glomeration of primary particles to promote the growth of uniform secondary particles (mechanism of controlled agglomeration). The presence of a convenient lyophilic polymer prevents the intercontact recrystallization and agglomeration among growing crystals or secondary particles, respectively.

The formation and growth of stable crystals or secondary particles are governed by the reaction conditions in the bulk of well-stirred crystallizer. The selection of reaction conditions enables one to modify the properties of formed crystals or secondary particles: size distribution, average size, habit, internal composition, and epitaxy.

Second-Order Nonlinear Optical Properties of Poled Polymers of Vinyl Chromophore Monomers: Styrene, Methacrylate, and Vinyl Benzoate Derivatives Having One-Aromatic-Ring Push–Pull Chromophores

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Vinyl monomers having a nonlinear optical one-aromatic-ring chromophore were synthesized and polymerized with a radical initiator. The polymers (S-1 and M-1a,b) having nitro and amino groups showed high second harmonic generation (SHG) of d_{33} coefficients over 22–30 pm/V and d_{31} of 7.0–8.8 pm/V, after corona poling, respectively. These values gradually decreased over a period of a few weeks. The d_{33} of S-1 reached a level of about 65% of the initial value of d_{33} = 14 pm/V after about 2500 h and stayed constant after that, to the end of our observation after 14 months at room temperature. The chromophore copolymer of S-1 with M-1 had a lower T_g than those of the each homopolymer; therefore, the SH wave intensity of the copolymer showed larger temporal decay than those of the homopolymers. The chromophore copolymers (CS-75, -86) with a bifunctional chromophore monomer (S-9) showed lower decay of SH wave intensity than that of the homopolymer. Poly(vinyl (dimethylamino)benzoate) showed d_{33} = 2.2 pm/V and has an excellent low absorption cutoff wavelength of $\lambda_{\mathrm{cutoff}}$ = 360 nm.

Introduction

In recent years interest in nonlinear optical properties of organic materials has rapidly increased in the fields of telecommunication technologies and integrated optics. Nonlinear optics is expected to be a novel key technology in these fields. It is already known that organic compounds essentially have much larger nonlinear optical coefficients and faster response times than inorganic ones. There have been many investigations to estimate molecular hyperpolarizability, β, using various molecular orbital calculations. It has become possible to predict β values accurately for given molecular structures. However, for the potential application to optical devices, e.g., the frequency doubler, all optical signal switching, and so on, it is necessary to further examine properties of the aggregation state of these molecules.

Many types of molecular aggregation systems have been investigated as possible nonlinear optical organic materials, e.g., single crystals,[1–4] L–B films,[5] ferroelectric polymers such as PVDF–TrFe[6] and PVDCN-VAc,[7] polymer blend systems,[8] and polymers possessing chromophores as pen-

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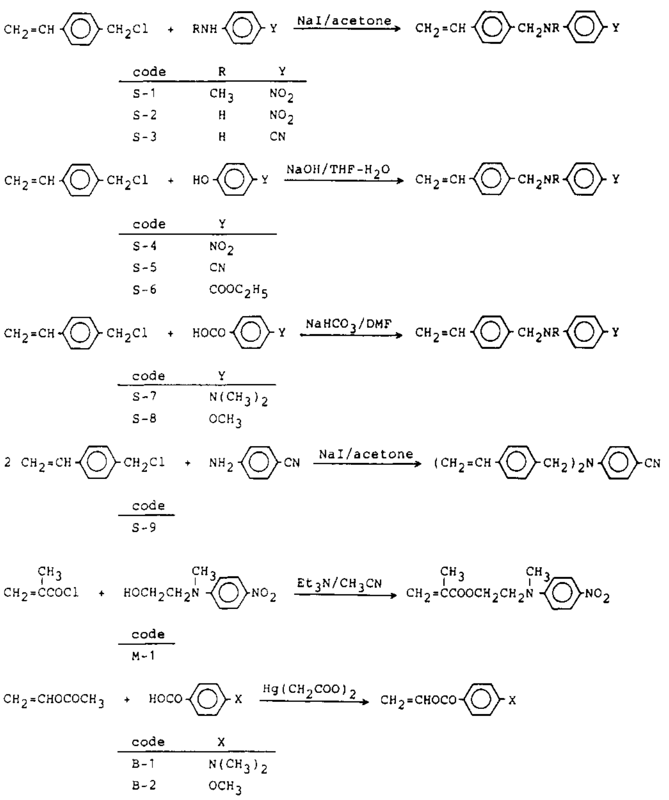
dant groups[9,10] or in a main chain.[11] Polymeric materials have drawn considerable interest because of their mechanical and thermal stabilities as well as easy processability to form waveguides and integrated optics devices.[12] It is desired to prepare polymeric materials with low propagation loss caused by small scattering and absorption, high *d* coefficients, and high temporal stability of poling induced chromophore alignment. Some efforts have been made to obtain poled polymer films with high *d* coefficients by introducing chromophores with large β values at high concentration and by highly orienting the introduced chromophores. A polymer-bonded chromophore can be more highly concentrated and also has better stability than a chromophore-doped polymer.

Many poled polymers reported previously[10] have a large β value, a long spacer group, and low chromophore concentration. The chromophores having large β contain (1) a long π-electron conjugation with aromatic rings such as stilbene, azobenzene, or biphenyl, (2) an electron-donating group such as amino, alkoxy groups on the para position of one aromatic ring, (3) an electron-withdrawing group such as nitro, cyano, or carbonyl groups on the para position of the other ring. On the other hand, the longer π-conjugated molecules show generally the longer absorption wavelength, and the lower solubility in organic media. Therefore, it is difficult for the large β compounds to be applied to optical devices such as frequency doublers of YAG or some semiconductor lasers, although recently a methacrylate polymer having a Disperse Red 1 (DR1, 4-([*N*-ethyl-*N*-(2-hydroxyethyl)]amino)-4′-nitroazobenzene) moiety as the pendant group has been used for a Cherenkov type phase matching SHG device with a IR and visible laser.[13]

Recently, to obtain higher SHG conversion efficiency, increasing the propagation length by preparation of periodically domain inverted structure[14] has been studied in inorganic[15] and organic materials.[16] We believe that enhancement of transparency by minimization of absorption to obtain low propagation loss media is very important.

Scheme I



Since *p*-nitroaniline (pNA) was found to have a relatively high β value[10] for one-aromatic-ring chromophore with a short maximum absorption wavelength of about 380 nm and a cutoff wavelength of about 480 nm, several polymers having pNA units were prepared to obtain polymeric materials with large *d* coefficients. Marks et al.[17] and Eich et al.[7,18] 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. Polymeric materials investigated hitherto[10] contained long spacers to facilitate alignment of chromophore groups under an electric field. But the long spacer units are also thought to increase the relaxation of the alignment 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 alignment as well as with a high chromophore concentration per unit volume. In our previous report[19] polystyrene with a nitroaniline unit was prepared and its optical properties were studied.

