The design of new copolymers for $\chi^{(3)}$ applications

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Several electroactive π-conjugated polymers have recently shown promising non-linear optical (NLO) properties. However, long conjugation sequences in such polymers as polyacetylene (PA), polythiophene (PT), poly(*p*-phenylene vinylene) (PPV) and poly(2,5-thienylene vinylene) (PTV) often result in solubility, processability and optical transparency problems that make their use in electro-optic devices difficult. In this paper it is outlined how copolymers in which oligomeric segments of PTV, alternating with saturated spacer units, can be synthesized and cast as optical-quality films for NLO applications. The design of oligomeric PTV monomers and preliminary NLO characterization of the copolymers are also described.

(Keywords: poly(2,5-thienylene vinylene) oligomers; polyamide; non-linear optics; electron delocalization; ultraviolet–visible absorption)

INTRODUCTION

The chemistry and physics of highly conjugated π-electron polymers continue to be of interest due to their fascinating properties which range from metallic conductivity, upon chemical or electrochemical doping, to the more recently studied NLO properties under intense laser irradiation. In both cases, extensive electron delocalization seems to be involved in the physical processes observed. Large optical non-linearities have been observed by several research groups in neutral π-electron systems (undoped) such as polyacetylene, polythiophene, poly(*p*-phenylene vinylene), poly(2,5-thienylene vinylene) and polydiacetylenes[1–3]. All of the above polymers have characteristically broad absorption bands extending well into the visible region. Since it is desirable that polymers for non-linear optical applications should not absorb at the laser fundamental frequency or harmonics, these absorption characteristics can lead to large optical losses, photochemical degradation of the polymer and declining performance over time. However, if copolymer structures in which segments with high NLO activity alternate with spacer segments with low NLO activity are envisaged, it is possible that the u.v.–visible absorption characteristics can be controlled and tailored to the laser fundamental. The type of spacer used may also confer enhanced solubility to the copolymer structure with regard to the extended π-electron homopolymer.

SYNTHETIC STRATEGY

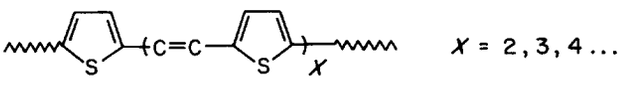
We have previously described a general approach to the design of copolymers for non-linear optics applications in which oligomeric electroactive segments can be alternated with hydrocarbon spacer groups[4]. The electroactive oligomeric units can be joined to the spacer segments by either electron-donating or electron-withdrawing functionalities. A general formulation is illustrated in *Figure 1*.

DESIGN OF THIENYLENE VINYLENE COPOLYMERS

We have previously shown that thienylene vinylene oligomers can successfully model PTV in chemical doping studies, forming polaron and bipolaron states in solution[6,7]. There remains the question, then, whether short oligomeric segments of electroactive polymers can display reasonably large non-linear susceptibilities in copolymer form. Beratan *et al.*[8] have previously shown that in a conjugated polyene series, the third-order hyperpolarizability, γ, increases rapidly up to 10–15 repeat units and then more slowly up to 40 units. After that there was little additional change up to the infinite polyene limit. This would imply that long conjugation sequences are not necessary for high NLO activity. In a similar fashion, Prasad[9] and Garito *et al.*[10] have shown that γ/N levels off with increasing N. In addition, Prasad has shown that γ/N reaches a limiting value faster in poly(*p*-phenylene) than in polythiophene. Thus we have focused our attention on PTV in our copolymer studies after early indications that PPV oligomers did not display good NLO behaviour[4,5].

SYNTHESIS OF MONOMER UNITS

PTV oligomeric repeat units can be defined as follows:



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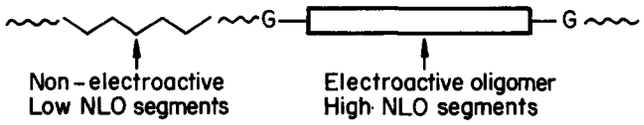
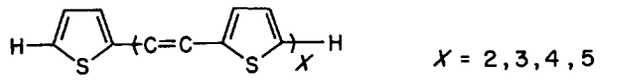


