Oligomers containing carbocyanine/flexible chain segments as non-linear optical materials

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(*Received 26 March 1990; accepted 17 May 1990*)

As part of a search for new non-linear optical (NLO) materials, we have synthesized new oligomers containing carbocyanine units linked by flexible chain segments. The oligomers can be cast into films and have an improved miscibility with other host polymer matrices compared to the simple carbocyanine molecules. Degenerate four-wave mixing (DFWM) measurements showed that a pure oligomer film has a $\chi^{(3)}/\alpha$ value of 9.0×10^{-13} esu cm at $\lambda = 532$ nm. Furthermore, the reaction of acidic protons in a quinolidine quaternary salt with diethyl squarate has been utilized to synthesize a polymer. The polymer, containing 13 repeat units, has a diffuse and strong absorption in the visible region and does not exhibit a detectable DFWM signal at 532 or 1064 nm.

(Keywords: oligomers; carbocyanine copolymer; non-linear optical materials)

INTRODUCTION

In the past decade, optical non-linearities of organic materials have been intensely investigated[1–3]. This research has been strongly motivated in part by the potential for application of these materials in optoelectronic devices. Attractive characteristics of organic materials include their ultrafast non-linear optical (NLO) response time, high laser damage threshold and large NLO susceptibilities. Unfortunately the materials investigated to date do not meet all the requirements for practical applications[4]. Therefore, considerable effort continues to be focused on developing new materials. It has been realized that NLO effects for different organic materials have different origins, and that π-electron delocalization and charge-transfer phenomena contribute to the NLO response[5,6]. Materials with electron clouds of enhanced anharmonicity are expected to give rise to large NLO effects.

In efforts carried out in this laboratory, it has been found that copolymers containing NLO-active units with flexible chain spacers can exhibit third-order NLO properties comparable to those with extended conjugation systems[7,8]. Furthermore, the processibility of the copolymers can be improved. These results are consistent with theoretical results[9,10]. As an extension of this work, we are effecting the incorporation of NLO units into polymer backbones and as pendants to flexible polymer backbones.

Carbocyanine dyes, discovered more than 100 years ago, are known as sensitizing dye materials in photography[11–13]. Recently these materials have been tested for NLO activity in the solution state[14]. We have designed a reaction scheme to incorporate carbocyanine units into a polymer backbone to study the NLO properties in the solid state (see *Schemes 1, 2* and *3* below). In contrast to our expectation, we were unable to prepare polymers since the reaction media left even oligomers insoluble. Oligomers with two or three repeat units were obtained. Although these materials were not high-molecular-weight polymers, they still possessed interesting potential as NLO materials since they were film-forming, as well as being miscible with many host polymers such as polycarbonate, poly(4-vinylpyridine), etc., to form optical-quality films. Degenerate four-wave mixing (DFWM) measurements revealed a high optical non-linearity: a $\chi^{(3)}/\alpha$ value of 9×10^{-13} esu cm was observed for a pure oligomer film. Meanwhile, we tried to react quinolidine bis-quaternary salts with diethyl squarate to prepare new polymers (see *Scheme 4* below). Unfortunately the resulting materials have strong, diffuse absorptions in the visible region and a significant DFWM signal for these materials cannot be detected at 532 or 1064 nm.

EXPERIMENTAL

Materials

p-Anisidine 1,5-dibromopentane, crotonaldehyde, ethyl iodide, triethyl orthoformate, diethyl squarate and quinoline were purchased from Aldrich Chemical Co. and used as received. All other chemicals were obtained from Fisher Scientific and used without further purification unless otherwise stated. All melting points are uncorrected.

Monomers

2-Methyl-6-methoxyquinoline (*1*). This compound was prepared according to the known procedure with m.p. 63–65°C (lit. 67°C)[15]. Analysis: calculated for $C_{11}H_{11}NO$, C 76.30, H 6.35, N 8.09%; found, C 76.09, H 6.43, N 8.45%.

2-Methyl-6-hydroxyquinoline hydrogen bromide (**2**).

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This compound was prepared by reflux of compound **1** (9.03 g, 0.058 mol) in hydrobromic acid (48%, 20 ml) for 16 h. The resulting solution was evaporated to dryness, another 20 ml of hydrobromic acid was added, and the mixture was refluxed again for 4 h. After cooling, a solid formed and was collected by filtration. Recrystallization from ethanol (95%) gave 13.61 g of compound **2** (91%, m.p. 272–275°C). Analysis: calculated for $C_{10}H_{10}NOBr \cdot H_2O$, C 46.51, H 4.65, N 5.41%; found, C 46.69, H 4.64, N 5.18%.

