

cement composite materials under conditions of careful temperature control. According to mercury intrusion porosimetry data currently being analyzed, the superior mechanical properties observed for the magnesia triphosphate cement are not molecular in origin, but instead have their origin in lower porosity arising from a lower water-to-solids ratio (g of water/g of MgO) determined by the superior solubility of the triphosphate precursor. If longer polyphosphate chains are employed, however, it is possible that molecular structure may play a role in determining bulk properties, and we are currently investigating this possibility.

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Second Harmonic Generation of Poled 4-[*N*-Methyl-*N*-(4'-nitrophenyl)amino-methyl]styrene Polymer Film

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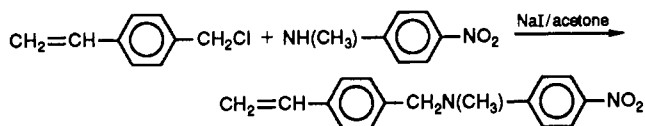
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Since *p*-nitroaniline (pNA) was found to have relatively high hyperpolarizability¹ for one aromatic ring chromophores with a short maximum absorption wavelength of ca. 375 nm and a cutoff wavelength of ca. 480 nm, several polymers having pNA units were prepared to obtain high second-order nonlinearity, i.e., second harmonic generation (SHG). Marks et al.^{2,3} and Eich et al.⁴ introduced pNA units into polystyrene or poly(allylamine) through polymer

reactions. However, it is usually difficult to obtain a high functionalization level or high chromophore concentration through polymer reactions. Most polymers previously reported^{5,6} have long spacer units, which facilitate the orientation of the chromophore unit by electrical poling. But the long spacer units are also considered to increase the relaxation of the orientation when the electric field is removed, leading to a decrease of SHG characteristics. Therefore, the polymerization of a chromophore-linked polymerizable group with a short spacer is expected to provide a polymer with a suppressed relaxation of the orientation as well as with a high chromophore concentration per unit volume.

To obtain this, we synthesized a new styrene derivative, MNPAMS, 4-[(*N*-methyl-*N*-(4'-nitrophenyl)amino-methyl]styrene, a pNA unit linked by only one methylene carbon, and examined the polymerization behavior. The optical properties of the polymer were also studied.

MNPAMS was obtained by the reaction of *p*-chloromethylstyrene with *N*-methyl-*p*-nitroaniline in acetone in the presence of sodium iodide (yield 71%):



The crude MNPAMS was purified by recrystallization in ethanol to obtain a yellow prismatic crystal (mp 121 °C).

Polymerization of MNPAMS was carried out in a glass ampule in a nitrogen atmosphere. Table I shows the results of polymerization. We obtained polymers with radical and anionic initiators but not a cationic catalyst. With a radical initiator a polymer prepared in a polar solvent, such as dimethylformamide (DMF) or dimethylacetamide (DMAc), had a higher molecular weight than one prepared in benzene. The polymers prepared were soluble in polar solvents such as DMF, DMAc, and dimethyl sulfoxide and insoluble in less polar solvents such as benzene, tetrahydrofuran, and chloroform.

A thin polymer film was cast on ITO coated glass from a DMAc solution of polymer 3 (Table I) by using a spin coater. The film had a maximum absorption of 393 and a cutoff wavelength of 480 nm. These values are almost equal to those of pNA. The short cutoff wavelength indicates the possibility of using this polymer for frequency doubling in waveguide devices of IR lasers such as neodymium-YAG and some semiconductor lasers and for some electrooptical modulators and switches. The refractive indices n were measured by the m -line method,⁷ as shown in Table II. The refractive index of this film at 532 nm could not be measured using an optical prism ($n = 1.7936$ at 532 nm), because the refractive index of the polymer at this wavelength was near or higher than that of the prism. The d coefficients were calculated by using a refractive index of 632.8 nm instead of 532 nm. The film thickness, $l = 0.85 \pm 0.02 \mu\text{m}$, was determined from interference fringes and refractive indices, $l = [2\bar{n}(1/\lambda_1 - 1/\lambda_2)]^{-1}$, where \bar{n} is the average refractive index.

The pNA units in the polymer film were aligned by corona poling, keeping the film at 110 °C (T_g 103 °C) under a dc electric field of 5 kV (ca. 59 MV/cm) for 1 h and then cooling to room temperature. The orientation of the thin

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Table I. Polymerization of MNPAMS

no.	initiator	solvent	concn of initiator, mol %	temp, °C	time, h	yield, %	\bar{M}_n	\bar{M}_w	\bar{M}_w/\bar{M}_n
1	AIBN	benzene	1	80	86	7.5	5000	6500	1.3
2	AIBN	DMAc	1	80	86	15	6400	10000	1.5
3	AIBN	DMAc	5	80	168	33	7400	12000	1.6
4	AIBN	DMAc	1	60	168	4.4	6200	8700	1.4
5	BF ₃ OEt ₂	CH ₂ Cl ₂	3.3	25	144	0			
6	<i>n</i> -BuLi	THF	0.8	60	72	tr ^a			
7	AlEt ₃	THF	4	60	72	tr ^a			

^aTrace.