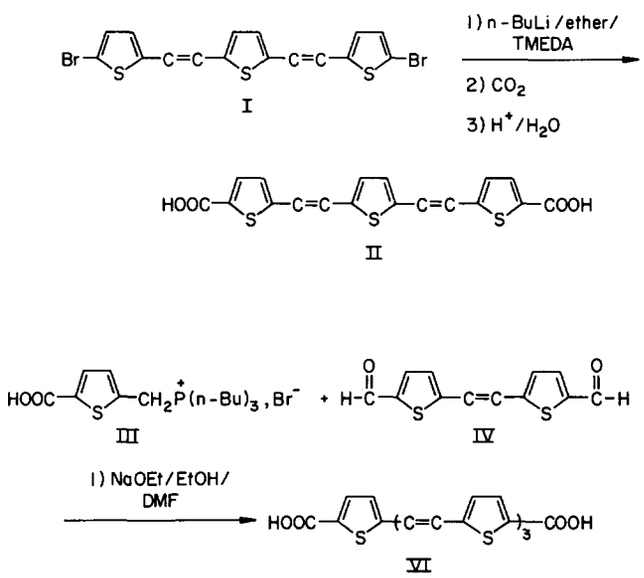
Figure 1 General formulation of NLO-active copolymers (G is a mesomerically interactive functional group)

The parent oligomers with $n = 2-5$ have been synthesized and doping behaviour will be discussed in a future publication[11]. Owing to their relative ease of formation via interfacial polymerization techniques, polyamide

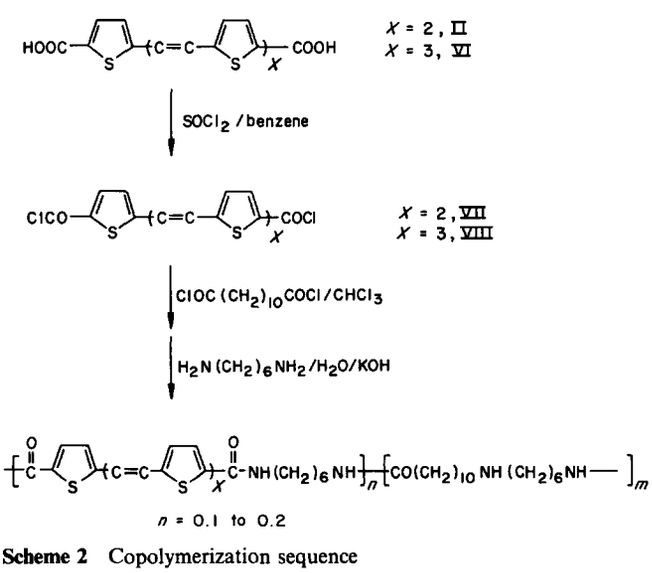


structures were chosen for the incorporation of PTV segments in formal copolymer structures. To this end, two PTV-biscarboxylic acids (II and VI) were synthesized, as outlined in *Scheme 1*.

The copolyamides were synthesized via conventional interfacial techniques, as described in the following Experimental section and illustrated in *Scheme 2*.



Scheme 1 Synthesis of PTV oligomer diacids



Scheme 2 Copolymerization sequence

EXPERIMENTAL

PTV dimer bis-carboxylic acid (II)

A solution of butyllithium (1.6 M solution in hexane) (12.5 ml, 0.02 mol) was added dropwise to a solution of I (2.29 g, 0.005 mol) in a mixture of ether (300 ml) and tetrahydrofuran (100 ml) while maintaining the temperature at −35°C. The resulting mixture was stirred for 30 min, after which dry ice (8.8 g, 0.2 mol) was added. The product mixture was stirred for 30 min and then hydrolysed by addition of 150 ml of 3 N HCl. The product was obtained by vacuum filtration and recrystallization from DMF (1.27 g, 66%): m.p. >300°C; λ_{max} (DMF) 436; 457 (sh) nm. Calculated for $C_{18}H_{12}O_4S_3$: C, 55.67; H, 3.09. Found: C, 55.03; H, 3.65.

PTV trimer bis-carboxylic acid (VI)

A solution of sodium ethoxide (30 ml, 1 M solution, 0.03 mol) was added dropwise to a solution of IV (0.98 g, 0.003 mol) and III (3.09 g, 0.007 mol) in a 1:1 mixture of DMF–ethanol while maintaining the temperature at 90°C. The resulting mixture was poured into 100 ml cold water and the product isolated by filtration. Pure VI was obtained by recrystallization from DMF (0.79 g, 53%): m.p. >340°C; λ_{max} (DMF) 479; 504 (sh) nm. Calculated for $C_{24}H_{16}O_4S_4$: C, 58.06; H, 3.23. Found: C, 58.03; H, 3.38.