1,5-Bis(2-methylquinolin-6-oxy)pentane (*3*). The mixture of compound **2** (13.0 g, 0.05 mol), 1,5-dibromopentane (5.75 g, 0.025 mol), potassium carbonate (13.8 g), potassium iodide (2 g) and acetone (100 ml) was refluxed for 20 h. After cooling, the mixture was poured into cold water. The precipitate was collected by filtration and then washed with water. Recrystallization from ligorin yielded 4.1 g of compound **3** (42%, m.p. 112–114°C). ^1H n.m.r. ($CDCl_3$): δ (ppm) = 1.83 (multiplet, 6 H, $-C-(CH_2)_3-C-$), 2.70 (s, 6H, $-CH_3$), 4.10 (t, 4 H, $J = 5.86$ Hz, $-OCH_2-$), 7.00–8.00 (multiplet, 10 H, aromatic proton). ^{13}C n.m.r. ($CDCl_3$): δ: (ppm) = 22.6 (C1), 24.7 (C13), 28.7 (C2), 67.5 (C3), 105.8 (C6), 122.0 (C5,11), 127.1 (C8), 129.7 (C7), 134.9 (C10), 143.5 (C9), 156.0 (C12), 156.4 (C4). Analysis: calculated for $C_{25}H_{26}N_2O_2$, C 77.72, H 6.73, N 7.25%; found, C 77.48, H 7.00, N 7.18%.

*1,5-Bis(2-methyl-*N*-ethylquinolin-6-oxy)pentane diiodide* (*4*). A tube containing compound **3** (4.90 g, 0.013 mol) and ethyl iodide (5.96 g, 0.038 mol) was sealed under vacuum after being frozen in liquid nitrogen, and was then heated at 100°C for 24 h. The mixture was poured out after breaking the tube and digested with acetone. The solid was collected by filtration and recrystallized from methanol, yielding 9.06 g of compound **4** (95%, m.p. 119–121°C). ^1H n.m.r. and ^{13}C n.m.r. spectra are shown in *Figures 1* and *2*. Analysis: calculated for $C_{29}H_{36}N_2O_2I_2 \cdot 2H_2O$, C 47.41, H 5.45, I 34.60%; found, C 47.83; H 5.56, I 34.92%.

*2-Methyl-6-methoxy-*N*-ethylquinoline iodide* (*5*). This compound was prepared according to the same procedure as for compound **4**. The yield of compound **5** was 93% (m.p. 119–121°C). ^1H n.m.r. (DMSO-d_6): δ (ppm) = 1.5 (t, 3 H, $J = 6.8$ Hz, $-NCCH_3$), 3.1 (s, 3 H, $-CH_3$), 4.0 (s, 3 H, $-OCH_3$), 4.9 (q, 2 H, $J = 6.8$ Hz, $-NCH_2-$), 7.6–9.0 (multiplet, 5 H, aromatic proton). ^{13}C n.m.r. (DMSO-d_6): δ (ppm) = 13.5 (C1), 22.0 (C13), 47.5 (C12), 56.5 (C11), 108.0 (C5), 121.0 (C7), 126.5 (C4), 130.0 (C10), 133.5 (C9), 144.0 (C8), 157.0 (C6), 158.5 (C2). Analysis: calculated for $C_{13}H_{16}NOI$, C 47.41, H 4.86, I 38.58%; found, C 47.38, H 4.94, I 38.64%.

Model compound 6. A mixture of compound **5** (0.60 g, 1.82 mmol), triethyl orthoformate (1.08 g, 7.28 mmol) and pyridine (10 ml) was refluxed for 30 min. Green crystals formed, which were collected, washed with cold ethanol and dried under vacuum, yielding compound **6** (0.36 g, 72.6%). The ^1H n.m.r. spectrum is shown in *Figure 3* (curve A). Analysis: calculated for $C_{27}H_{29}N_2O_2I \cdot H_2O$, C 58.07, H 5.55, I 22.76%; found, C 58.13, H 5.62, I 22.49%.

Oligomer 7. The polymerization was tested in two solvents.

(a) In pyridine: a mixture of compound **4** (1 g, 1.48 mmol), triethyl orthoformate (1.37 g, 11.84 mmol) and pyridine (15 ml) was refluxed for 1 h as the colour of the solution changed from yellow to green and then to blue. The oligomers were collected by filtration, and washed with tetrahydrofuran (THF) and finally methanol. The blue solids were extracted using methanol in a Soxhlet extractor for 24 h and the residue dried under vacuum yielding 0.6 g of oligomer **7** (80%). Analysis: calculated for $C_{89}H_{100}N_6O_{10}I_4 \cdot 4H_2O$ (two repeat units + end-group + $4H_2O$), C 55.01, H 5.92, I 26.18; found, C 55.10, H 5.74, I 26.19%.

