Optical nonlinearities in substituted conjugated polymers

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Conjugated polymers with sidegroups such as methyl, trimethylsilyl, p-methoxy phenyl, o-methoxy phenyl, and hexyl groups on a polyphenylacetylene chain are studied in an attempt to understand the contribution of factors such as the backbone, conformation of the chain, sidegroups and polymerization catalyst on the optical nonlinearities. The results of degenerate four-wave mixing experiments at 532 nm with nanosecond pulses indicate that the substitution of an electron-donating group away from the backbone can enhance the third-order susceptibility. Some of the polymers show optical limiting action at this wavelength. The thermal contribution to the measured susceptibility is also determined.

1. Introduction

There have been a multitude of investigations reported on optical nonlinearities in organic molecules directed towards the understanding of the fundamental processes as well as the development of devices [1, 2]. Organic molecules with \( \pi \)-electrons resulting in bond alternation on the backbone possess unique advantages for the study of higher-order optical nonlinear processes [3]. Polyphenylacetylene (PPA) is a \( \pi \)-conjugated polymer which we have previously investigated [4-6] in both the undoped and iodine-doped states. In the present work, we study polymers that are similar to PPA as far as the backbone structure is concerned but contain differing sidegroups both on the backbone and on the phenyl ring. These modifications appear to throw light on the different contributions to nonlinearity.

Optical nonlinearity in undoped conjugated polymers arises from the one-dimensional long-chain nature of the delocalized \( \pi \)-electron cloud. The merit is decided by the conjugation length, defined as the distance over which the \( \pi \)-electron cloud extends without breaks. The conjugation length is affected by factors such as (a) the backbone, (b) the conformation of the chain, (c) the sidegroups and (d) the process of polymerization. The polymers chosen for this study are such that they provide each of these contributions independently in a fairly satisfactory way. In (a), we consider only the effect of \( \pi \)-electron conjugation due to the alternation of single and double bonds on the backbone. Comparison
of polyphenylacetylene with polystyrene helps to isolate the backbone contribution due to conjugation since the two polymers have otherwise identical structures.

The form-dependent (conformation) contribution is estimated by studying a single sample of PPA in various states such as (i) a liquid film sandwiched between two glass slides, (ii) in solution, (iii) a solution-cast solid film on a glass substrate and (iv) a melt-cast solid film. While in solution, all the polymeric molecules are independent of each other with no fixed order; the liquid film sandwich form perhaps leaves the molecules independent owing to the dilution but some amount of orientation is added due to the restraining glass slides slid one over the other. The polymer in the form of a solution-cast solid film is free of the effects of the solvent to a large extent. The melt-cast film, though quite homogeneous and easy to form, does not show any optical nonlinearity, presumably owing to the coagulation of the long-chain molecules above the melting point.

The contribution of the sidegroup is estimated by substituting different groups directly onto the backbone and also by substitutions made away from the backbone. PPA has hydrogen and phenyl ring as the sidegroups. In the first case, hydrogen is substituted by methyl and trimethylsilyl groups while the phenyl sidegroup is unchanged. In the second case, hydrogen on the backbone is retained and a hydrogen on the phenyl group is substituted by methoxy groups in both the ortho- and para-positions. In the third case, hydrogen is retained and the phenyl ring is replaced by a hexyl group.

In order to find the effect of the polymerization catalyst on the nonlinear optical characteristics of a polymer, a single polymer is prepared with three different catalysts, namely tungsten, molybdenum and chromium. We do observe a variation in the characteristics based on the catalyst, and the route of polymerization is thus seen to play a role in the effectiveness of a polymer for nonlinear optical studies.

2. Experiment

Table I lists the polymers used in this work and their structures. Poly(methylphenylacetylene) (poly(MPA)) and poly(trimethylsilylphenylacetylene) (poly(TMSPA)) differ from PPA because of the replacement of the hydrogen in PPA by methyl and trimethylsilyl groups, respectively. In poly(p-methoxyphenylacetylene) (poly(p-MOPA)-1, poly(p-MOPA)-2 and poly(p-MOPA)-3) and poly(o-methoxyphenylacetylene) (poly(o-MOPA)-1), one hydrogen in the phenyl ring is replaced by methoxy group in the para- and ortho-positions, respectively. In poly(hexylacetylene) (poly(HA)), the phenyl ring in PPA is replaced by the hexyl group. There are some reported studies [7, 8] on picosecond degenerate four-wave mixing in polyphenylacetylene and substitutions such as o-methyl, o-ethyl, o-octyl and o-trimethylsilyl groups on the phenyl ring of PPA. In addition to substitutions on the phenyl sidegroup, we varied the sidegroups themselves, in effect substituting on the backbone directly. We expect this to have a larger effect on the properties of the polymer since the conjugation length is dependent on the conformation of the chain, which in turn is decided to a large extent by the bulkiness and the electronic properties of the sidegroups attached to the backbone.

All the polymers are obtained in the form of amorphous powders and they dissolve well in many organic solvents. The absorption spectra of the polymer solutions in the solvent 1,2-dibromoethane shown in Figs 1a and 1b were recorded on a Hitachi U-3400 UV-Vis-NIR spectrophotometer. The monomers were also studied in the same solvent. An increase in the third-order susceptibility \( \chi^{(3)} \) is anticipated if substitutions on the polyene chain alter its symmetric structure. This is true of all the substitutions we have studied.