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13. ABSTRACT *(Maximum 200 Words)*

One-pot post-polymerization modification reactions such as azo-coupling and tricyanovinylation reactions were employed to synthesize a series of polymers containing different nonlinear optical (NLO) chromophoric as well as ionic functionalities. We have extended and established the versatility of our earlier reported post-modification strategy to incorporate various heteroaromatic chromophores as well as ionic functionalities in the polymers, at the final stage of synthesis. The correlation between different heteroaromatic chromophore structures and the NLO properties of the polymers was extensively studied, Polymers containing heteroaromatic chromophores exhibit improved temporal stability and enhanced NLO activity. Polymers with ionic chromophores were employed to fabricate NLO active ultra-thin films using electrostatic self-assembling (ESA) technique. Attempts were also made to synthesize second order NLO active polydiacetylene derivatives using post azo-coupling reaction.

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DESIGN, METHODOLOGY AND PREPARATION OF NOVEL POLYMERS FOR NONLINEAR OPTICS

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ABSTRACT

One-pot post-polymerization modification reactions such as azo-coupling and tricyanovinylation reactions were employed to synthesize a series of polymers containing different nonlinear optical (NLO) chromophoric as well as ionic functionalities. We have extended and established the versatility of our earlier reported post-modification strategy to incorporate various heteroaromatic chromophores as well as ionic functionalities in the polymers, at the final stage of synthesis. The correlation between different heteroaromatic chromophore structures and the NLO properties of the polymers was extensively studied. Polymers containing heteroaromatic chromophores exhibit improved temporal stability and enhanced NLO activity. Polymers with ionic chromophores were employed to fabricate NLO active ultra-thin films using electrostatic self-assembling (ESA) technique. Attempts were also made to synthesize second order NLO active polydiacetylene derivatives using post azo-coupling reaction.

I. INTRODUCTION

Polymeric materials have advantages over inorganic crystals for nonlinear optical (NLO) applications, because of their low dielectric constant, large optical nonlinearity, low cost, and ease of processability. Stable NLO polymeric materials are potential candidates for electro-optic (EO) devices such as high bandwidth electro-optic modulators [1], and optical interconnects [2]. Second-order NLO properties in polymers are present when the chromophores are aligned in a non-centrosymmetric manner, using various approaches including electric field poling [3], formation of acentric Langmuir-Blodgett films [4], and sequential synthesis [5]. Recently, we have reported a new approach using electrostatic self-assembly to achieve acentric alignment of the chromophores in thin films. The process is very simple and involves alternate dipping of appropriate substrates into dilute aqueous solutions of oppositely charged polymers [6].

Chromophores with enhanced NLO susceptibilities can be obtained by increasing electron-donating and/or accepting effects [7], by extending the conjugation length between the donor and acceptor groups [8] and by replacing the phenyl groups in the chromophores with thiophene groups [9]. Efforts were made by our group [10] and various other groups [9, 11] to synthesize and optimize the properties of the chromophore functionalized polymers with high optical nonlinearity. NLO chromophores with large nonlinearity are crucial components in the formulation of photorefractive (PR) materials. PR effect occurs in materials that are photoconducting and in addition exhibit an electro-optic response [12]. This effect results from the formation of light induced space charge fields and consequently the spatial modulation of refractive index through the electrooptic effect. There is a growing interest in the development of fast responding photorefractive polymers with high charge carrier mobilities [13]. Polydiacetylenes are very good photoconductors and exhibit a charge carrier mobility of as high as 100 $cm^2 \cdot V^{-1} \cdot s^{-1}$ [14]. Chromophore functionalized polydiacetylenes may be ideal candidates for PR applications.

We have employed one-pot post-polymerization azo coupling reaction as well as tricyanovinylation, to synthesize a series of NLO polymers containing different heteroaromatic NLO chromophores as well as ionic functionalities, from epoxy and diacetylene based precursor polymers. The effect of the chromophore structure on the bulk NLO and other physical properties was discussed in some detail. The synthesized ionic polymers were assembled as NLO active thin films using ESA technique. Synthesized NLO chromophore functionalized polydiacetylene derivatives are potential candidate materials for PR applications. The synthesis and properties of the synthesized polymers are discussed in this work.

II. EXPERIMENTAL

2.1 Post azo-coupling reaction

The diazonium salts of appropriate chromophoric units were prepared by adding the corresponding amines directly into the nitrososulfuric acid solution at 5 °C, followed by decomposition of excess nitrous acid by addition of suitable amount of sulfamic acid in water. The freshly prepared diazonium salt solution was added dropwise into a solution of appropriate precursor polymer in N,N'-dimethylformamide (DMF) at 0 °C. The solution was stirred at 0 °C for 12 h. Chromophore functionalized polymers were obtained by precipitation in water followed by repeated washing of the polymer with acetone and drying under vacuum at least for 24 h.