(b) In quinoline: the same procedure as above was followed. The oligomers were obtained in the yield of 83%. Analysis: calculated for $C_{122}H_{132}N_8O_{14}I_5 \cdot 5H_2O$ (three repeat units + end-group + $5H_2O$), C 56.48, H 6.11, N 4.43, I 25.12%; found, C 56.43, H 5.78, N 4.40, I 26.11%.

Polymer 8. The compound **4** (1.256 g, 1.80 mmol) and diethyl squarate (0.205 g, 1.80 mmol) were dissolved in butanol (15 ml) and heated to reflux. Sodium butoxide solution (5 ml, 5.5% of sodium) was then added dropwise and the mixture was refluxed for 30 min. After cooling, the solid formed was collected by filtration, and washed with water and finally ethanol. The material obtained was extracted with ethanol using a Soxhlet extractor, yielding 0.35 g of polymer. Analysis: calculated for 13 repeat units + end-group + $13H_2O$, C 71.45, H 6.21, N 5.10, I 3.30%, calculated for 14 repeat units + end-group + $14H_2O$, C 71.59, H 6.22, N 5.10, I 3.08%; found, C 70.94, H 6.24, N 4.93, I 2.83%.

Characterization of compounds

N.m.r. spectra were recorded on a JEOL FX 90 Q *FT*n.m.r. spectrometer. *FT*i.r. spectra of pressed KBr pellets were taken using a Perkin–Elmer 1760 *FT*i.r. spectrometer. U.v./vis. spectra were obtained using a Perkin–Elmer Lambda 4C u.v./vis. spectrophotometer. Thermal analyses were performed using Perkin–Elmer DSC-7 and TGA-7 systems under nitrogen with a heating rate of 20°C min^{-1}. NLO measurements were performed employing the degenerate four-wave mixing technique. A detailed description of DFWM measurements has been given previously[16].

RESULTS AND DISCUSSION

Carbocyanine oligomers

Monomer **4** was synthesized in four steps as shown in *Scheme 1* and was obtained as reddish crystals. Elemental analysis showed this to be a dihydrate. The assignments of the ^1H and ^{13}C n.m.r. spectra (see *Figures 1* and *2*) support this structure[17]. When the monomer was heated under vacuum at 80°C, the associated water was dispelled and a yellow powder was obtained. The compound 5,6-methoxy-2-methyl-*N*-ethylquinoline iodide was prepared in the same way as for monomer **4** and was reacted with triethyl orthoformate to prepare the model compound (compound **6** of *Scheme 2*). The model compound reaction has been carried out using both pyridine and quinoline as solvents. Spectroscopic and elemental analyses showed that the product obtained in both solvents is model compound **6**.

Polymerizations were attempted by heating a mixture of compound **4** and triethyl orthoformate in both quinoline and pyridine (see *Scheme 3*). Pyridine and