PTV dimer bis-acyl chloride (VII)

PTV-dimer diacid (II) (0.50 g, 0.0013 mol) was mixed with benzene (10 ml) and freshly distilled thionyl chloride (0.50 g, 3.3 equivalents) in a 50 ml flask equipped with condenser and drying tube. The mixture was heated at 95°C for 18 h or until evolution of HCl gas was undetectable at the condenser head. After solvent removal the residue was washed with 5 ml benzene to remove excess thionyl chloride. VII can purified by recrystallization from $CHCl_3$/hexane (0.54 g, 99%): m.p. 175–80°C; i.r. (KBr pellet), 1734 (C=O), 1653, 1636, 1605 (C=C–Ar), 1429 (C–S, ring) cm^{-1}; ^1H n.m.r., 7.70 (d, 2H), 7.42 (s, 2H), 7.35 (d, 2H), 7.18–7.45 (quintet, 4H).

PTV trimer bis-acyl chloride (VIII)

The synthesis is essentially as that described above for VII. The crude product can be purified by dissolving in $CHCl_3$ (*ca.* 200 ml g^{-1}), filtering to remove insoluble material and removal of solvent by evaporation. Thus in a typical preparation, 0.50 g VI yields 0.51 g VIII (crude, 95%; purified, 80%): m.p. 83–85°C; i.r. (KBr pellet), 1732 (C=O), 1583, 1504 (C=C–Ar), 1420 (C–S ring) cm^{-1}; n.m.r. 7.1–8.3 (series of overlapping multiplets).

Copolymerization procedure

The copolyamides were synthesized by first dissolving the bis-acyl chloride monomers in chloroform (approximately 0.2 wt% solution) followed by the addition of dodecanedioyl dichloride (30:70 to 90:10 molar ratio to electroactive monomer, as dilution and solubilizing agent). To this vigorously stirred solution was added hexamethylene diamine dissolved in an equal volume of water with an appropriate excess of sodium hydroxide (2 equivalents based on HCl evolution). The copolymers precipitated immediately and the solutions were stirred

for an additional 2 h, after which the chloroform layer was essentially colourless. The chloroform layer was then separated and the polymers filtered off the aqueous layer with repeated water washing, and finally an acetone wash and drying. For example, the 20% incorporated thienylvinylene ($X = 2$) copolymer was prepared by first dissolving the diacyl chloride (0.10 g, 2.35×10^{-4} mol) in chloroform (50 ml) followed by the addition of dodecanedioyl dichloride (0.25 g, 9.40×10^{-4} mol). To this vigorously stirred solution was added in one shot a solution of hexamethylene diamine (0.1136 g, 1.18×10^{-3} mol) in water (50 ml) containing approximately 0.20 g of sodium hydroxide. The polymer precipitated at once and the solution was stirred for an additional 12 h. The aqueous layer was carefully decanted and the polymer collected on a fine-fritted glass funnel, washed with approximately 100 ml of water and finally with acetone. The dried polymer weighed 0.34 g (85%).

CHARACTERIZATION

Infrared spectra. The i.r. spectra of polymers and polymer intermediates were recorded on a Perkin-Elmer model 1760 Fourier transform spectrophotometer with a nominal resolution of 4 cm^{-1} and a total of 16 scans.

U.v.–visible spectra. The u.v.–visible spectra were obtained on either a Perkin-Elmer Lambda 4C spectrophotometer with a slit width of 1 (0.5 nm resolution) and a scan speed of 120 nm min^{-1}, or with a guided wave model 200-25 visible–near-infrared spectrometer via fibreoptic cable link to a remote sample cell at a scan rate of 7 nm s^{-1}. Spectra were obtained in solution (CH_2Cl_2, DMF or NMP) for monomers and in NMP solution for polymers.

Thermal measurements. A Perkin-Elmer TGA7 thermogravimetric analyser was used to investigate the thermal stability of the polymers between ambient and 900°C compared to a standard sample of Nylon 6-12. A nitrogen purge was employed to exclude oxidative decomposition.