2.2 Post tricyanovinylation reaction

Recrystallized tetracyanoethylene was added slowly into the precursor polymer solution in DMF under vigorous stirring. After the addition of tetracyanoethylene, the reaction temperature was raised to 45 °C, at which the reaction solution was stirred for 12h. The solution was subsequently precipitated in water. The precipitate was collected by filtration. The polymer was repeatedly washed with water, dried and further purified by repeated extraction with toluene. The polymer was dried under vacuum at least for 24 h before use.

III. RESULTS AND DISCUSSION

The precursor polymers were functionalized to introduce different chromophores at the final stage of the polymer preparation, using post azo coupling reaction as well as post tricyanovinylation reaction. Heteroaromatic chromophore functionalized epoxy based NLO polymers synthesized by post azo-coupling reaction are shown in Figure 1. Post tricyanovinylation reaction was employed as shown in Figure 2, to synthesize tricyanovinyl functionalized NLO polymers. Second order NLO properties and other physical properties of the synthesized epoxy polymers are listed in Table 1. The first part of the polymer nomenclature is an abbreviation to distinguish between precursor polymers from diglycidyl ether of bisphenol-A (BP) and other epoxide compounds (CH). The following parts refer to the different conjugation bridges and electron acceptor moieties of the chromophores.

Most of the synthesized polymers are solution processable. The glass transition temperatures (Tg's) of the polymers were studied using differential scanning calorimetry (DSC) and are listed in Table 1. Polymer, BP-IM-DC exhibit the highest Tg of 179 °C, among the series and the high Tg is attributed to possible presence of intermolecular hydrogen bonds between imidazole units and hydroxyl groups, causing physical networks. The precursor polymers, BP-AN and BP-TA, have very similar thermal stability as studied by thermogravimetric analysis (TGA) and are stable up to 330 °C under nitrogen atmosphere. Thermal stability of the formed NLO polymers declines, upon functionalization. The magnitude of the decrease depends on the type of heteroaromatic chromophores present in the polymer. BP-TA-TC starts to decompose in the temperature range between 270 and 280 °C, which is as stable as the epoxy based polymer containing 4-tricyanovinylaniline chromophores. Most of the polymers with heteroaromatic azo chromophores studied in this work do not show improved thermal stability over the epoxy based polymers with azobenzene type chromophores. However, BP-TA-TC polymer with highly enhanced NLO activity due to the presence of 2-(4-aminophenyl)-(5-tricyanovinyl)thiophene chromophores was developed, while maintaining thermal stability.

Corona poling was carried out at temperatures 10 to 15 °C higher than Tg of the polymers, to achieve non-centrosymmetric alignment of the chromophores in the polymer films. Second order NLO coefficients (d_{33}) were measured by second harmonic generation (SHG) technique. The measured d_{33} values are enlisted in Table 1. BP-TA-TC with 2-(4'-aminophenyl)-5-(tricyanovinyl) thiophene chromophores exhibited significantly larger optical nonlinearities due to the presence of strong electron-withdrawing tricyanovinyl group. The temporal stabilities of the synthesized polymers are good at 80 °C for 1000 h.

Precursor polymer, CH-AN, was synthesized from 1,4-cyclohexane -dimethanol diglycidyl ether (CH) and aniline (AN) and was functionalized with ionic chromophores using post azo coupling reaction as shown in Figure 3. All the synthesized polymers shown in Figure 3 are highly soluble in water at appropriate pH.