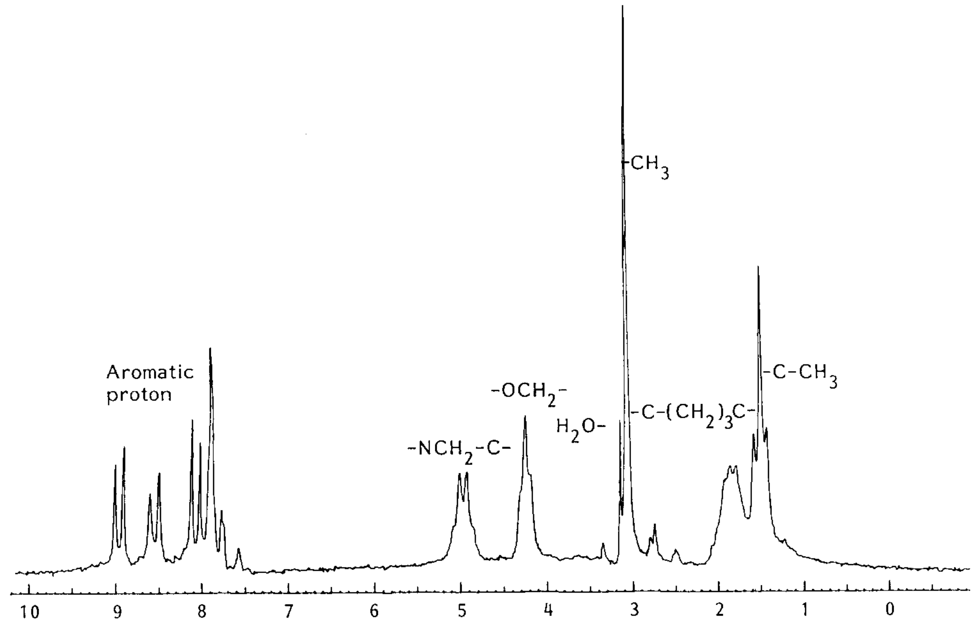


Figure 1 ^{1}H n.m.r. spectrum of monomer **4** in DMSO-d$_6$

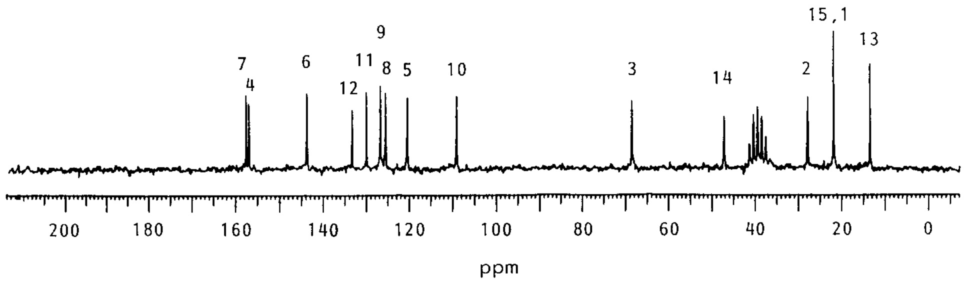
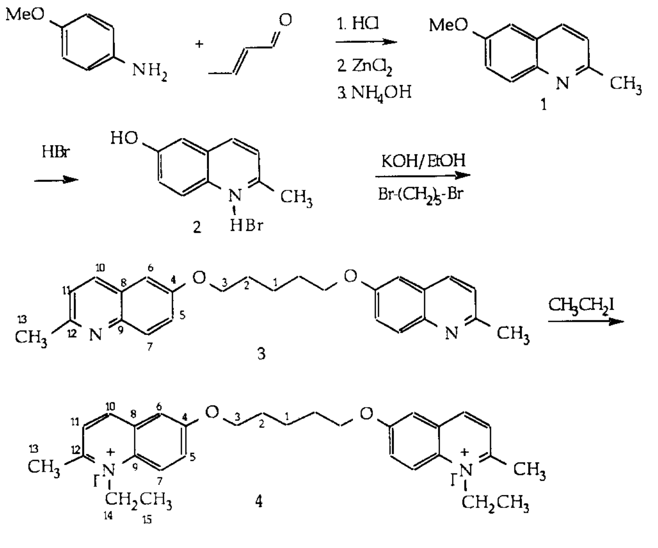
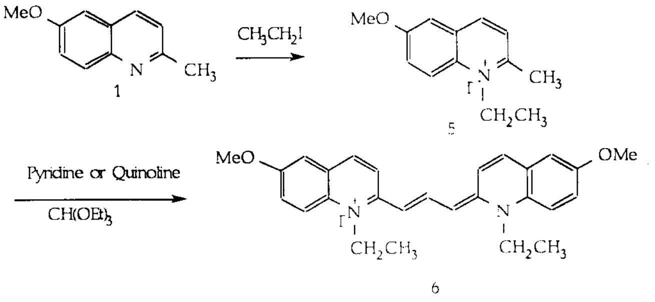


Figure 2 ^{13}C n.m.r. spectrum of monomer **4** in DMSO-d$_6$ (the assignments of the spectrum refer to ref. 17)



