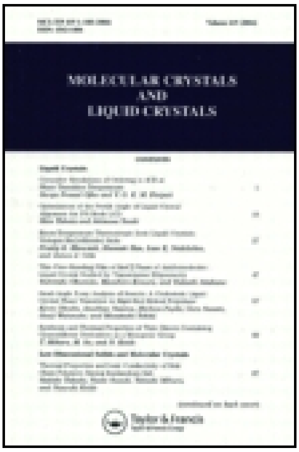

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis of Second-Order Nonlinear Optical Polymers Containing Stilbazolium Salt Chromophore in the Side Chain

Dong Hoon Choi [a], Sangyup Song [a], Sun Jin Lim [a], Soo Young Park [a] & Nakjoong Kim [a]

[a] Division of Polymer Research Korea, Institute of Science and Technology, P.O. Box 131, Cheongryang, Seoul, 130-650, KOREA

To cite this article: Dong Hoon Choi, Sangyup Song, Sun Jin Lim, Soo Young Park & Nakjoong Kim (1995): Synthesis of Second-Order Nonlinear Optical Polymers Containing Stilbazolium Salt Chromophore in the Side Chain, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 267:1, 53-58

To link to this article: http://dx.doi.org/10.1080/10587259508033972

Mol. Cryst. Liq. Cryst. 1995, Vol. 267, pp. 53–58
Reprints available directly from the publisher
Photocopying permitted by license only

SYNTHESIS OF SECOND-ORDER NONLINEAR OPTICAL POLYMERS CONTAINING STILBAZOLIUM SALT CHROMOPHORE IN THE SIDE CHAIN

Dong Hoon Choi*, Sangyup Song, Sun Jin Lim, Soo Young Park,
and Nakjoong Kim
Division of Polymer Research
Korea Institute of Science and Technology
P.O. Box 131 Cheongryang, Seoul 130-650, KOREA

Abstract We synthesized novel side chain copolymers containing the stilbazolium tetraphenylborate for the linear electro-optic coefficient measurement. These polymers are very soluble in common organic solvents such as acetone, cyclohexanone, dimethylformamide etc. The second-order nonlinear optical properties of poly [1-[(N-ethylenepiperazyl)-stilbazolium tetraphenylborate]-N-[(1,1-dimethyl-*m*-isopropenyl)benzyl]carbamate-co-methylmethacrylate] (POLYMER Ia & Ib), poly [1-[(N-ethylenepiperazyl)-stilbazolium tetraphenyl borate]-N-[(1,1-dimethyl-*m*-isopropenyl)benzyl]carbamate-co-N-vinylcarbazole] (POLYMER II), and poly [1-[(N-ethylenepiperazyl)-stilbazolium tetraphenyl borate]-N-[(1,1-dimethyl-*m*-isopropenyl)benzyl]carbamate-co-4-hydroxyphenyl maleimide] (POLYMER III) were improved due to the change of the nonlinear optical chromophore in the side chain.

INTRODUCTION

The field of photonics has drawn much interest as a frontier science that has many applications to the future technology. Nonlinear optics (NLO) is an essential part of photonics whose technology includes acquisition, storage, process, and transmission of photons instead of electrons in signal processing. For this purpose, organic materials have been highlighted in this field mainly due to their inherent advantageous material properties since a decade ago. Organic NLO materials provide strong potential advantages for second harmonic generation and electro-optic applications. [1-7]

Particularly, side-chain polymers have drawn remarkable interest in recent years as promising candidates for application in electro-optic and photonic devices. [1-9] In this work, we selected the stilbazolium salt chromophore as a second-order NLO active group. In an attempt to enhance both the poling induced optical nonlinearity and temporal stability of the side chain NLO polymers, we have designed and synthesized some novel α-methylstyrene copolymers containing stilbazolium tetraphenylborate chromophore in the side-chain, which can show high glass transition temperatures with an aid of robust comonomers such as N-vinylcarbazole, 4-hydroxyphenylmaleimide etc.

