $\underline{b}_i$ as following equation, $\langle \underline{R}^2 \rangle = Nb$ where N and b represent the degree of polymerization and the absolute value of $\underline{b}_i$, respectively. The radius of gyration $\langle \underline{R}_g^2 \rangle$ of random coil of the polymer is also related to $\underline{R}$ as following equation, $\langle \underline{R}_g^2 \rangle = \langle \underline{R}^2 \rangle/6$, then $\langle \underline{R}_g^2 \rangle = Nb/6$ can be obtained. Since the $(\langle \underline{R}_g^2 \rangle)^{1/2}$ is proportional to $N^{1/2}$, the volume occupied by random coil is proportional to $N^{3/2}$. This can be interpreted that if a polymer has a longer main-chain, the number of chromophore per unit volume decreases more and the interaction between the chromophore and the main-chain becomes weaker. Assuming that extending chromophore absorption is derived from the interaction, a series of polymers with regular length cause interaction with almost the same intensity to chromophores. As a result, the absorptions are localized within narrow wavelength region.

CONCLUSION

EO polymer, polystyrene with DR-1 as a side-chain, was synthesized by Williamson method using chloromethylated polystyrene and sodium salt of DR-1. Narrower dispersed EO polymer showed weaker absorptional tail, suggesting that waveguides fabricated from these polymers have less optical losses in this region. However, polystyrene doped with DR-1 showed no significant difference in absorption influenced by dispersity of polystyrene. For more practical study, it is necessary to perform the measuring of propagating losses in the waveguides.

Acknowledgments

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