Scheme 1

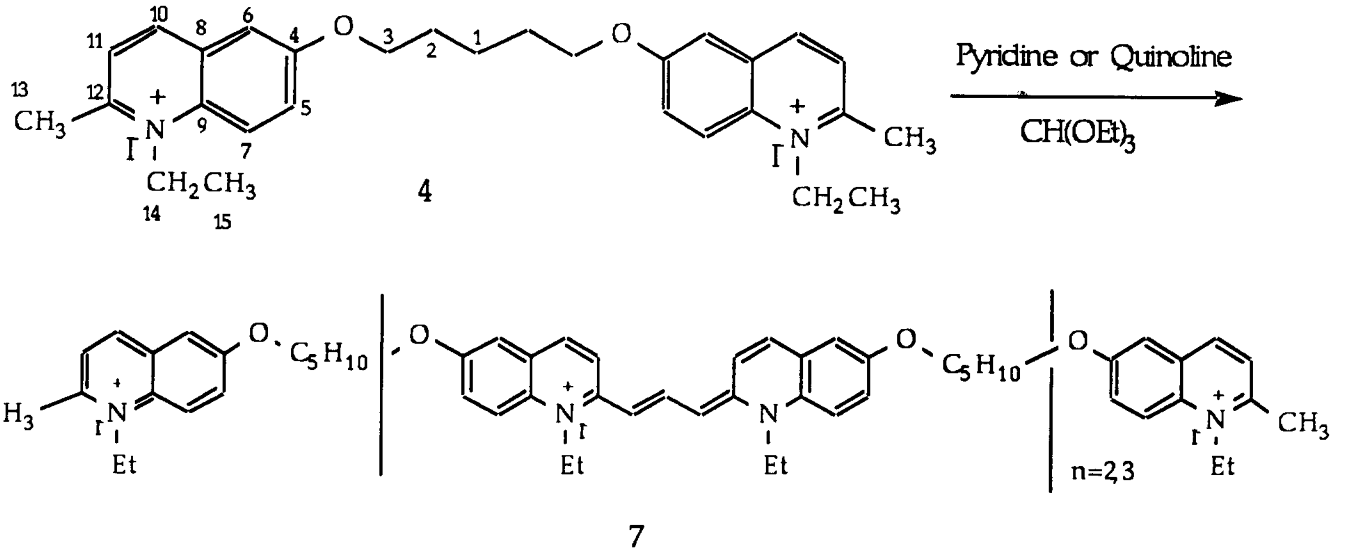


Scheme 2

quinoline appeared to be poor solvents for the final products, and hence the molecular weights of the materials obtained were low. Both final materials were identical in terms of spectroscopic analyses. Elemental analyses showed that materials obtained from quinoline media exhibit higher molecular weight. This is reasonable with respect to the better solvation properties of quinoline in general over pyridine. Elemental analysis results further suggested that, in oligomer systems, each quaternary salt unit is associated with one water molecule.

The ^{1}H n.m.r. spectra of both model compound **6** and oligomer **7** are shown in *Figure 3*. It can be seen that the chemical shift at 6.4 ppm due to methine bridge proton, H_α ($-CH_\alpha{=}CH_\beta{-}CH_\alpha{=}$), occurs in both model compound and oligomer[18]. The chemical shift at 7.3 ppm is a new feature compared to the monomer (*Figure 1*), which is related to the chemical shift of aromatic protons without quaternary salt unit (see structure of compound **7**). Chemical shifts of H_β appear at ~8.2 ppm, but this peak is overlapped by the aromatic proton chemical shift, as is observed for other carbocyanine compounds[18].

The *FT*i.r. spectra of the model compound **6** and oligomer **7** are shown in *Figure 4*. These two spectra are very similar to each other and *Table 1* summarizes the



Scheme 3

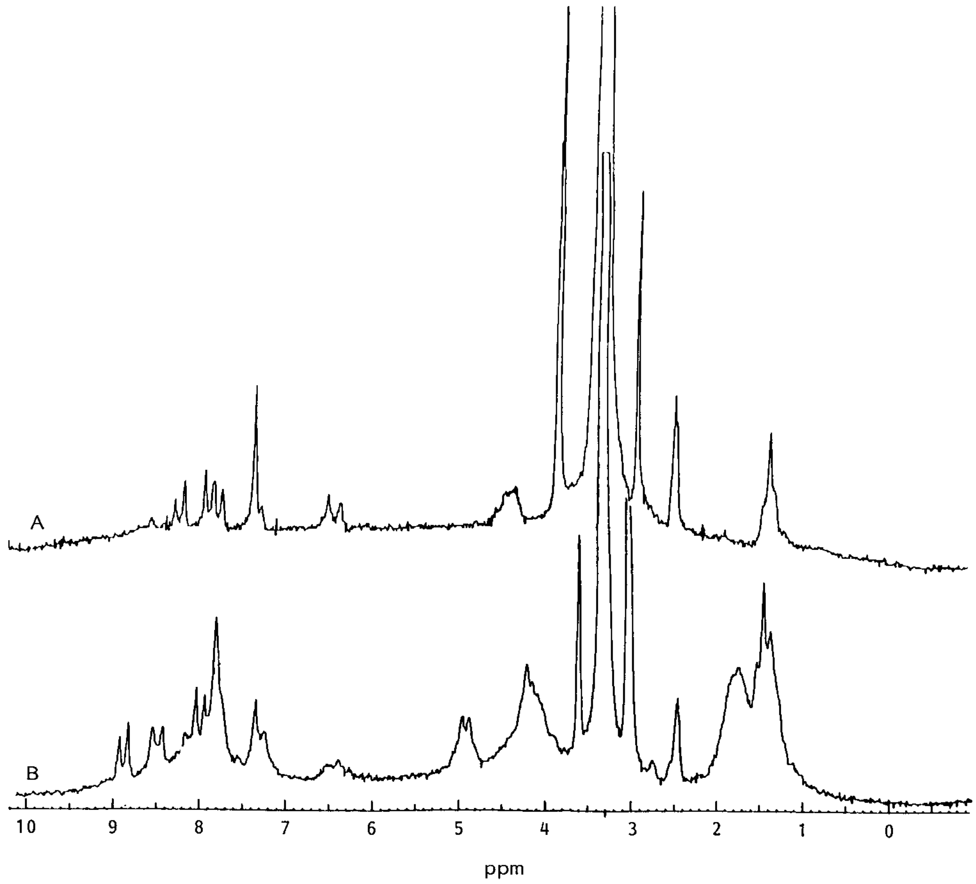


Figure 3 ^1H n.m.r. spectra of (A) model compound **6** and (B) oligomer 7 in DMSO-d_6

*FT*i.r. spectroscopic features related to the carbocyanine unit[19]. One can note that the specific absorption bands related to the carbocyanine structures exist in both model compound and oligomer. Since the oligomer contains different lengths of repeat units and end-groups, its *FT*i.r. spectrum showed some overlap in the aromatic related absorption region at ~750–850 cm^{-1}, two singlet bands being observed. For the model compound, these are two doublet bands.