EXPERIMENTAL

The syntheses of monomers are well illustrated in Figure 1. 4-[N-(2-hydroxyethyl)piperazyl]benzaldehyde (II) was prepared by reported method.(10) Additionally, we synthesized 4-hydroxyphenyl maleimide (HPMI) following the known procedure. (11)

1,4-Dimethylpyridinium iodide (I)

Iodomethane (3.36 g, 23.7 mmole) and 4-picoline (2 g, 21.5 mmole) were mixed in dichloromethane (30 ml). The mixture was refluxed for 12 hours. The concentrated solution was added dropwise to hexane. The solid product was filtered and purified in ether/ethanol. Product is quite hygroscopic. Percent yield is 85%, m.p. 150-153°C
^{1}H NMR (DMSO-d^6) δ 2.55 (s, 3H), 4.24 (s, 3H), 7.93 (d, 2H), 8.83 (d, 2H)

1-Methyl-4-{2-[N-(2-hydroxyethyl)piperazyl]vinyl}pyridinium iodide (III)

4-[N-(2-hydroxyethyl)piperazyl]benzaldehyde (1 g, 4.2 mmole) and 1,4-dimethylpyridinium iodide (1.004 g, 4.2 mmole) were dissolved in absolute ethanol (20 ml). After heating the solution to 60°C, piperidine (0.364 g, 4.2 mmole) was added dropwise. The solution was refluxed for 12 hours at 90°C. The solution was kept in cold room (0°C-4°C) overnight. The solid crystals could be collected. Recrystallization was done from methanol. Percent yield was 65 %. m.p. 230-233 °C.
^{1}H NMR (DMSO-d^6) δ 8.74 (d, 2H), 8.10 (d, 2H), 7.95 (d, 1H), 7.60 (d, 2H), 7.27 (d, 1H), 7.06 (d, 2H), 4.49 (t, 2H), 4.21 (s, 3H), 3.57 (t, 2H), 3.37 (4H), 2.58 (4H)
Anal. Cald. $C_{20}H_{26}N_3OI$ (451.35): C, 53.22; H, 5.81; N, 9.31. Found; C, 53.01; H, 5.70; N, 9.25.

[1-[(N-ethylenepiperazyl)-stilbazolium iodide]-N-[(1,1-dimethyl-*m*-isopropenyl)benzyl]] carbamate (IV)

1-Methyl-4-{2-[N-(2-hydroxyethyl)piperazyl]vinyl}pyridinium iodide (III) (20.0 g, 44 mmole) was dissolved in 80 ml of dried dimethylformamide and a trace of dibutyltin dilaurate was introduced into the mixture as a catalyst. *m*-Isopropenyl-α,α-dimethylbenzylisocyanate (13.5 g, 67 mmole) was added dropwise into the mother solution over a period of 30 minutes. The mixture was kept stirring at 60°C for 10 hours. It was poured into the cold ethanol (500 ml). Recrystallization was done from ethanol. Percent yield was 62%. m.p. 190-193 °C.
^{1}H NMR δ 8.74 (d, 2H), 8.10 (d, 2H), 7.95 (d, 1H), 7.65 (d, 2H), 7.47 (s, 1H), 7.27 (m, 4H), 7.06 (d, 2H), 5.42 (s, 1H), 5.08 (s, 1H), 4.21 (s, 3H), 4.04 (t, 2H), 3.47 (6H), 2.58(4H), 2.10 (s, 3H), 1.55 (s, 6H)

Anal. Cald. $C_{33}H_{41}N_4O_2I$ (652.62): C, 60.73; H, 6.33; N, 8.58. Found; C, 60.54; H, 6.09; N, 8.52.

[1-[(N-ethylenepiperazyl)-stilbazolium tetraphenyl borate]-N-[(1,1-dimethyl-*m*-isopropenyl)benzyl]]carbamate (V)

[1-[(N-ethylenepiperazyl)- stilbazolium iodide]-N-[(1,1-dimethyl-*m*-isopropenyl)benzyl]] carbamate (7.6 g, 11.6 mmole) was dissolved in methanol (500ml). At room temperature, the methanol solution of tetraphenyl boron sodium was added dropwise in the mother solution. Solid product came out after 30 minute stirring. Yellow solid material can be isolated. Recrystallization was done in ethanol/ acetone. Percent yield was 92%. m.p. 182-184°C

^{1}H NMR δ 8.74 (d, 2H), 8.10 (d, 2H), 7.95 (d, 1H), 7.60 (d, 2H), 7.47 (d, 1H), 7.30-6.70 (26H), 5.42 (s, 1H), 5.08(s, 1H), 4.21 (s, 3H), 4.04 (t, 2H), 3.49 (6H), 2.57 (4H), 2.10 (s, 3H), 1.55 (s, 6H)

Anal. Cald. $C_{57}H_{61}N_4O_2B$ (844.95)): C, 81.03; H, 7.28; N, 6.63. Found; C, 80.9; H, 7.31; N, 6.68.