In this report we synthesized several vinyl monomers having a one-aromatic-ring chromophore with electron

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donor and acceptor groups, linked with a short spacer. The polymerization behavior and optical properties of the obtained polymers were examined.

Experimental Section

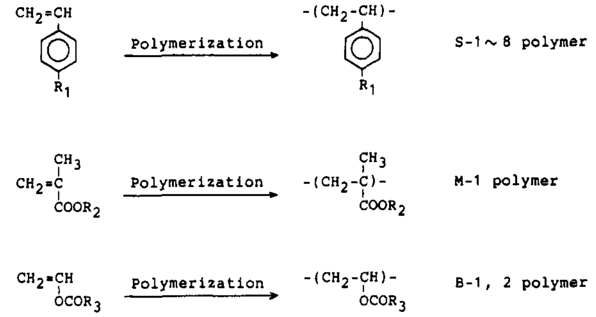
(a) Preparations of Monomers (Scheme I). *Styrene Derivatives.* (Phenylamino)methylstyrene derivatives such as 4-[(*N*-methyl-*N*-(4′-nitrophenyl)amino)methyl]styrene (MNPAMS, S-1) and 4-[(*N*-(4′-nitrophenyl)amino)methyl]styrene (S-2), and *N*,*N*-bis((4-vinylphenyl)methyl)-4-cyanoaniline (S-9) were obtained by the reactions of 4-(chloromethyl)styrene with aniline derivatives for 24 h in acetone in the presence of sodium iodide at room temperature of approximately 25 °C. (Phenoxymethyl)styrene derivatives of 4-((4′-nitrophenoxy)methyl)styrene (S-4), 4-((4′-cyanophenoxy)methyl)styrene (S-5), and 4-((4′-(ethoxycarbonyl)phenoxy)methyl)styrene (S-6) were obtained by the reactions of 4-(chloromethyl)styrene with phenol derivatives for 48 h in water–THF heterogeneous phase solution in the presence of sodium hydroxide at 40 °C. Benzenecarbomethoxystyrene derivatives of 4-[4′-(dimethylamino)benzenecarbomethoxy]styrene (S-7) and 4-(4′-methoxybenzenecarbomethoxy)styrene (S-8) were obtained by the reactions of 4-chloromethylstyrene with substituted benzoic acids for 48 h in the presence of sodium hydrogen carbonate in DMF at 40 °C.

These compounds were recrystallized from appropriate solvents and then identified by using ^{1}H NMR (JEOL FX-200) spectra. ^{1}H NMR (TMS/DMSOd_6) S-1: δ 3.19 (s, 3 H, $\mathrm{>NC}H_3$), 4.74 (s, 2 H, $\mathrm{>NC}H_2\mathrm{Ar}$), 5.22 (d, 1 H, *trans*-$\mathrm{CH_2}$=, J = 10.6 Hz), 5.78 (d, 1 H, *cis*-$\mathrm{C}H_2$=, J = 16.6 Hz), 6.70 (tetra, 1 H, $\mathrm{CH_2{=}C}H\mathrm{Ar}$—, J = 4.5 Hz), 6.80, 8.02 (dd, 4 H, $\mathrm{>N}Ph\mathrm{NO_2}$, J = 9.1 Hz), 7.18, 7.42 (dd, 4 H, $\mathrm{CH_2{=}CH}Ph$—, J = 7.5 Hz); S-2: δ 4.40 (s, 2 H, $\mathrm{>NC}H_2\mathrm{Ar}$), 5.21 (d, 1 H, *trans*-$\mathrm{C}H_2$=, J = 10.9 Hz), 5.75 (d, 1 H, *cis*-$\mathrm{C}H_2$=, J = 17.2 Hz), 6.70 (tetra, 1 H, $\mathrm{CH_2{=}C}H\mathrm{Ar}$—, J = 5.5 Hz), 6.64, 7.93 (dd, 4 H, $\mathrm{>N}Ph\mathrm{NO_2}$, J = 8.6 Hz), 7.28, 7.38 (dd, 4 H, $\mathrm{CH_2{=}CH}Ph$—, J = 7.8 Hz), 7.70 (b, 1 H, $\mathrm{>N}H$); S-3: δ 4.30 (s, 2 H, $\mathrm{>NC}H_2\mathrm{Ar}$), 5.21 (d, 1 H, *trans*-$\mathrm{C}H_2$=, J = 10.9 Hz), 5.72 (d, 1 H, *cis*-$\mathrm{C}H_2$=, J = 16.4 Hz), 6.72 (tetra, 1 H, $\mathrm{CH_2{=}C}H\mathrm{Ar}$—, J = 5.5 Hz), 6.65, 7.30 (dd, 4 H, $\mathrm{>N}Ph\mathrm{CN}$, J = 8.6 Hz), 7.36 (m, 4 H, $\mathrm{CH_2{=}CH}Ph$—), 6.96 (b, 1 H, $\mathrm{>N}H$); S-4: δ 5.24 (s, 2 H, $\mathrm{{-}OC}H_2\mathrm{Ar}$), 5.26 (d, 1 H, *trans*-$\mathrm{C}H_2$=, J = 15.5), 5.84 (d, 1 H, *cis*-$\mathrm{C}H_2$=, J = 19.9), 6.75 (tetra, 1 H, $\mathrm{CH_2{=}C}H\mathrm{Ar}$—, J = 4.4 Hz), 7.20, 8.18 (dd, 4 H, $\mathrm{{-}O}Ph\mathrm{NO_2}$, J = 8.8), 7.47 (m, 4 H, $\mathrm{CH_2{=}CH}Ph$—); S-5: δ 5.18 (s, 2 H, $\mathrm{{-}OC}H_2\mathrm{Ar}$), 5.28 (d, 1 H, *trans*-$\mathrm{C}H_2$=, J = 11.1 Hz), 5.82 (d, 1 H, *cis*-$\mathrm{C}H_2$=, J = 19.9 Hz), 6.74 (tetra, 1 H, $\mathrm{CH_2{=}C}H\mathrm{Ar}$—, J = 3.3 Hz), 6.15, 7.70 (dd, 4 H, $\mathrm{{-}O}Ph\mathrm{CN}$, J = 12.2 Hz), 7.44 (m, 4 H, $\mathrm{CH_2{=}CH}Ph$—); S-6: δ 1.39 (tri, 3 H, $\mathrm{{-}COOCH_2C}H_3$, J = 10.5 Hz), 4.26 (tetra, 2 H, $\mathrm{{-}COOC}H_2\mathrm{CH_3}$, J = 6.5 Hz), 5.16 (s, 2 H, $\mathrm{{-}OC}H_2\mathrm{Ar}$), 5.25 (d, 1 H, *trans*-$\mathrm{C}H_2$=, J = 13.1 Hz), 5.84 (d, 1 H, *cis*-$\mathrm{C}H_2$=, J = 19.6 Hz), 6.76 (tetra, 1 H, $\mathrm{CH_2{=}C}H\mathrm{Ar}$—, J = 3.9 Hz), 7.09, 7.92 (dd, 4H, $\mathrm{{-}O}Ph\mathrm{COOEt}$, J = 10.9 Hz), 7.43 (m, 4 H, $\mathrm{CH_2{=}CH}Ph$—); S-7: δ 3.00 (s, 6 H, $\mathrm{ArN(CH_3)_2}$), 5.25 (s, 2 H, $\mathrm{{-}COOC}H_2\mathrm{Ar}$), 5.25 (d, 1 H, *trans*-$\mathrm{C}H_2$=, J = 6.5 Hz), 5.82 (d, 1 H, *cis*-$\mathrm{C}H_2$=, J = 17.4 Hz), 7.73 (tetra, 1 H, $\mathrm{CH_2{=}C}H\mathrm{Ar}$—, J = 5.4 Hz), 6.71, 7.82 (dd, 4 H, $\mathrm{{-}OCO}Ph\mathrm{N(CH_3)_2}$, J = 8.7 Hz), 7.43 (dd, 4 H, $\mathrm{CH_2{=}CH}Ph$—, J = 4.5 Hz); S-8: δ 3.84 (s, 3 H, $\mathrm{ArOC}H_3$), 5.32 (s, 2 H, $\mathrm{{-}COOC}H_2\mathrm{Ar}$), 5.26 (d, 1 H, *trans*-$\mathrm{C}H_2$=, J = 15.2 Hz), 5.86 (d, 1 H, *cis*-$\mathrm{C}H_2$=, J = 17.4 Hz), 6.74 (tetra, 1 H, $\mathrm{CH_2{=}C}H\mathrm{Ar}$—, J = 3.5 Hz), 7.04, 7.95 (dd, 4 H, $\mathrm{{-}OCO}Ph\mathrm{OMe}$, J = 6.5 H), 7.43 (dd, 4 H, $\mathrm{CH_2{=}CH}Ph$—, J = 4.8 Hz); S-9: δ 4.73 (s, 4 H, $\mathrm{Ar(C}H_2\mathrm{)_2N}$—), 5.22 (d, 1 H, *trans*-$\mathrm{C}H_2$=, J = 11.8 Hz), 5.74 (d, 1 H, *cis*-$\mathrm{C}H_2$=, J = 16.5 Hz), 6.70 (tetra, 1 H, $\mathrm{CH_2{=}C}H\mathrm{Ar}$—, J = 7.1 Hz), 6.79, 7.44 (dd, 4 H, $\mathrm{>N}Ph\mathrm{CN}$, J = 8.7 Hz), 7.20, 7.38 (dd, 8 H, $\mathrm{CH_2{=}CH}Ph$—, J = 8.3 Hz).