U.v./vis. spectra of both model compound **6** and oligomer 7 are identical (see *Figure 5*). Three absorption peaks can be seen in the visible region at ~533, 577 and 631 nm. This is further evidence for the structural similarity of model compound and oligomer. The oligomer is sensitive to the acid as are other carbocyanine compounds[18], and decolorization was observed when the material was dissolved in methanesulphonic acid.

D.s.c. studies showed that the oligomer has a melting transition at ~250–253°C. The t.g.a. trace of the oligomer showed that it was thermally stable up to ~420°C (first breakdown) under nitrogen (see *Figure 6*, curve A).

The oligomers were soluble in polar organic solvents such as dimethylformamide (DMF) and dimethylsulphoxide (DMSO) and films could be cast on glass slides. The film quality of the pure oligomer was usually poor due to aggregation, but, after a few repeat preparations, a (macroscopically) uniform film was obtained, and such films were used for DFWM measurements. An alternative way to prepare optical-quality films was to put the oligomer into a host polymer matrix of either polycarbonate or poly(4-vinylpyridine). For the model compound, aggregation is observed in polycarbonate composite at very low concentration, and only poor optical-quality films in poly(4-vinylpyridine) were obtained due to gradual aggregation.

DFWM measurements at $\lambda = 532$ nm showed that the oligomer has a $\chi^{(3)}/\alpha$ value of 9×10^{-13} esu cm. It was estimated that the value of the absorption coefficient α of this material is $\sim 10^4$–10^5 cm^{-1}, which gives a $\chi^{(3)}$ value of $\sim 10^{-10}$–10^{-9} esu. Since the measurements were performed in regions of absorption, these values contain a large resonant contribution. *Figure* 7 gives a plot of the DFWM signal $\chi^{(3)}/\alpha$ as a function of the laser beam delay time. It can be noted that there exists a permanent grating (a constant signal after 50 ps delay time), which likely reflects a photochemical reaction. The films prepared from DMF solution of polycarbonate with 10% (w/w) oligomers also showed a $\chi^{(3)}/\alpha$ value of 0.85×10^{-13} esu cm. In these composite samples no permanent grating was observed.

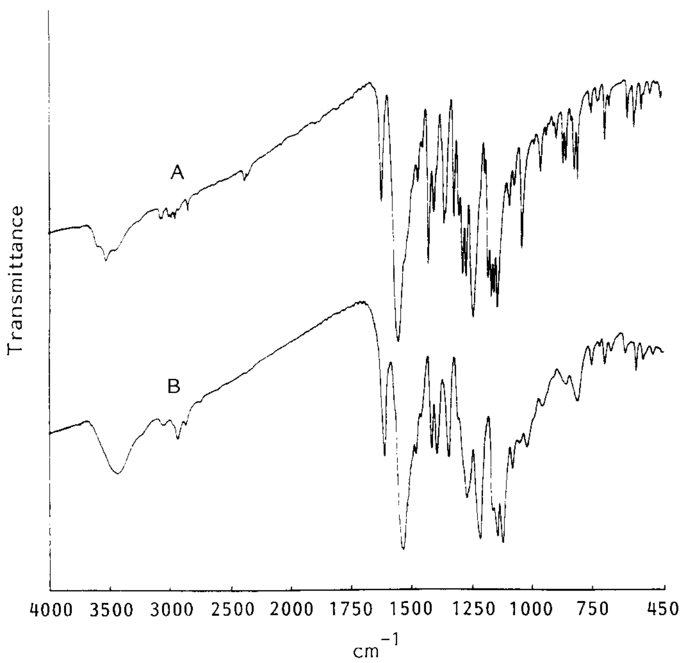


Figure 4 *FT*i.r. spectra of (A) model compound **6** and (B) oligomer **7** (in KBr pellets) from 450 to 4000 cm^{-1}

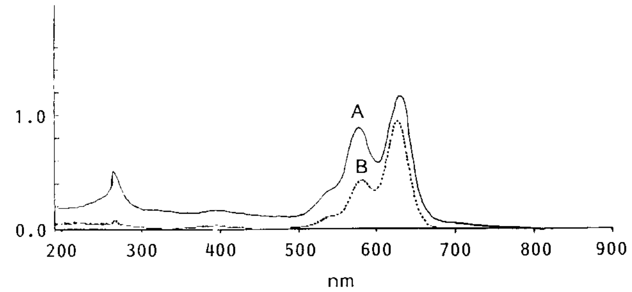
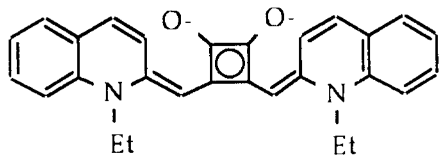