Poly [1-[(N-ethylenepiperazyl)-stilbazolium tetraphenylborate]-N-[(1,1-dimethyl-*m*-isopropenyl)benzyl]]carbamate-co-methylmethacrylate (POLYMER Ia)

[1-[(N-ethylenepiperazyl)-stilbazolium tetraphenylborate]-N-[(1,1-dimethyl-*m*-isopropenyl)benzyl]]carbamate (V) (0.796 g, 0.942 mmole) was dissolved in 18 ml of dried dimethylformamide in a vacuum ampule. To the solution, are added 0.283 g of methylmethacrylate and one mole percent of azobisisobutyronitrile. The mixture was thoroughly degassed by freeze-vacuum-thaw technique and heated at 70°C for 48 hours. The resulting viscous mixture was cooled and poured into hot methanol to precipitate the red solid. The copolymer was purified by reprecipitation from dimethylformamide into ether. Then, it was dried *in vacuo* at 90°C for 48 hours. Percent yield 45%. Polymer Ib, Polymer II, and polymer III were prepared in a same way. Specifications of other polymerizations are illustrated in Table 1.

RESULTS AND DISCUSSION

The synthesis of the α-methylstyrene monomers is illustrated in the Figure 1. Compound III was synthesized using 4-[N-(2-hydroxyethyl)piperazyl]benzaldehyde (II) and 1,4-dimethylpyridinium iodide (I) with an equivalent of piperidine. Well known reaction of urethane formation using isocyanate and alcohol can give us to prepare the monomer IV. This reaction yield and the reaction rate is strongly dependent on the temperature. At room

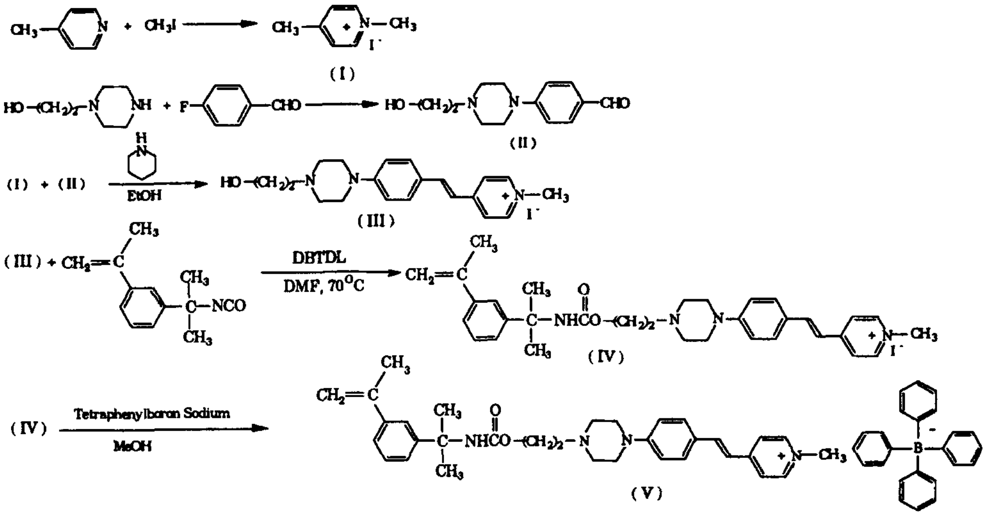

Figure 1. Synthetic procedure of α-methylstyrene containing stilbazolium salt chromophore.

temperature, the reaction yield was achieved 50% after the reaction was kept for 24 hours. At 60°C for 5 - 6 hours, the yield was improved to 65%.

The compositions of copolymers (Ia & Ib) can be calculated by integration of proton NMR signal. The copolymer compositions were not consistent with the monomer feeding concentrations. When methylmethacrylate (MMA) was used as a comonomer, 1: 3 (monomer V: MMA) feeding ratio gave 1 : 2.2 resultant mole ratio. In the case of N-vinylcarbazole as a comonomer, NMR spectrum does not give useful information about the composition because the chemical shift of the protons in aromatic ring of carbazole were all overlapped with the other chemical shifts of the protons in the stilbazolium structure. The resultant mole ratio of *p*-hydroxyphenyl maleimide and NLO monomer was calculated 1 : 0.95 with the NMR spectral analysis with the monomer feeding mole ratio of 1 : 2 (HPMI: monomer V).

Thermal Properties of Copolymers

Differential scanning calorimetry was utilized for studying the thermal transition behaviors of new copolymers. The glass transition temperature of polymer Ia was determined 125-128 °C. The polymer Ib showed the glass transition behavior around 120-122°C which is lower than that of polymer I. It is seeing that the higher composition of MMA can lower the T_g of polymer Ib. In the case of polymer II, T_g was observed around 144-146°C which is relatively higher than those of copolymers with MMA because the N-vinyl carbazole unit lead to increase T_g due to

Table 1. Specification of α-methylstyrene copolymers.