Methacrylate Derivative. Methacrylate derivative was prepared by reacting methacryloyl chloride with *N*-(2-hydroxyethyl)-*N*-methyl-4-nitroaniline in acetonitrile for 3 h at 80 °C. The aniline derivative was obtained by the reaction of 4-fluoronitrobenzene with 2-(methylamino)ethanol in the presence of sodium hydrogen carbonate in DMSO for 24 h at 100 °C.

This compound was recrystallized from ethanol and then identified by using ^{1}H NMR spectra. ^{1}H NMR (TMS/DMSOd_6) M-1: δ 1.82 (s, 3 H, $\mathrm{CH_2{=}C(C}H_3\mathrm{)}$—), 3.09 (s, 3 H, $\mathrm{>NC}H_3$), 3.80 (tri, 2 H, $\mathrm{{-}COOCH_2C}H_2\mathrm{N{<}}$, J = 6.2 Hz), 4.32 (tri, 2 H, $\mathrm{{-}COOC}H_2\mathrm{CH_2N{<}}$, J = 6.2 Hz), 5.56 (s, 1 H, *trans*-$\mathrm{C}H_2$=), 5.94 (s, 1 H, *cis*-$\mathrm{C}H_2$=), 6.80, 8.00 (dd, 4 H, $\mathrm{>N}Ph\mathrm{NO_2}$, J = 9.5 Hz).

Scheme II



R_1, R_2, R_3: the corresponding chromophore units

Vinyl Benzoate Derivatives. Vinyl benzoate derivatives were prepared by ester interchange between benzoic acids and vinyl acetate. Vinyl 4-(dimethylamino)benzoate (B-1) and vinyl 4-methoxybenzoate (B-2) were obtained by the reactions of vinyl acetate with substituted benzoic acids in the presence of mercury(II) diacetate.

These compounds were recrystallized from ethanol or methanol solvents and then identified by using ^{1}H NMR spectra. ^{1}H NMR (TMS/DMSOd_6) B-1: δ 3.00 (s, 6 H, $\mathrm{ArN(C}H_3\mathrm{)_2}$, 4.59 (d, 1 H, *trans*-$\mathrm{C}H_2\mathrm{{=}CH}$—, J = 5.0 Hz), 4.98 (d, 1 H, *cis*-$\mathrm{C}H_2\mathrm{{=}CH}$—, J = 13.5 Hz), 6.64, 7.95 (dd, 4 H, $\mathrm{(CH_3)_2N}Ph\mathrm{COO}$—, J = 9.2 Hz), 7.50 (tetra, 1 H, $\mathrm{CH_2{=}C}H$—, J = 6.4 Hz); B-2: δ 3.86 (s, 3 H, $\mathrm{ArOC}H_3$, 4.69 (d, 1 H, *trans*-$\mathrm{C}H_2\mathrm{{=}CH}$—, J = 6.4 Hz), 5.04 (d, 1 H, *cis*-$\mathrm{C}H_2\mathrm{{=}CH}$—, J = 14.2 Hz), 6.94, 8.06 (dd, 4 H, $\mathrm{CH_3O}Ph\mathrm{COO}$—, J = 9.6 Hz), 7.52 (tetra, 1 H, $\mathrm{CH_2{=}C}H$—, J = 6.4 Hz).