Figure 5 U.v./vis. spectra of (A) oligomer **7** and (B) model compound **6** in DMF

Cyanine dye polymer containing squaric acid units

Sprenger *et al.*[20] first studied the reactions of diethyl squarate with quinolidine quaternary salts leading to dye materials with a reported structure as **9** below:



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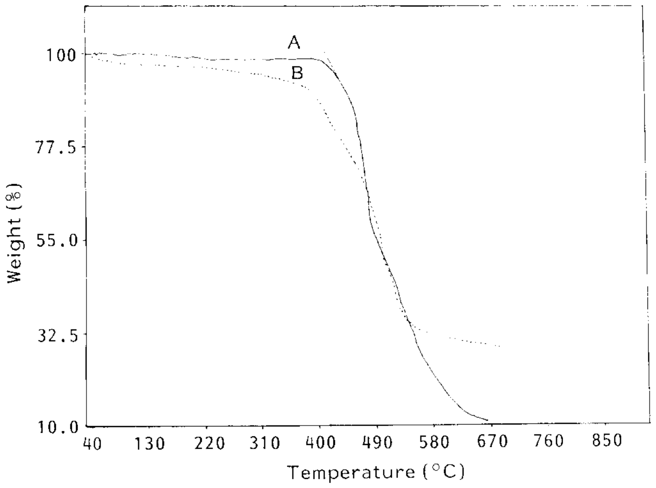


Figure 6 T.g.a. diagram of (A) oligomer **7** and (B) polymer **8** under nitrogen atmosphere at heating rate of 20 C min^{-1}

Table 1 *FT*i.r. spectroscopic data of oligomer **7** and model compound **6** (in cm^{-1})

	Resonant conjugated unsaturated C=C (st)	Aromatic quinolyl (st)	C=C (*trans*) out-of-plane bending	Hetero ring (C–H)	Benzene ring (C–H)	–CH$_2$–, –CH$_3$ (st)	Ar–O–R (st)
Model compound **6**	1538	1611	953 (m)	861	827	3058–2859	1230 (s)
	1460	1503		848	814		
	1416	1460					
Oligomer **7**	1533	1608	956 (m)	857	809	3040–2808	1218
	1478	1501					
	1414	1457					

We utilized the monomer **4** to react with diethyl squarate to attempt an analogous polymer (*Scheme 4*).

The reaction was carried out in n-butanol with sodium butoxide as catalyst according to the literature procedure[20]. The resulting polymeric material was a black powder, which was partially soluble in DMF and DMSO. Elemental analysis showed that the final material contained 2.83% iodide. The best-fit structure to the elemental analysis corresponds to structure **8** in which each repeat unit is associated with a water molecule. Indeed, we observed weight loss of 3.6% in a t.g.a. trace of the polymer before 200°C (see *Figure 6*, curve B). The *FT*i.r. spectrum of the polymer shows strong absorption at 1750 and 1726 $\mathrm{cm^{-1}}$ due to carbonyl stretching, at 1662 $\mathrm{cm^{-1}}$ due to $>C{=}C<$ stretching and at 1616 $\mathrm{cm^{-1}}$ due to aromatic stretching. The u.v./vis. spectrum of the polymer showed a broad absorption at ~630, 576, 532, 485 (sh), 399, 383 (sh) and 267 nm (see *Figure 8*, curve A). This material is also sensitive to the acid as indicated in the optical absorption spectrum in DMF with methanesulphonic acid (see *Figure 8*, curve B).

Although the best-fit structure of the polymer shows 13 repeat units, an optical-quality film cannot be obtained due to aggregation. Optical-quality films can be prepared using a poly(4-vinylpyridine) composite matrix. Unfortunately, DFWM measurements cannot detect visible signals at 532 or 1064 nm. This inability to detect a phase conjugate signal could reflect either or both a weak optical non-linearity or strong absorption of the generated signal.