Preliminary NLO characterization. Third-order susceptibilities reported here were measured with degenerate four-wave mixing (DFWM) by employing a variation of this technique by Hellwarth and co-workers that permits measurements of all tensor components of the third-order susceptibility including fast and slow components, which gives, among other things, the acoustic velocity and damping coefficients. A phase-conjugation geometry for DFWM is employed in which all beam polarizations and delays can be varied to give independent data. Three input beams are formed from 532 nm laser pulses (derived from 5 Hz repetition-rate mode-locked pulses from a Quantel model YG471-C Nd:YAG laser frequency doubled to 532 nm) having an energy of about 2 mJ and duration of about 25 ps.

COPOLYMER CHARACTERIZATION

The copolymers were analysed by u.v.–visible and i.r. spectroscopy and by thermogravimetric analysis (t.g.a.) compared to Nylon 6-12. The conversion of the diacyl dichloride to copolyamide can be followed easily by tracing the changes in the C=O stretching frequency (*Figure 2*). Thus in the conversion of VI to VIII, the C=O frequency shifts from 1650 to 1732 cm^{-1}. Conversion of VIII to the 20% copolyamide shifts the C=O absorption to 1642 cm^{-1}. The u.v.–visible spectra of the diacid and copolyamide were essentially identical in NMP solution, as illustrated in *Figure 3*. T.g.a. analysis for the $X = 2$ copolyamide (10% in composition) shows that thermal degradation begins at *ca.* 350°C *versus* 410°C for Nylon 6-12. The $X = 3$ copolyamide (10% in composition) is stable to *ca.* 400°C, while the $X = 3$ (20% in composition) copolyamide is stable to *ca.* 420°C. These results are illustrated in *Figure 4*.

The molecular weights of the copolymers were measured to be of the order 100 000 amu as polystyrene equivalent molecular weights.

DISCUSSION AND CONCLUSIONS

The results of this study clearly indicate that oligomeric segments of well-known electroactive polymers can be incorporated in copolymer structures by conventional copolymer synthetic techniques. This approach will thus allow a number of different electroactive segments to be evaluated for potential non-linear optical activity. Several postulated advantages[4,5] of this approach have now been confirmed. First, it is now possible to synthesize polymer structures in which the delocalization length of the electroactive segment is well-defined and invariant, thus the absorption bands tend to be much sharper than for the fully conjugated electroactive polymer. Secondly, the absorption characteristics of the copolymer can be predetermined or 'tailored' since there is little difference in the u.v.–visible spectra of the monomer *versus* the copolymer. Thirdly, the copolymerization process can be varied to include different lengths (and structures) of spacer groups as well as NLO-inactive diluents (in the copolyamide case, a saturated bis-acyl dihalide).

Preliminary measurements of $\chi^{(3)}/\alpha$ for thin films cast from NMP (10% and 20% incorporation) show strong initial phase conjugate signals of the order of 10^{-13} esu cm^{-1}. Absorption measurements at several different film locations indicate an α of 10^{-2}–10^{-3} cm^{-1}, which yield $\chi^{(3)}$ values in the range 10^{-10}–10^{-11}. There is some decay in this signal, which may indicate possible photochemical oxygen interaction. Studies to test this hypothesis are currently under way. It is interesting to note that similar-size oligomers of PPV are much less active than the PTV segments[4]. This may be additional evidence that the phenyl ring, with regard to thiophene, is not a good transmitter of electron delocalization over moderate-to-long distances in conjugated segments, as first suggested by Prasad[9].

Another advantage of the copolymer approach is that it allows a direct evaluation of the effect of conjugation length on $\chi^{(3)}$. We are currently synthesizing a series of oligomers where $X = 4$, 5 and 6, which we will attempt to incorporate in copolymers similar to those described in the present study. This will allow a direct evaluation of how $\chi^{(3)}/\alpha$ varies with delocalization length and identity of repeat unit. The current study is also being expanded to include $\chi^{(3)}/\alpha$ measurements at a number of different laser fundamentals to evaluate how $\chi^{(3)}$ varies in terms of resonant *versus* non-resonant contributions.