Table II. Refractive Indices

λ , nm	n
632.8	1.730
1064	1.663

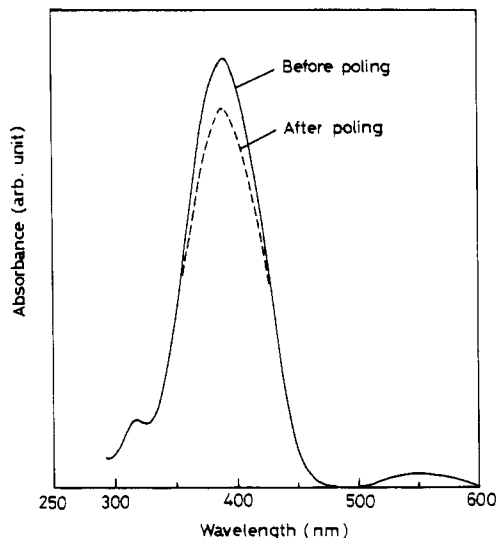


Figure 1. Absorbance of MNPAMS polymer film before (—) and after (---) poling.

film was also confirmed by a UV-visible absorption spectra measurement⁸ before and after the corona poling as shown in Figure 1. The absorption of the phenyl group around 400 nm decreased to 0.87 of the original value through poling, indicating that the pNA units were arranged perpendicular to the glass plane. The order parameter was determined to be 0.130, $\Phi = 1 - (A_{\perp}/A_0)$, where A_{\perp} is the absorbance perpendicular to the poling direction of a poled film, and A_0 is the absorbance of an unpoled film. This poled film system possesses relative low orientation. The second-order nonlinear d coefficients can be estimated with the oriented gas model⁹ using absorbance before and after poling:

$$d_{33} = N\beta f^2 \omega(f\omega)^2 \langle \cos^3 \theta \rangle / 2 \quad (1)$$

where N is chromophore density, 28.5×10^{20} units/cm³, and f is Lorentz local field factor, $(n^2 + 2)/3$. The θ is the angle between the dipole moments of each chromophore molecule and the poling direction, and $\langle \cos^2 \theta \rangle$ is obtained by the following equation, $\Phi = (3\langle \cos^2 \theta \rangle - 1)/2$.⁸ The value of $\langle \cos^3 \theta \rangle$ was determined to be 0.280 assuming Langevin function. The β of *N,N*-dimethyl-*p*-nitroaniline at 1890 nm, 2.15×10^{-20} pm/V,¹⁰ was used for the β of

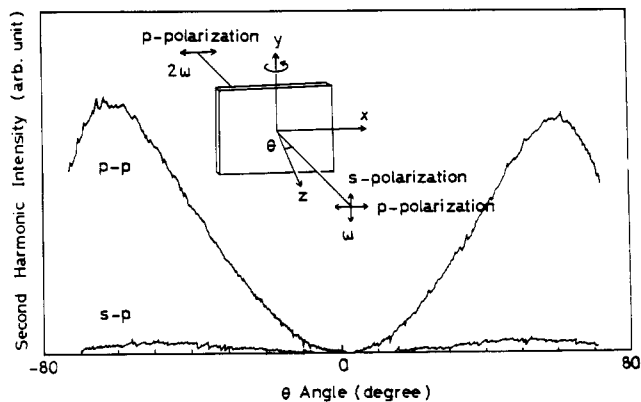


Figure 2. Fringe pattern of MNPAMS polymer film.

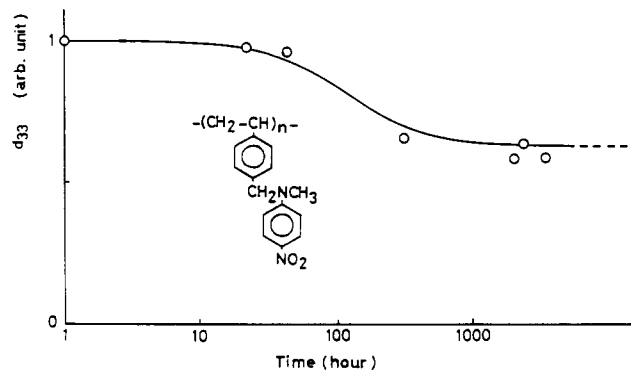


Figure 3. Temporal decay of the second harmonic coefficient.

MNPAMS. By substituting these values for the eq 1, $d_{33} = 36.0$ pm/V was obtained.

