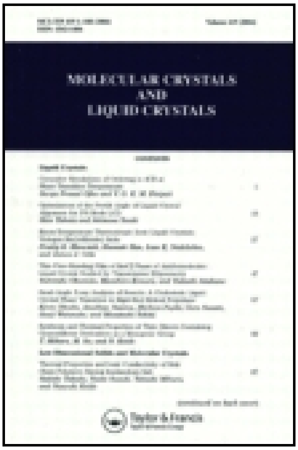

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Nonlinear Optical Polymers with Novel Benzoxazole Chromophores. 1. PMMA Copolymers with Good Thermal and Temporal Stability

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NONLINEAR OPTICAL POLYMERS WITH NOVEL BENZOXAZOLE CHROMOPHORES. 1. PMMA COPOLYMERS WITH GOOD THERMAL AND TEMPORAL STABILITY

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Abstract New copolymers (PMBz) from the benzoxazole-based vinyl monomer and methylmethacrylate as a comonomer, were synthesized for an improvement of thermal stability of second-order nonlinear optical activity. The thermal stability of the chromophores in PMBz copolymers monitored by IR and UV-visible spectroscopy was much better than in PMSt copolymer bearing general pendant stilbene units. The electro-optic coefficient r_{33} of the poled PMBz film exhibited as large as 45 pm/V at 632 nm of He-Ne laser. Thermal relaxation behavior of the poled PMBz films at 100 °C showed that the PMBz having more rigid benzoxazole structure had better temporal stability of r_{33} compared to the general stilbene structure.

INTRODUCTION

Organic nonlinear optical (NLO) polymers provide strong potential to the optoelectronics area. Particularly, side chain polymers are promising candidates as the second-order nonlinear optical materials. The major problems of the organic polymers for the practical applications are thermal and photochemical stabilities of NLO response. Most of the conventional chromophores of in organic second-order NLO polymers are based on the azo or stilbene structure as a conjugated π-framework because of their large hyperpolarizability (β) and facile synthetic method.[1,2] To improve the thermal stability of NLO chromophores, new chromophores having heterocyclic ring instead of general azo or stilbene structures have been designed by others.[3,4]

Recently, we successfully developed several novel chromophores having a benzoxazole π-conjugation system, which have good thermal stability of the benzoxazole units [5] and large μβ values comparable to azo and stilbene chromophores. In this study, we compared the thermal stability of polymethylmethacrylate copolymers (PMBz) bearing the benzoxazole chromophore with a copolymer (PMSt) bearing general stilbene chromophores using UV-visible and infra-red (IR) spectroscopy. The electro-optic coefficients and their temporal stability at 100 °C of poled copolymer films are presented.

EXPERIMENTAL

Materials

The synthesis of a novel vinyl monomer containing the benzoxazole chromophore, 2-(4-nitrophenyl)-6-[N-methyl-N-(2-methacryloy)amino] benzoxazole (1) and copolymers will be reported seperately.[6] Copolymers of PMBz and PMSt as shown in FIGURE 1, were prepared by general radical copolymerization with 1 and methylmethacrylate as a comonomer.

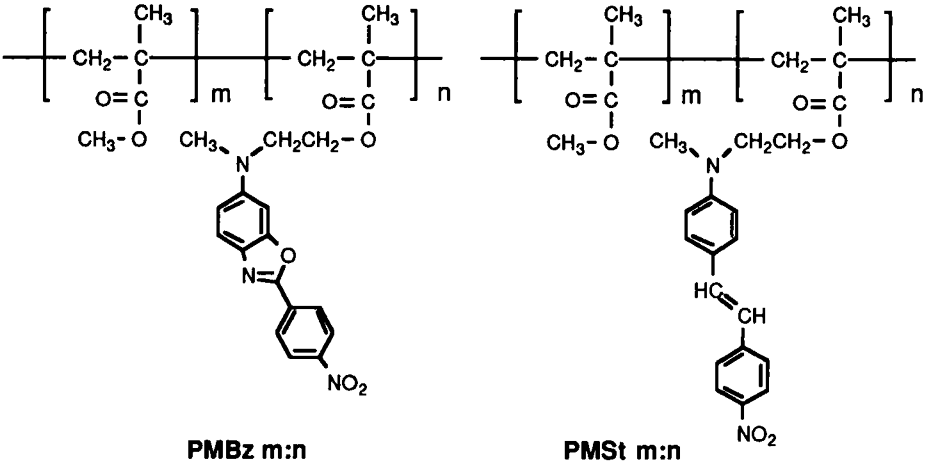

FIGURE 1 Chemical structures of NLO copolymers in this study.