The relative thermal stability of the copolymers is acceptable, but it is interesting to note that stability seems to be increasing both as the oligomer length increases and as the percentage incorporation increases. Thus it

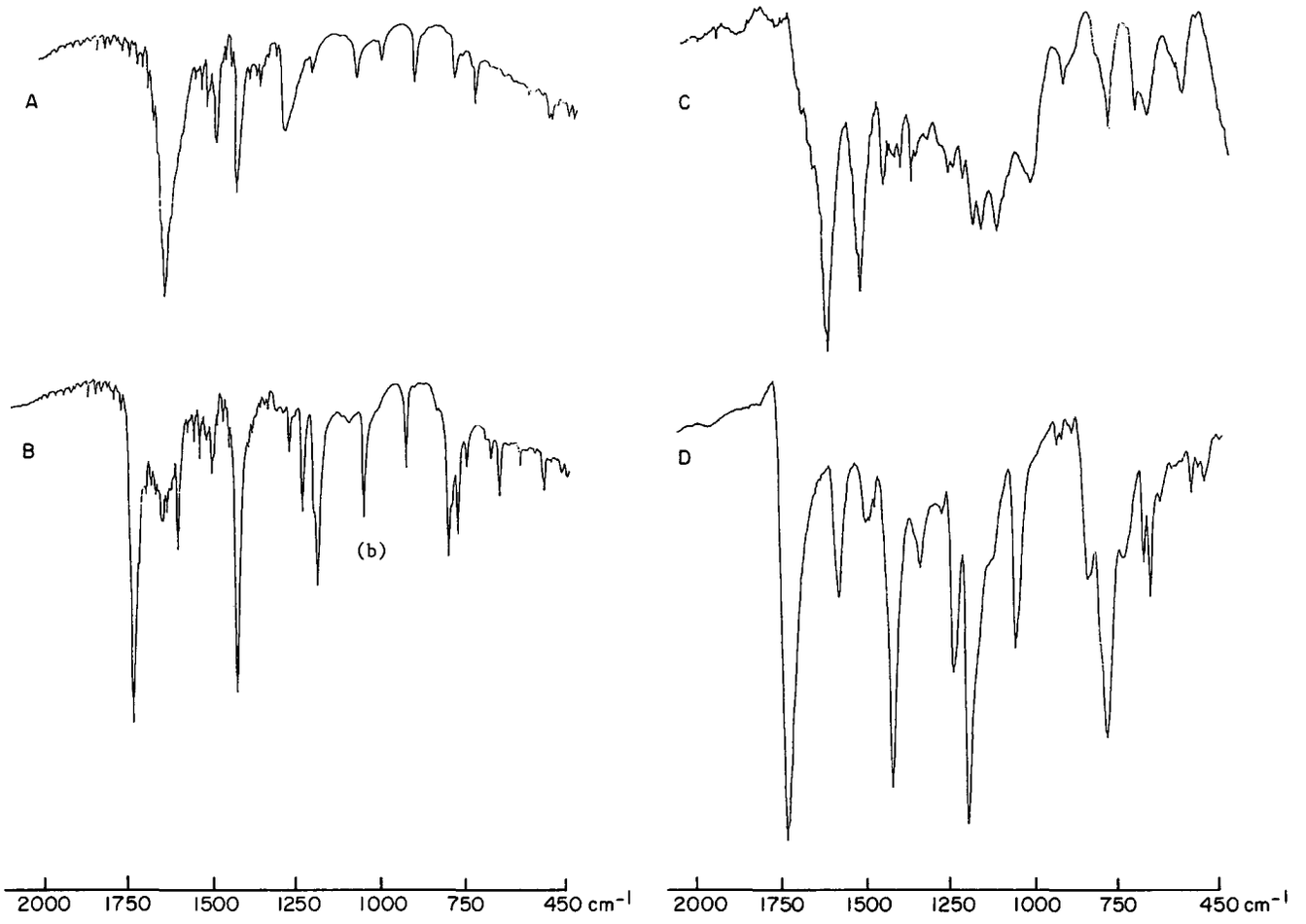


Figure 2 I.r. spectra of monomers and polymer: (A) $X = 2$ diacid (II); (B) $X = 2$ diacyldichloride (VII); (C) $X = 3$ 20% copolyamide; (D) $X = 3$ diacyl dichloride (VIII)