(b) Preparation and Characterization of Polymers (Scheme II). Polymerization was carried out in a glass ampule under nitrogen atmosphere using AIBN as an initiator. ^{1}H NMR spectra were used to determine the structures of each polymer and also the molar fraction of the copolymers. The glass transition temperatures (T_g) and average molecular weights of the polymers were measured by using DSC (Rigaku TAS-200) and gel permeation chromatography (Jasco 880-PU, 830-RI), respectively. The absorption maxima and cutoff of the polymer films on fused silica plates were measured by UV–visible absorption spectra instrument (Jasco Ubest30).

(c) Calculation of β Values. The β values of chromophore unit molecules were calculated by using MOPAC program using semiempirical AM1 Hamiltonian.

(d) Film Preparation. Polymer films for SHG measurement were prepared by casting from DMAc, DMF, or THF solution onto hot ITO glass plates using a spin-coater. The films were dried in a vacuum oven at about T_g for about 2 days. The film thickness l was determined from interference fringes and refractive indexes:

$$l = [2\bar{n}(1/\lambda_1 - 1/\lambda_2)]^{-1}$$

where $\bar{n}$ is the average refractive index, and λ_1 and λ_2 are the neighboring mode wavelength of interference fringe. The film thickness were 0.31–0.85 μm.

Films for refractive indexes measurement were prepared by casting onto hot fused silica or Pyrex plate. The refractive indices were estimated using the m-line method,[20] which measures input or output beam angle of some guided modes existed on condition of a wavelength light and a film thickness. The prism coupling method was used to measure refractive index on the basis of the theory of guided waves in the isotropic film waveguide.

(e) Poling Procedure. The polymer films were poled normal to the surface by corona discharge. The poling process was carried out at several degrees above T_g of the polymers. The distance of the corona needle from the surface is 8 mm. The needle side was set to 4.5–5 kV positive to the ITO glass surface. After alignment of the films, they were cooled to room temperature under the electric field.

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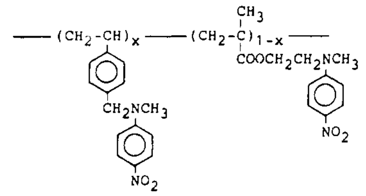
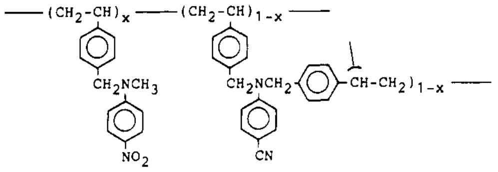
Table I. Radical Polymerization of Chromophore Monomers[a]

code	solvent	concn of initiator, mol %	temp, °C	time, h	yield, %	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
S-1	benzene	1	80	86	7.5	5 000	6 500	1.3
	THF	1	80	48	4		14 000	
	DMF	1	80	48	4		9 000	
	DMF	2.5	80	300	29	4 500	5 400	1.2
	DMAc	1	80	86	15	6 400	10 000	1.5
	DMAc	5	80	168	33	7 400	12 000	1.6
S-2	DMF	1	80	48	2		15 000	
	THF	1	80	48	5.9		15 000	
S-3	DMF	3	80	48	70	36 000	250 000	6.9
	DMF	10	80	48	42	30 000	170 000	5.7
	DMF	1	80	48	38		230 000	
	THF	1	80	48	47		280 000	
S-4	DMF	1.5	80	48	23	10 000	17 000	1.7
	THF	1	80	48	7		12 000	
S-5	DMF	1	80	48	72	27 000	69 000	2.6
	THF	1	80	48	64		51 000	
S-6	DMF	1	80	48	67	35 000	89 000	2.5
	THF	1	80	48	54		71 000	
S-7	DMF	1	80	48	86	22 000	58 000	2.6
	THF	1	80	48	82		37 000	
S-8	DMF	1	80	48	71	24 000	47 000	2.0
	THF	1	80	48	65		28 000	
M-1a	DMAc	5	80	58	73	13 000	17 000	1.3
M-1b	DMAc	20	80	31	63	8 800	11 000	1.3
B-1	benzene	1	65	74	74	5 000	7 600	1.5
B-2	benzene	1	65	74	94	21 000	36 000	1.7

[a] Initiator: AIBN.

Table II. Radical Copolymerization of Chromophore Monomers[a]

code	solvent	concn of initiator, mol %	temp, °C	time, h	yield, %	x	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
									
SM-1	DMF	5	80	48	55	0.74	8 800	12 000	1.3
									
CS-86	DMF	3	80	48	16	0.86	46 000	89 000	2.0
CS-75	DMF	3	80	48	20	0.75	42 000	97 000	2.3

[a] Initiator: AIBN.

(f) Measurements of SHG Intensity. The SHG measurement system is depicted in Figure 1. The neodymium:YAG laser beam (1064 nm, 10 ns/pulse, 0.8 ± 0.2 mJ/pulse, 10 Hz) was introduced to the sample in the rotation stage after being polarized and focused by a polarizer and a lens, respectively. The generated second harmonic wave was detected by a photomultiplier and a Maker fringe pattern was obtained by plotting SH wave intensity against the angle between the plate and incident beam. The second-order nonlinear optical coefficients were determined from the relative SH wave intensity of the observed Maker fringes by comparing them to that of a y-cut quartz (d_{11} = 0.4 pm/V).

Results and Discussion

The several styrene, methacrylate, and vinyl benzoate derivatives were synthesized by reacting 4-(chloromethyl)styrene, methacryloyl chloride, and vinyl acetate, respectively, with various chromophores. The chromophores were benzenes having both a donor, such as amino, methylamino, and alkoxy, and an acceptor, such as nitro, cyano, and carboxyl at the para position. These monomers were polymerized using 2,2′-azobisisobutyronitrile (AIBN) as an initiator. The polymerization results are shown in Table I. All monomers provided high molecular weight polymers in high yield, except those containing a nitro group, such as S-1, S-2, M-1, and S-4, which gave polymers with molecular weight of several thousands in lower yield. The lower polymerizability of nitro-containing monomers can be attributed to degradative radical chain transfer to the nitro group.[21] The molecular weight and yield of S-1 polymer could be increased by changing the solvent from THF to DMAc, and with higher AIBN concentration or a longer polymerization time. The radical copolymerization results of S-1 with M-1, and bifunctional S-9 monomers are shown in Table II. All the polymers were soluble in polar solvents such as DMF, DMAc, and DMSO. Less-polar polymers, S-4–8 and B-1,2, were also

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(21) Tudos, F.; Kende, I.; Azori, M. *J. Polym. Sci.* **1963**, *A-1*, 1353–1368.