The SHG characteristics of the film was measured by an irradiating pulsed neodymium-YAG laser beam (1064 nm, 10 ns/pulse, 0.8 ± 0.2 mJ/pulse, 10 Hz). Figure 2 shows the Maker fringe pattern of the p-p measurement of this film, i.e., the p-polarized second harmonic (SH) wave intensity with irradiating p-polarized incident wave, and s-p measurement of this film, i.e., the p-polarized SH intensity with irradiating s-polarized incident wave. The SHG coefficients were determined to be $d_{33} = 56d_{11}$ (quartz) and $d_{31} = 17d_{11}$ (quartz) relative to the second harmonic wave intensity of quartz. Therefore, the SHG d_{33} and d_{31} coefficients were estimated to be 28 and 8.8 pm/V, respectively, assuming the d_{11} of quartz to be 0.5 pm/V.^{3,11} These values are similar to those of other polymers having pNA as a chromophore.^{2-4,12} The d_{33} value determined from SHG measurement showed good agreement with that estimated from the order parameter determined by the UV-visible spectrum.

The temporal decay curve of the SH intensity is shown in Figure 3. We assume that the initial decay occurred very fast, within 1 h, due to rigid polymer side chains. The

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relative SH intensity remained almost unchanged for several days after poling and then gradually decreased over a period of a few months, and d_{33} reached a level of about 60-70% of the initial value and $d_{33} = 18$ pm/V at 2500 h (3.5 months) after poling and stayed constant after that, to the end of our observation at 3600 h (5 months). This value is considered very high compared with other polymers previously reported, although temporal decay of only a short period has been reported (ca. 70% after 800 h,² ca. 60% after 120 h,⁴ and ca. 70% after 670 h¹²). The slow temporal decay of this polymer may be attributed to the short spacer group between the polymer and the chromophore unit. The propagation loss of this film was determined to be about 10 dB/cm at 632.8 nm for the prism coupling intensity of a waveguide using He-Ne laser beam.

In conclusion, MNPAMS, the vinyl monomer having a pNA unit, provided glassy polymers transparent in the wavelength region longer than 480 nm. Although the order parameter of this poled polymer was low, high d coefficients and slow temporal decay were obtained by high chromophore concentration and a short spacer.

Registry No. MNPAMS (homopolymer), 130525-38-1; $H_2C=CHC_6H_4-p-CH_2Cl$, 1592-20-7; $H_3CNHC_6H_4-p-NO_2$, 100-15-2; MNPAMS, 130525-37-0.

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Selective Synthetic Routes to Electroconductive Organosilicon Polymers Containing Thiophene Units

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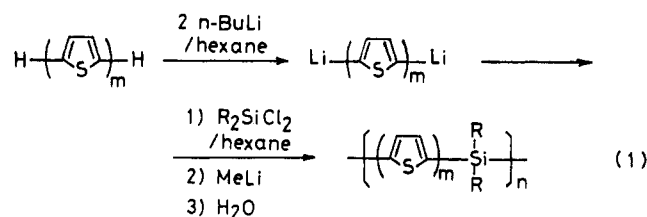
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Our current interest in organosilicon polymeric materials containing alkyne diyl segments¹ led us to investigate the preparation of other new unsaturated polymers containing silylene and thienylene units. Polythiophene, prepared by electrochemical^{2,3} or chemical⁴ methods, and related polyheterocyclic polymers⁵ constitute an important class of

organic electroconductive materials. The properties can be tuned by varying the molecular composition of the polymer.⁶ Various studies have been performed in modifying the chain unit^{7,8} and preparing copolymers,⁹ and composites¹⁰ in order to assess the molecular properties for various uses and to study the rules governing transport properties in these polymeric materials.

We were interested in investigating the introduction of silicon atoms into the polymer chain. Polymers with alternating silylene and thienylene units would be of interest in terms of properties based on a structure capable of $d\pi$ - $p\pi$ conjugation.¹¹ Delocalization of the π -electron density along the main chain can lead to an electroactive material by oxidative doping. Interestingly, related carbon-bridged thiophene polymer precursors to multiblock conjugated copolymers exhibiting semiconductivity and third-order nonlinear optical properties have been recently described.¹² Moreover, the introduction of a silicon atom along the polymer chain can allow attachment of a variety of functional groups. Functionalized poly(thiophenes) with original properties have been recently described.¹³ Also, owing to the photochemical reactivity of polysilane units,^{14,15} related polymers might be of interest for photolithographic applications.¹⁶ In connection to this, a poly-[2,5-bis(dimethylsilyl)thiophene] with high thermal stability was recently reported to undergo degradation upon photolysis.¹⁷

We report here the synthesis of molecularly defined poly[2,5-silylthiophene] with one to five thienylene and up to six silylene units in the polymer chain. Our objective was to prepare a variety of polymers with alternating thienylene and silylene units that can be used as models for conductivity studies. To achieve a selective synthesis of the various desirable chain units, two methods have been used: (i) We first studied the coupling reactions of dilithio derivatives of mono-, di-, and terthiophene with chlorosilanes (eq 1).



The lithiation was achieved in hexane, and the condensation was carried out by slow addition of the required

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