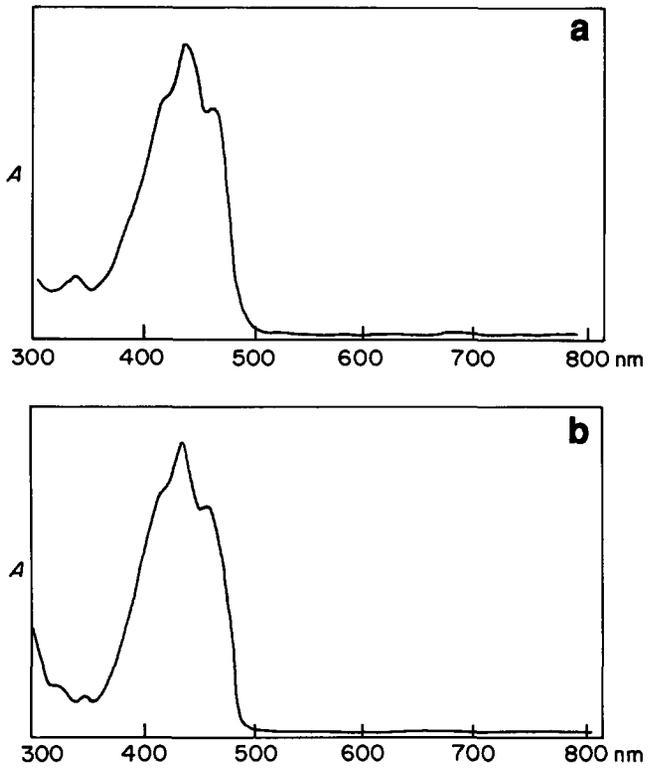


Figure 3 U.v.–visible absorption spectra: (a) compound II in NMP solution; (b) $X = 2$ copolymer (10% incorporation) in NMP solution

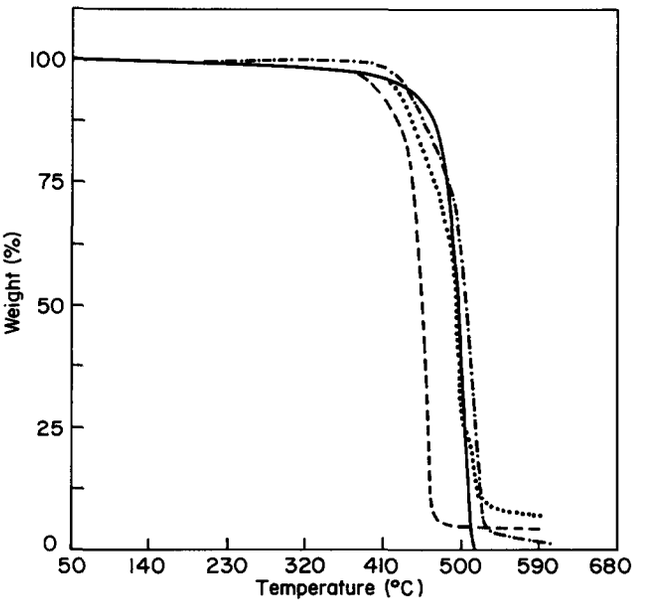
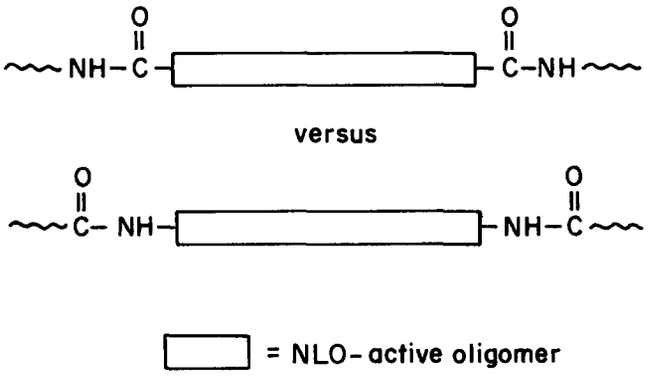


Figure 4 T.g.a. traces for: Nylon 6-12 (——); 10% incorporated $X = 2$ PTV oligomer (– – – –); 10% incorporated $X = 3$ PTV oligomer (○); and 20% incorporated PTV (●)

would appear that thermal stability in excess of 500°C could be expected for $X > 3$ and $n > 0.2$ (see *Scheme 2*). As mentioned above, these copolymers are currently being prepared in our laboratories. In a similar fashion, it is interesting to speculate how polymer stability and $\chi^{(3)}$ may vary if the electron demand in the copolymer sequence is inverted. This can be accomplished by reversing the amide orientation:



This can be accomplished by synthetic manipulation of II and VI by standard organic synthetic methodology

$$-COOH \longrightarrow -COCl \longrightarrow -CON_3 \longrightarrow -C-N=C=O \longrightarrow -CNH_2$$

These new monomers have been prepared[12] and are currently being converted into the inverted copolyamides. Characterization and NLO evaluation of these new materials will be reported at a later time.

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