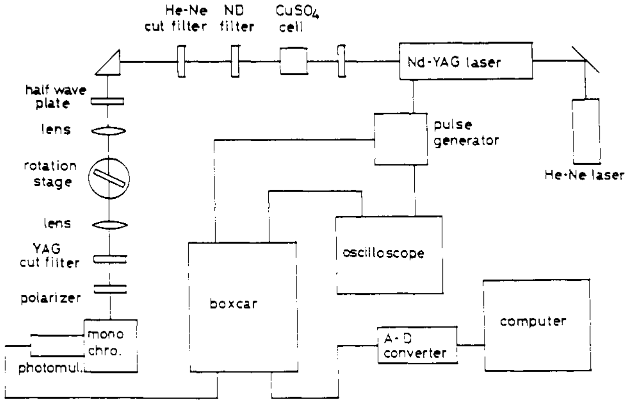

Figure 1. Schematic drawing of the laser system for SHG measurement.

Table III. Characteristics of Polymers

code	λ_{max}, nm	λ_{cutoff}, nm	$10^{30}\beta$, esu	T_g, °C
S-1	383	480	15.7	103
S-2	383	480	14.3	123
S-3	288	338	9.2	132
S-4	310	380	2.5	115
S-5	250	300	0.9	182
S-6	255	295	2.2	101
S-7	310	353	12.9	129
S-8	258	295	2.4	125
M-1	390	490	15.7	100
B-1	310	360	12.9	126
B-2	265	300	2.4	82
copolymer				
SM-1	390	490	15.7	48
CS-86	383	480		80
CS-75	383	480		84

soluble in THF and chloroform.

The structures of each polymer were identified, and the molar fraction of the copolymers were determined by ^1H NMR spectra measurements. A H signal of unreacted methacryl group could not detect in measurements of CS-86 and CS-75 polymers.

The polymers were cast into films on fused quartz plates or on ITO-coated glass using a spin-coater.

The UV–visible spectra of polymer films were measured, and their absorption maxima and cutoff wavelengths are listed in Table III. The polymer containing both amino and nitro groups (S-1, S-2, M-1, SM-1, CS-86, and CS-75) had the longest λ_{max} and cutoff wavelengths of about 390 and 490 nm, respectively. Other polymers showed an absorption maximum at shorter than 310 nm and colorless in the visible region. It has been reported that the larger difference of Hammett σ values for para substituents, the larger β values for a series of para-substituted benzenes.[22] It has also been known that the larger difference of σ, the longer λ_{max}. Polymer films displayed almost the same UV–visible spectra to those of corresponding low molecular weight chromophores. For example, λ_{max} and cutoff wavelengths of S-1 are almost equal to those of pNA in methanol. This finding indicates that the chromophore unit in the polymer has the same electronic structure as the corresponding low molecular weight compound. Therefore, the β value per one monomer unit of the polymer was assumed to the same as the low molecular weight corresponding, which is shown in the third column of Table III. The β values of monomers were calculated by using the MOPAC program.

Table IV. Refractive Indexes of Polymers

code	refractive indexes		
	1064 nm	632.8 nm	532 nm
S-1	1.658	1.693	1.716
S-2	1.645	1.698	1.784
S-3	1.623	1.648	1.715
S-4	1.610	1.633	1.656
S-5	1.607	1.622	1.629
S-6	1.580	1.599	1.615
S-7	1.610	1.634	1.655
S-8	1.589	1.604	1.621
M-1a	1.609	1.664	1.713
M-1b	1.606	1.652	1.702
B-1	1.585	1.605	1.641
B-2	1.563	1.586	1.592
copolymer			
SM-1	1.636	1.687	1.715

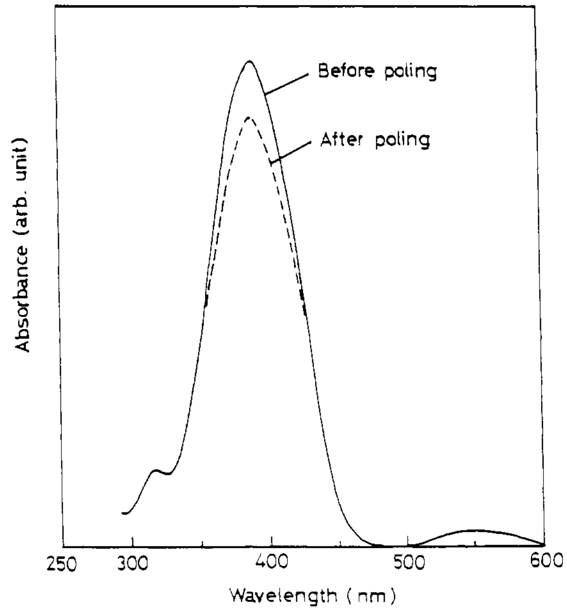

Figure 2. Absorbance before and after poling of S-1 polymer film.

The thermal properties of the polymer were measured by differential scanning calorimetry (DSC). The homopolymers and copolymers showed glass transition temperature in the ranges 82–182 and 48–84 °C, respectively, as listed in the last column of Table III. None of the polymers exhibited melting points, indicating that they were amorphous polymers.

The refractive indexes of the polymers were measured by the *m*-line method at 1064, 632.8, and 532 nm, which are listed in Table IV.

The chromophore units in the polymer film coated on the ITO glass were aligned by corona poling, keeping the films at about 5 °C above T_g under a dc electric field of 4.5–5 kV (about 60 MV/cm) for about 1 h and then cooling to room temperature. In the case of these polymers, SH wave intensity gradually increased and it reached a maximum level after 30–60 min, indicating that the orientation of the pendant group leveled off after 30–60 min of poling. Therefore, the poling time was set to 40 min for all the films. The orientation of the thin film of S-1 polymer was also confirmed by a UV–visible absorption spectra measurement before and after the corona poling as shown in Figure 2. The absorption of the phenyl group around 380 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 is expressed as $\Phi = 1 - (A_{\perp}/A_0)$, where $A_{\perp}$ is the absorbance perpendicular to the poling direction of a poled film, and A_0 is the

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(22) Li, D.; Ratner, M. A.; Marks, T. J. *J. Am. Chem. Soc.* 1988, *110*, 1707–1715.

absorbance of an unpoled film. The order parameter of poled S-1 polymer was determined to be 0.13 by substituting the absorbance before and after the poling. The low-order parameter shows that this poled film system possesses relatively low alignment. When the poled film was heated at 105 °C for 48 h, absorbance increased to 0.93–0.95 of that of unpoled film, which indicates that the decrease of absorbance is due to the reversible alignment of pendant groups.