Measurements

FT-IR spectra were recorded on a Mattson Alpha Centauri spectrophotometer. UV-visible spectroscopy was performed by a Shimadzu UV-240. Differential scanning calorimetry (DSC) was performed with a Dupont thermal analyzer DSC 2910 at a heating rate 20 °C/min in nitrogen. The electro-optic coefficients at 632.8 nm of He-Ne laser were measured by the simple reflection technique proposed by C. C. Teng et. al.,[7] and the thin film processing, poling, and the electro-optic measurement procedure was reported by our recent literature in detail .[8]

RESULTS AND DISCUSSION

1. Solubility

PMBz was less soluble than PMSt since the benzoxazole structure of PMBz is more rigid than the stilbene structure of PMSt. The PMBz 1:1 was slightly soluble in dichloroethane and exhibited good solubility in highly chlorinated solvent such as 1,1,2-trichloroethane (TCE) and 1,1,2,2-tetrachloroethane. All the films for a measurement electro-optic coefficient was spin coated at 2000 rpm on ITO glass using TCE as a solvent.

TABLE I Properties of copolymers in this study.

Code	m : n feeded	λmax [a] (nm)	T_g [b] (°C)	Solubility [c]
PMMA	1 : 0	-	117	THF, Chloroform
PMBz 2:1	2 : 1	434	140	DCE, TCE, TtCE
PMBz 1:1	1 : 1	434	134	TCE, TtCE
PMBz 1:2	1 : 2	434	126	TCE, TtCE
PMSt 1:1	1 : 1	430	130	THF, Chloroform

a) film.
b) were determined by DSC at a heating rate of 20 °C/min in nitrogen.
c) THF; tetrahydrofuran, DCE; 1,2-dichloroethane, TCE; 1,1,2-trichoroethane, TtCE; 1,1,2,2-tetrachloroethane.

2. Thermal Property

The thermal properties of all the polymers are presented in TABLE I. All the polymers showed distinct glass transition temperatures by DSC. The PMBz had high T_g values in the range of 120 - 140 °C. The PMBz 1:2 having higher chromophore contents had lower T_g values, probably due to lower degree of polymerization. Due to more rigid side-chain structure of PMBz, the Tg of PMBz 1:1 was a little higher than that of PMSt 1:1. The thermal stability of PMBz and PMST were investigated by IR spectroscopy. Each of IR samples was prepared by spin coating on KBr pellet. FIGURE 2 shows the IR-spectra of PMBz and PMSt before and after heat-treatment at 210 °C for 3 h, respectively. While characteristic benzoxazole absorptions at 1631 and 1606 cm^{-1} (C=N, C=C) showed no remarkable difference after hear-treatment, a characteristic stilbene absorption at 1583 cm^{-1} (C=C) was considerably decreased. It implied that benzoxazole structure is more stable at higher temperature than the stilbene structure. A new absorption band appearing at 1018 cm^{-1} of PMSt after heat-treatment was probably ascribed to the thermal decomposition of stilbene units.

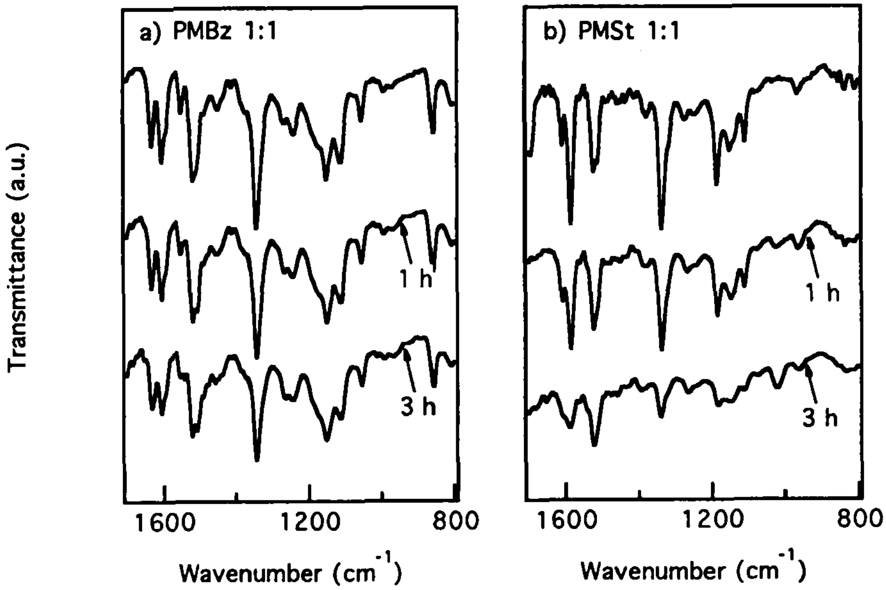

FIGURE 2 FT-IR spectra of (a) PMBz 1:1 and (b) PMSt 1:1 films stored at 210 °C, respectively.