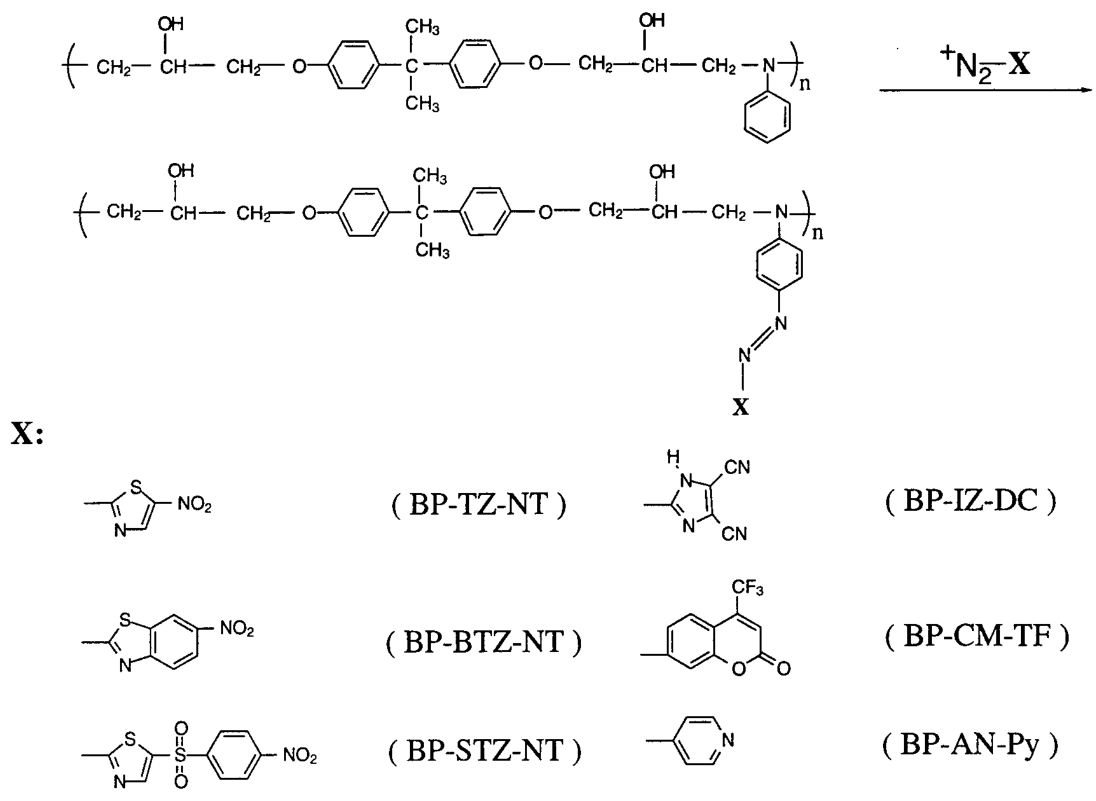

Figure 1. Synthesis of hetero-aromatic chromophore functionalized epoxy polymers by post azo-coupling reaction.

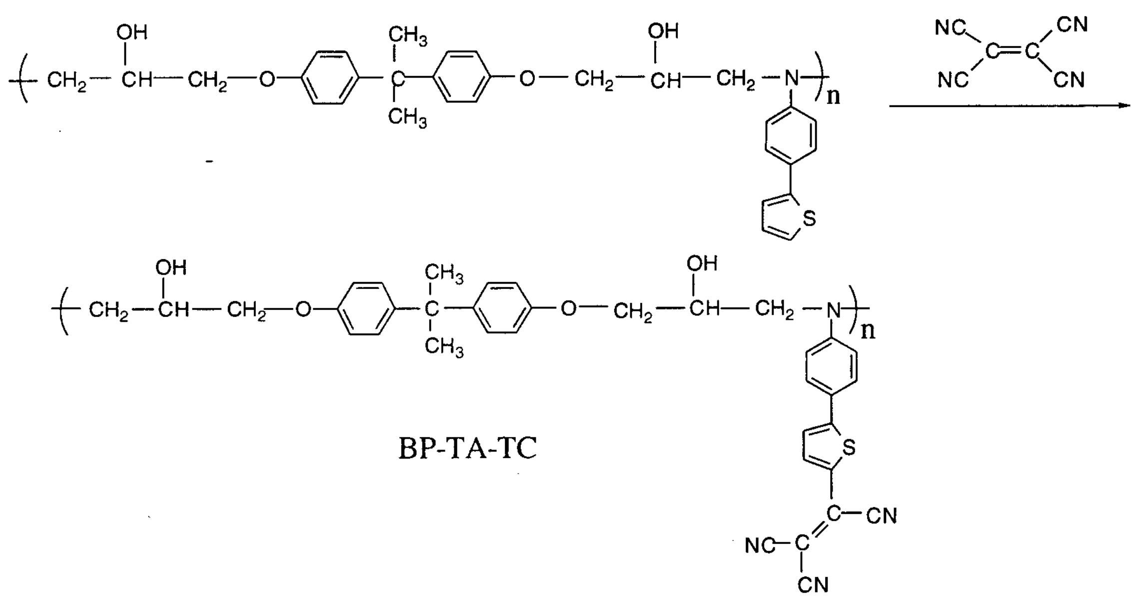

Figure 2. Synthesis of NLO chromophore functionalized epoxy polymers by post tricyanovinylation reaction.