The second-order nonlinear *d* coefficient can be estimated with the oriented gas model[23] by using absorbance before and after poling:

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

where N is chromophore density, 28.5 × 10^{20} units/cm^3 calculated from the density of 1.27, and f is the Lorentz local field factor, $(n^2 + 2)/3$. θ is the angle between the dipole moments of each chromophore molecule and the poling direction, and $\langle \cos^2 \theta \rangle$ is obtained from the following equation: $\Phi = (3\langle \cos^2 \theta \rangle - 1)/2$.[24] The value of $\langle \cos^3 \theta \rangle$ was determined to be 0.28 assuming a Langevin function. The β value of pendant chromophore was assumed to be equal to that of (dimethylamino)-4-nitroaniline, i.e., 15.7 × 10^{-30} esu calculated by the MOPAC program. By substituting these values in eq 1, d_{33} = 11.0 pm/V was obtained. This calculated value was comparable to the observed value.

After the poling, absorbance of S-2 polymer film decreased to 0.40 of the original value, showing a larger decrease than for S-1 polymer. However, it was not recovered by annealing around T_g without an electric field. This irreversible absorption change may indicate that the decrease of the absorbance by poling was attributed not only to alignment of the pendant group but also to the decomposition or chemical change of the polymer. With other styrene and vinyl benzoate polymers, orientation by corona poling could not be detected by UV measurement, because the polymers possess absorption only in the range where ITO has absorption.

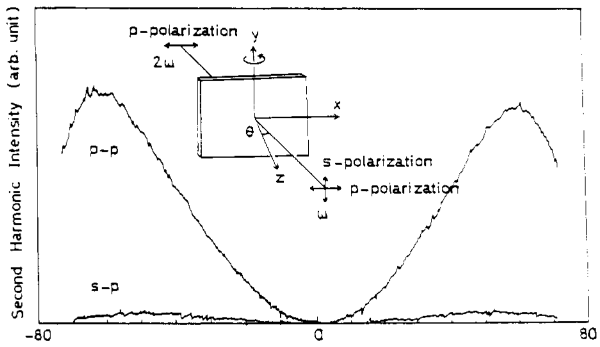

Figure 3. Maker fringe of poled S-1 polymer film.

Table V. Optical Properties of Polymers

code	l, μm	d_{33},[a] pm/V	$d_{31}(t = 0.5$ h),[a] pm/V
S-1	0.85 ± 0.02	22	7.0
S-2	0.54 ± 0.02	10.4	4.2
S-3	0.32 ± 0.02	1.0	0.4
S-4	0.31 ± 0.02	whitening	
S-5	0.50 ± 0.02	<0.5	<0.2
S-6	0.68 ± 0.02	whitening	
S-7	0.72 ± 0.04	whitening	
S-8	0.62 ± 0.03	whitening	
M-1a	0.93 ± 0.05	28	7.0
M-1b	0.59 ± 0.04	30	8.8
B-1	0.58 ± 0.02	2.2	0.96
B-2	0.68 ± 0.02	0.54	0.23
copolymer			
SM-1	0.63 ± 0.02	14	4.4
CS-86	0.32 ± 0.02	8.0	1.8
CS-75	0.36 ± 0.02	6.4	1.8

The SH wave intensity of poled polymer film is given by the following equation.[24,26] The relative SH wave intensity of the polymer against that of quartz leads to the *d* coefficients of the polymer:

$$I(2\omega) = (512\pi^3/A)t_g{}^4 t(\omega)^4\, T(2\omega)\, d_p{}^2 2I(\omega)^2[1/(n(\omega)^2 - n(2\omega)^2)^2] \sin^2 \Psi(\theta)$$

where $I(2\omega)$ is the transmitted SH wave intensity, $I(\omega)$ is the incident fundamental wave intensity, A is the laser beam area, d_p is the product of appropriate SH coefficients with angular factors resulting from projection of the nonlinear polarization components onto the direction of $E(2\omega)$ in the film, $t(\omega)$ and $T(2\omega)$ are transmission factors, t_g is the transmission factor of the fundamental light through the glass substrate, and n is the refractive index at the indicated frequencies. Ψ is an angular factor resulting from interference between free and bound waves. For $l < l_0$

$$\sin^2 \Psi(\theta) \sim [(\pi/2)(l/l_0)\{\bar{n}/(N^2 - \sin^2 \theta)^{1/2}\}]^2$$

where l is the film thickness, l_0 is the coherence length, $\lambda/4[n(2\omega) - n(\omega)]$, θ is the incident angle, $\bar{n} = [n(\omega) + n(2\omega)]/2$, and $N^2 = \bar{n}^2 + [n(\omega) - n(2\omega)/2]^2$. The d_P obtained from the p-polarized SH wave intensity with irradiating p-polarized incident wave is shown by

$$d_P = [d_{33} \sin^2 \theta(\omega)' + d_{31} \cos^2 \theta(\omega)'] \sin \theta(2\omega)' + 2d_{31} \cos \theta(\omega)' \sin \theta(\omega)' \cos \theta(2\omega)'$$

where the angles $\theta(\omega)'$ and $\theta(2\omega)'$ are the incident angle which convert from external to internal angle, $\sin \theta' = \sin \theta/n$. The d_P obtained from the p-polarized SH wave intensity with irradiating s-polarized incident wave is shown by

$$d_P = d_{31} \sin \theta(2\omega)'$$

Therefore, the *d* coefficients could be determined from refractive indexes and Maker fringe of both the p–p and s–p measurements, i.e., the p-polarized SH wave intensities with irradiating p-polarized and s-polarized incident waves, respectively.[26] A Maker fringe pattern for S-1 is shown in Figure 3. The *d* coefficients were calculated by using d_{11} of reference quartz. It was confirmed that the *d* values of the S-1 polymer increased with an increase of the applied voltage up to 5 kV. However, ITO on glass plate and/or polymer film became turbid when the applied field was higher than 5 kV. Therefore, all the experiments were carried out with the applied field lower than 5 kV. In the case of polymers S-4, -6, -7, and -8, polymer films became white and turbid even at 3.5 kV, and hence *d* values of these polymer films were not determined. The whitening may be caused by decomposition or crystallization under the electric field.

In this work, the initial SH wave intensities of the polymers were determined 0.5 h after poling. The second-order nonlinear optical coefficients measured from the initial intensities are shown in Table V. The second harmonic *d* coefficients of the poled S-1 polymer film showed the largest *d* coefficients of the styrene derivatives,

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(23) (a) Williams, D. J. *Nonlinear Optical Properties of Organic Molecules and Crystals*; Chemla, D. S., Zyss, J., Eds.; Academic Press: New York, 1987; Vol. 1, p 407.

(24) Mortazavi, M. A.; Knoesen, A.; Kowel, S. T.; Higgins, B. G.; Dienes, A. *J. Opt. Soc. Am.* **1989**, *B-6*, 733–741.