Polymer	Comonomer	Yield	m : n [a] feeding	m : n [b] polymer	$\eta_{inh.}$ (dl/g) [c]
POLYMER Ia	MMA	45%	1 : 3	1 : 2.2	0.26
POLYMER Ib	MMA	55%	1 : 6	1 : 4	0.39
POLYMER II	VK	40%	1 : 3	–	0.32
POLYMER III	HPMI	60%	2 : 1	0.95 : 1	0.43

* MMA: methylmethacrylate
VK: N-vinyl carbazole
HPMI: 4-hydroxyphenyl maleimide
[a] m: mole fraction of NLO monomer charge
n: mole fraction of comonomer charge
[b] m: mole fraction of NLO monomer in copolymer
n: mole fraction of comonomer in copolymer (Cal'd by NMR)
[c] Inherent viscosity was measured at 25°C in DMF.

its chain rigidity. When 4-hydroxyphenylmaleimide was used as a comonomer, the glass transition could not be observed upto 170°C. At higher temperature than 170°C, we could not observe the glass transition behavior because molecular ionic chromophore start to decompose around 160-170°C.

Linear Electro-optic Coefficients of α-Methylstyrene Copolymers

We measured the electro-optic coefficient following the simple reflection technique proposed by C. C. Teng et. al.(12) The electro-optic coefficient "r_{33}" could be calculated by following equation

$$r_{33} = \frac{3\lambda I_m}{4\pi V_m I_c n^2} \frac{(n^2 - \sin^2\theta)^{\frac{3}{2}}}{(n^2 - 2\sin^2\theta)} \frac{1}{\sin^2\theta} \qquad [1]$$

where I_m is the amplitude of modulation, V_m is the modulating voltage applied to the sample, and I_c is half the maximum intensity of modulation. Since the piperazyl group is likely to behave as a good electron donating group in the side chain, it can affect the second-order nonlinearity of the synthesized new polymers. Additionally, the α-methylstyrene backbone structure give some stiffness of polymer chain to improve thermal properties to which higher glass transition temperature can be attributed. The refractive indices of four polymers were measured by ellipsometric technique at 632 nm, wavelength which is same as the wavelength used in electro-optic study. Using the equation (1), the electro-optic coefficients of polymer Ia , Ib, II, and III were calculated to be 45, 36, 38, and 30 pm/V respectively. (See Table 2)

Table 2. Measured values of α-methylstyrene copolymers

POLYMER	Absorption Maximum, λ_{max} (nm)	T_g (°C)	Refractive Index[a]	r_{33} (pm/V)[b]
POLYMER Ia	456	125-128	1.638	45
POLYMER Ib	452	120-122	1.617	36
POLYMER II	465	144-146	1.717	38
POLYMER III	465	—	1.685	30

[a] Refractive Indices were measured using Rudolph Ellipsometry under 632.8 nm wavelength.

[b] EO coefficient was measured after electrode poling.

REFERENCES

1. P. N. Prasad and D. J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers; (Wiley: New York, 1991.)
2. D. J. Williams, Nonlinear Optical Properties of Organic and Polymeric Materials (ACS Symp. Ser. 233, 1983.)
3. D. S. Chemla and J. Zyss, Nonlinear Optical Properties of Organic Molecules and Crystals (Academic Press, Orlando, FL 1987.)
4. A. J. Heeger, J. Orenstein, and D. R. Ulrich, Nonlinear Optical Properties of Polymers.(Mater. Res. Soc. Symp. Proceedings, Pittsburgh, 1987; Vol 109.)
5. P. N. Prasad and D. R. Ulrich, Nonlinear Optical and Electroactive Polymers (Plenum Press, New York, 1988.)
6. R. A. Hann and D. Bloor, Organic Molecules for Nonlinear Optics; (The Royal Society of Chemistry Publication, London, 1989; Vol 69.)
7. J. Messier, F. Kajzar, P. N. Prasad, and D. R. Ulrich, Nonlinear Optical Effects in Organic Polymers; (NATO ASI series-vol. 162, Kluwer Academic Publishers, Netherlands, 1988.)
8. C. Ye, T. J. Mark, J. Yang, and G. K. Wong, Macromolecules, 20, 2322 (1987)
9. D. H. Choi, H. M. Kim, W. P. K. M. Wijekoon, and P. N. Prasad, Chem. Mat. 4, 6, 1253. (1992)
10. R. N. Martino, (Hoechst Celanese Corp.), Eur. Pat. 0 294 706 (1988) (Chem. Abstr., 110, 16. 1989)
11. J. O. Park and S. H. Jang, J. Appl. Polym. Sci., 30, 723 (1992)
12. C. C. Teng and H. T. Mann, Appl. Phys. Lett., 56(18), 30.(1990)