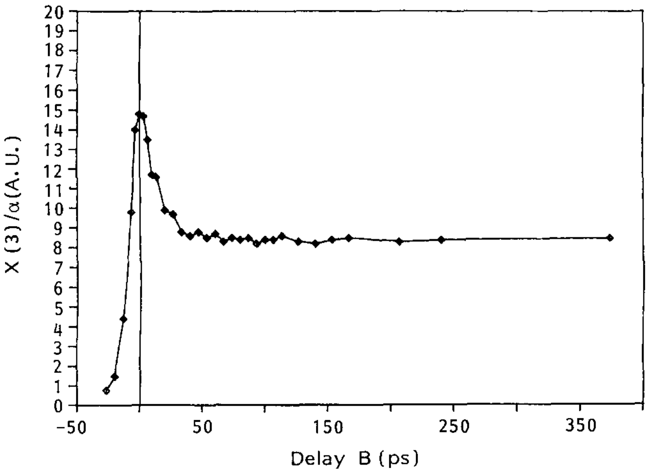


Figure 7 DFWM signal $\chi^{(3)}/\alpha$ of oligomer **7** as a function of laser beam delay time

CONCLUSIONS

A classic carbocyanine formation reaction has been adopted to synthesize NLO-active oligomers and polymers. Solubility limits the final products to oligomers. These oligomers have advantages over simple carbocyanine molecules due to their miscibilities with different transparent host polymers permitting optical-quality films to be prepared. DFWM measurements revealed a large optical non-linearity for a pure oligomer film as well as composite polymer films. The reaction of diethyl squarate with the active proton in a quinolidine quaternary salt was also employed to prepare a polymer. This material has a strong, diffuse absorption band in the visible region and no detectable DFWM signal.

ACKNOWLEDGEMENTS

This work was supported by Air Force Office of Scientific Research contracts F49620-87-C-0100 and F496-88-C-0071 and by National Science Foundation grant DMR-88-15508.

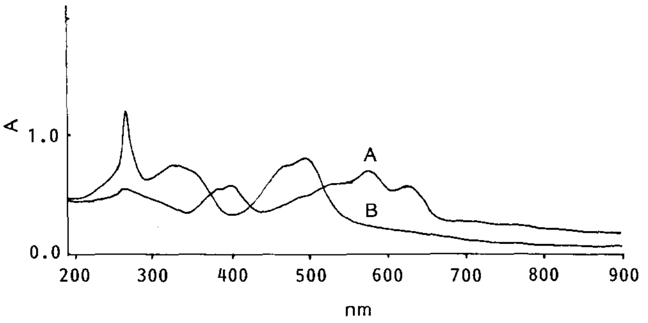
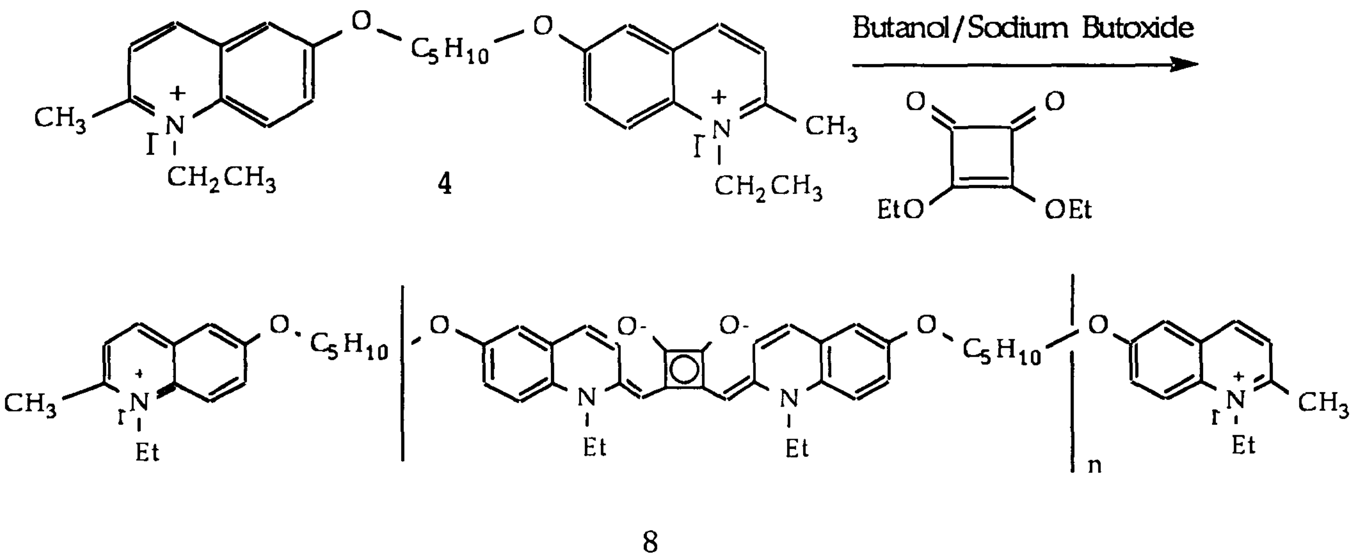


Figure 8 U.v./vis. spectra of (A) polymer **8** in DMF and (B) polymer **8** in acidic DMF (with methanesulphonic acid)



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Scheme 4

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