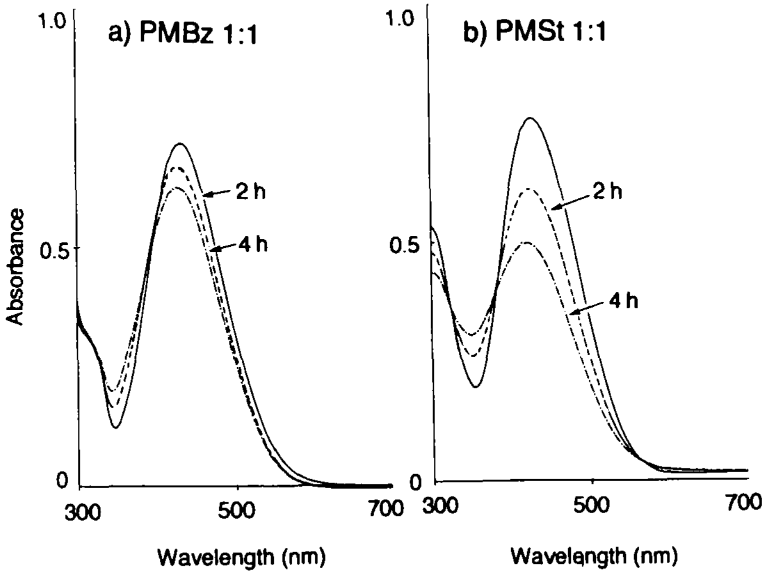

FIGURE 3 UV-visible spectra of (a) PMBz 1:1 and (b) PMSt 1:1 films stored at 170 °C, respectively.

To elucidate the decomposition of π-conjugated chromophores, UV-visible analysis of each films coated on glass with about 0.4 μm thickness was performed before and after stored at 170 °C for 2h and 4 h in air, respectively. FIGURE 3 shows the UV-visible spectra at this conditions. The normalized A (t) / A (0) value at λmax (430 nm) of PMSt for 4 h was remarkably decreased to 0.66 whereas that at λmax (434 nm) of PMBz was decreased to 0.93. The PMSt film after stored at 170 °C for 4 h was considerably bleached due to the cleavage of π-conjugation of stilbene unit. It imply that stilbene double bonded structure was not stable sufficiently enough even at 170 °C, and aromatic benzoxazole structure was evidently more stable.

3. Electro-optic Property

The r_{33} of contact poled PMBz 1:1 at 140 °C at a poling field of 0.7 MV/cm was measured as large as 45 pm/V (at 632.8 nm). The possibility exists of achieving even larger values of r_{33} at higher poling fields. Temporal stability of r_{33} values of the poled PMBz 1:1 films at 100 °C is shown in FIGURE 4. It was very noteworthy that the PMBz aged at 100 °C for 24 h exhibited 67 % of its original r_{33} under even non-crosslinking system. Both of run 1 and run 2 of PMBz films showed a good reproducibility. In contrast, PMSt 1:1 showed poorer temporal stability compared to PMBz 1:1, and the general PMSt under similar conditions exhibited 27 % of its original r_{33}. Though the Tg value of PMBz was a little higher, this outstanding improvement of thermal relaxation behaviors of PMBz was surprising. This improved temporal stability of PMBz film compared to PMSt film may be mainly attributed to its more rigid side-chain chromophore not to be relaxed at a elevated temperature.

CONCLUSIONS

New several NLO copolymers with large and stable r_{33} were synthesized from a new benzoxazole based vinyl monomer. The improved thermal stability of NLO benzoxazole chromophore compared to stilbene chromophores was well evaluated by IR and UV-visible spectroscopy. The r_{33} of poled polymer PMBz 1:1 was as large as 45 pm/V and had good temporal stability at 100 °C. This improved thermal relaxation behavior of PMBz film is attributed to its higher Tg and more rigid side-chain chromophores than conventional stilbene chromophores. From this results, polymers with benzoxazole chromophores are promising and potential candidates for thermally and temporally stable NLO materials that can find many useful high performance NLO applications.

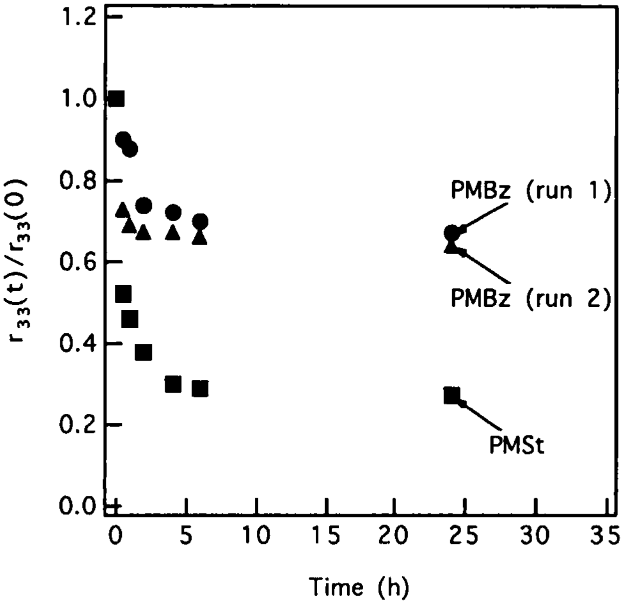

FIGURE 4 Temporal stability of r_{33} of poled PMBz 1:1 and PMSt 1:1 films stored at 100 °C; (●) PMBz 1:1 (run 1), (▲) PMBz 1:1 (run 2), and (■) PMSt 1:1.

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