(25) Singer, K. D.; Kuzyk, M. G.; Sohn, J. E. *Nonlinear Optical and Electroactive Polymers*; Prasad, P. N., et al., Eds.; Plenum Press: New York, 1988; pp 189–204.

(26) (a) Jerphagnon, J.; Kurtz, S. K. *J. Appl. Phys.* **1970**, *41*, 1667–1681; (b) *Phys. Rev.* **1970**, *B-1*, 1739–1744.

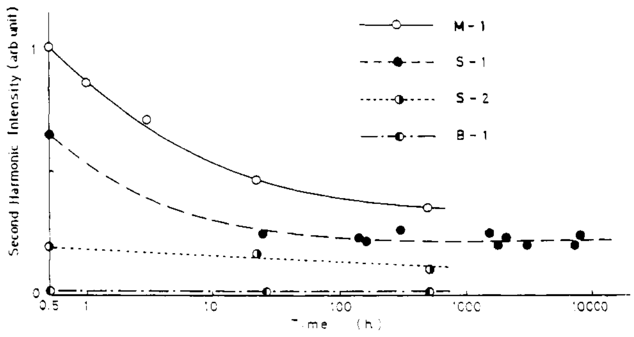

Figure 4. Temporal stability curves of SH wave intensity in polymer films after poling.

$d_{33} = 56d_{11}$(quartz) and $d_{31} = 18d_{11}$(quartz), which correspond to be 22 and 7.0 pm/V, respectively, assuming the d_{11} of quartz to be 0.4 pm/V. The M-1 polymers showed the largest d coefficients of d_{33} = 28–30 and 7.0–8.8 pm/V, respectively. The d coefficient was almost same in the range of $\bar{M}_n$ = 8 800–13 000 for the M-1 polymer. These values are similar to those of other polymers having pNA as a nonlinear optical chromophore, which possessed relatively high d values.[17,18,27] The d coefficients of S-2 were smaller than those of S-1. This difference is attributed to the decomposition or chemical or physical changes of S-2 when electric field was applied.

The d_{33} coefficients of the other styrene derivative polymers were less than 10% of S-1 or S-2 polymer, while β values of these polymers are half of S-1. The absorption maxima of the polymers having pNA were 480–490 nm, and those for the other chromophores were 250–310 nm. It was reported that β increase exponentially in or near the resonance absorption band of a chromophore.[22] Since the β values calculated by MOPAC using semiempirical AM1 were at frequency 0, i.e., not taken into account for wavelength dependence, it was considered that the polymers having pNA, such as S-1 and S-2, which have absorptions nearer the fundamental wavelength, have larger β values at 1064 nm than those listed in Table III. This consideration may indicate that the smaller d values for other polymers are not unreasonable. With consideration for the influence of the input wavelength upon the β, it could be shown that the d_{33} value determined from SH measurement was almost in agreement with that estimated from the order parameter determined after poling by the UV–visible spectrum. For films poled in a dc field (5 kV, ~60 MV/cm), d_{33} was almost 3 times d_{31}, which coincide with the prediction by the statistical average calculated using a Boltzmann orientational function to describe alignment of the chromophore in the poling field.

The temporal stability curves of the SH intensity for the S-1, M-1, B-1, and SM-1 polymers at room temperature are shown in Figure 4. The relative SH intensity of S-1 polymer gradually decreased over a period of a few weeks, and it reached a level of about 35–40% of the initial intensities and in the S-1 polymer d_{33} = 14 pm/V (65%) at 2 500 h (3.5 months) after poling and stayed constant after that, to the end of our observation at 10 000 h (14 months). In the case of the M-1 polymer, it reached d_{33} = 19 pm/V (65%) at about 1 000 h after poling. The relaxation behavior of the M-1 polymer was almost the same in the range of M_n = 8 800–13 000. The d values of S-1 and M-1 polymers were considered very high compared with other polymers previously reported, although a temporal stability of only a short period has been reported (about 70% after 800 h,[17] about 60% after 120 h,[18] and 70% after 670 h[27]). The other homopolymers exhibited a similar behavior to them. Copolymer SM-1 showed drastically low T_g as shown in Table III. Therefore, the d value was small because of large temporal decay at first time within 0.5 h. The good temporal stability of the homopolymers may be attributed to high T_g due to the regular repeating units by the short spacer group between the polymer and the chromophore unit and also completely 100% chromophore functionalization.

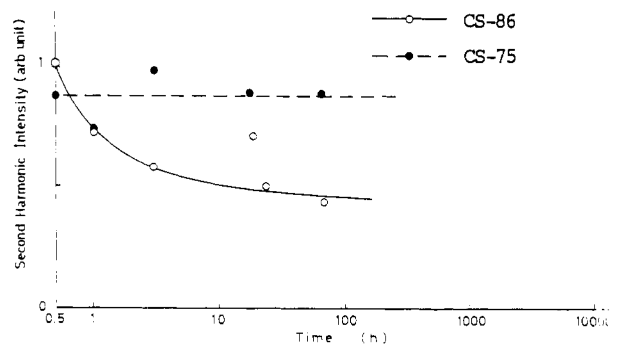

Figure 5. Temporal stability curves of SH wave intensity in polymer films after poling.

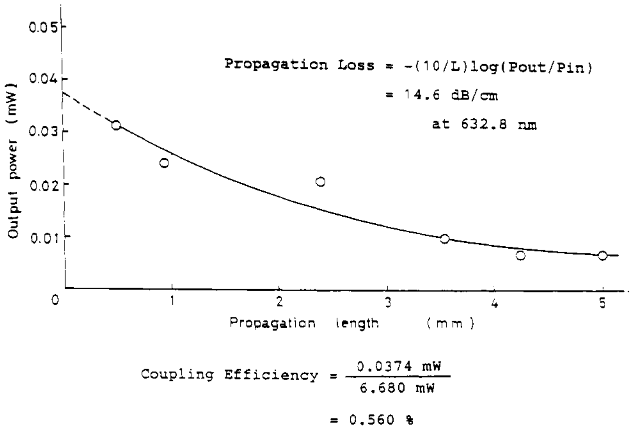

Figure 6. Measurements of propagation loss by prism sliding method.

To obtain polymers with larger temporal stability, S-1 polymer analogues were prepared by copolymerization of S-1 with bifunctional monomers. A bifunctional monomer with a CN group, S-9, was used as a comonomer because one having NO_2 did not provide. Copolymers CS-86 and CS-75, having bifunctional units in molar fraction of 0.14 and 0.25, respectively, possessed higher molecular weights than the S-1 homopolymer as shown in Table II. The were soluble in organic solvents such as DMF or DMSO in these molar fraction ranges of bifunctional units, because of chain transfer of nitro groups. As shown in Figure 5, the CS-75 copolymer showed more excellent stability of SH wave intensity than the CS-86 having less bifunctional sites and also the S-1 homopolymer. The very slow thermal disorientation may be explained by the partial crosslinking structure in the polymers which was determined by ^{1}H NMR, because the residual double bond of methacrylate was less than 18%.

The propagation loss was measured by using a prism sliding method on film waveguide at 632.8 nm. The incident power and output power were measured with a power meter. The propagation loss curve is shown in Figure 6. The prism coupling efficiency was estimated

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(27) Twieg, R. J.; Bjorklund, G.; Lee, V.; Baumert, C.; Looser, H.; Ducharme, S.; Moerner, W. E.; Willson, C. G.; Reck, B.; Swalen, J.; Eich, M.; Jungbauer, D.; Yoon, D. *Prepr. Int. Workshop Cryst. Growth Org. Mater.* **1989**, 262–277.

by extrapolation, 0.560%. Therefore, the propagation loss was 14.6 dB/cm.

In conclusion, S-1 and M-1, the vinyl polymer having a pNA unit, possessed a relative low molecular weight and provided glassy polymers transparent in the wavelength region longer than 480 nm. The poled S-1 and M-1 homopolymers possessed high *d* coefficients and good temporal stability at room temperature because of high chromophore concentration and a short spacer group between the polymer main chain and the chromophore unit, and also completely 100% chromophore functionalization. The copolymer of S-1 with M-1 showed drastically low T_g and large temporal decay. On the other hand, the cross-linked copolymer of S-1 with bifunctional S-9 chromophore exhibited more excellent stability than those homopolymers. These materials are expected to be applicable to frequency doubling and EO waveguide devices.

Registry No. S-1, 130525-37-0; S-1 (homopolymer), 130525-38-1; S-2, 139565-77-8; S-2 (homopolymer), 139565-94-9; S-3, 139565-78-9; S-3 (homopolymer), 139565-95-0; S-4, 125038-81-5; S-4 (homopolymer), 139565-96-1; S-5, 139565-79-0; S-5 (homopolymer), 139565-97-2; S-6, 139565-80-3; S-6 (homopolymer), 139565-98-3; S-7, 139565-81-4; S-7 (homopolymer), 139565-99-4; S-8, 139565-82-5; S-8 (homopolymer), 139566-00-0; S-9, 139565-83-6; S-9 (homopolymer), 139566-01-1; M-1, 133547-17-8; M-1 (homopolymer), 139566-02-2; B-1, 43033-22-3; B-1 (homopolymer), 139582-76-6; B-2, 13351-86-5; B-2 (homopolymer), 26375-86-0; (S-1)(M-1) (copolymer), 139566-03-3; (S-1)(S-9) (copolymer), 139566-04-4; $H_2C{=}CHC_6H_4\text{-}p\text{-}CH_2Cl$, 1592-20-7; $H_2C{=}C(CH_3)COCl$, 920-46-7; $HO(CH_2)_2N(CH_3)C_6H_4\text{-}p\text{-}NO_2$, 18226-16-9; $H_2C{=}CHOCOCH_3$, 108-05-4.

New Organosols of CuS, CdS, ZnS, HgS, NiS, and Mixed Metal Sulfides in *N*,*N*-Dimethylformamide and Dimethyl Sulfoxide. Preparation, Characterization, and Physical Properties

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Organosols of transition metal sulfides such as CuS, CdS, ZnS, HgS, and NiS in *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) are prepared by reactions of H_2S with the solutions of $Cu(OAc)_2$, $CdCl_2$, CdI_2, $Cd(OAc)_2$, $Zn(OAc)_2$, $HgCl_2$, and $Ni(OAc)_2$ (OAc = $OCOCH_3$), respectively. Organosols of mixed metal sulfides $Zn_xCd_{1-x}S$ are obtained by reactions of H_2S with DMF solutions of mixtures of $Cd(OAc)_2$ and $Zn(OAc)_2$ in various ratios. Rayleigh scattering studies of these organosols using an Ar laser beam (λ = 488 nm) show that the particle size of the colloidal metal sulfides and the stability of the organosols vary depending on the metal used and on the conditions of the organosol preparation. The organosol of CuS in DMSO shows a particle size of 13-nm diameter which does not change at 25 °C for 3 days. The organosol of CdS (0.1 M) in DMF has a particle size of 8–10-nm diameter. The particle size does not change for 2 weeks at −15 °C under argon atmosphere. Ar laser irradiation at 17 °C causes gradual increase in the particle size up to 30 nm in diameter and subsequent deposition of CdS. Addition of dodecanethiol or tetrabutylammonium bromide to the CdS organosol causes a blue-shift of the peak of the absorption spectrum. Organosols of ZnS, prepared by reaction of H_2S with a DMF solution of $Zn(OAc)_2$, are much less stable than those of CdS and begin to give a precipitate of ZnS after 1 h at room temperature. The light-scattering study reveals that the average particle size of ZnS increases from 17 to 500 nm in diameter during 70 min at room temperature. Addition of acetone, Et_2O, or methanol to these organosols causes precipitation of the corresponding metal sulfides, whose X-ray diffraction patterns agree with the authentic data. Black or orange organosols of HgS are obtained by reaction of H_2S with a DMF or DMSO solution of $HgCl_2$. Recovered solid from the orange organosol by addition of Et_2O shows a diffraction pattern identical with that of α-HgS, while the black organosol shows diffraction pattern due to β-HgS or those assignable to mixtures of α- and β-HgS depending on the preparation conditions. Organosols of NiS, obtained by reaction of H_2S with $Ni(OAc)_2$ in DMSO, do not show observable light scattering due to the relatively small particle size (<4-nm diameter). Electrophoresis of these organosols indicates the presence of negative charge on the metal sulfide particle surface that is similar to the colloidal particles of the metal sulfides in water.

Introduction

The chemistry and physics of the semiconducting metal sulfides have attracted increasing attention in view of the recent rapid development in the practical uses of semiconductor compounds.[1-4] Fine particles of the semiconducting metal sulfides are of particular interest in that their physical properties are not similar to those of the bulk metal sulfides due to the quantum size effect. Fine CdS colloidal particles (ca. 2–4 nm in the diameter) dispersed in water or organic solvents and stabilized by addition of

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[†] Tokyo Institute of Technology.

[‡] Gunma University.

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(3) Beghi, G., Ed. *Performance of Solar Energy Converters: Thermal Collectors and Photovoltanic Cells*; Reidel: Dordrecht, Holland, 1983.

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