The layer-by-layer deposition of CH-AZ-Ca was achieved by employing poly(diallyl-dimethylammonium chloride) [PDAC] as polycation. UV-Vis spectra of CH-AZ-Ca/PDAC films with increasing number of bilayers are shown in Figure 4. A linear increase of absorbance can be

Table 1. Second order NLO coefficient, d_{33}, of representative NLO polymers.

Polymer	λ_{max} (nm)	DF*	Tg (°C)	Td (°C)	d_{33} (pm/V, 1.064 μ)	d_{33} (pm/V, 1.550 μ)
BP-TZ-NT	571	77	141	210	104.5	24.5
BP-STZ-NT	545	70	139	222	108.4	14.1
BP-BTZ-NT	549	18	128	227	19.0	
BP-CM-TF	471	85	136	242	59.5	
BP-IZ-DC	489	72	179	224	24.3	
BP-TA-TC	615	58	126	273		80.0

*** DF - degree of polymerization (±3%) was determined using ^{1}H-NMR technique.**

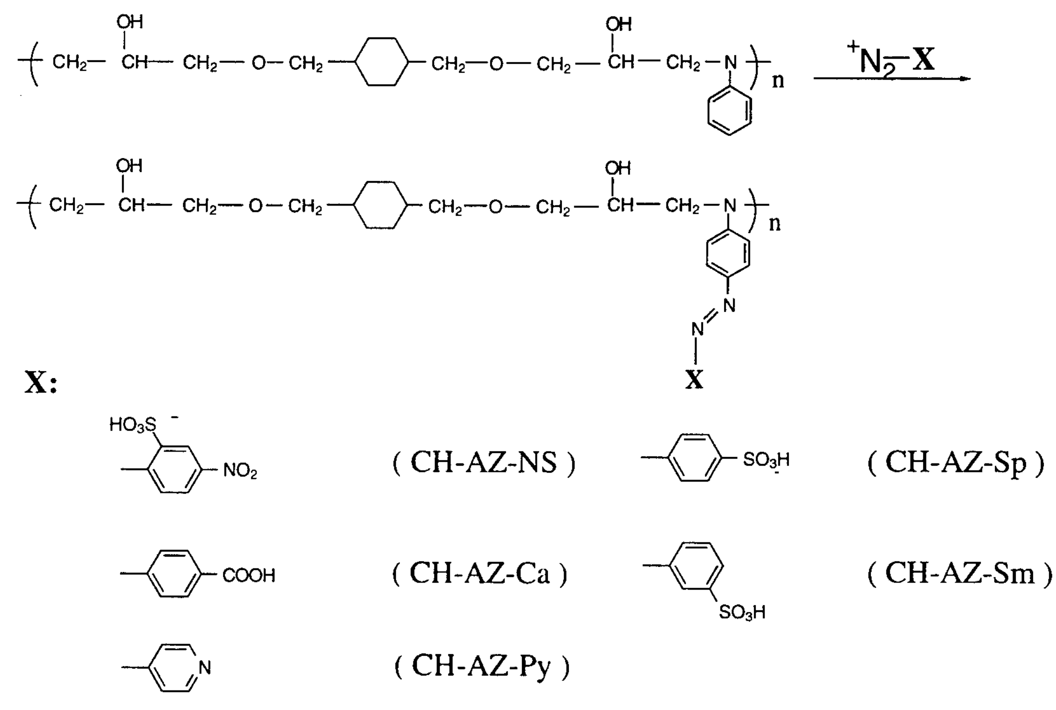

Figure 3. Synthesis of ionic polymers for electrostatic self-assembly (ESA) by post azo-coupling reaction.

seen as the number of bilayers increases. The linear relationship was observed up to at least 15 bilayers. The shape of the absorption curve of the multilayer is similar to that of spun cast films with an absorption maximum of 431 nm. The thickness of a 5 bilayer film was measured to be 72 Å by ellipsometry. The multilayer fabrication process was repeated several times to obtain films of the same exceptional optical quality. The second order NLO coefficients, d_{33}, of the self-assembled multilayers (5 bilayers) was determined to be 19 pm/V. This d_{33} value is in the same range as that of the electric field poled spin coated films of the same polymer. This result indicates that the azo chromophores in both the multilayers and poled spin coated films possess similar order of non-centrosymmetric alignment. Predominant orientation of the chromophores perpendicular to the surface of the substrate was inferred, using the relationship between the transmitted SHG intensity and the incident angle.

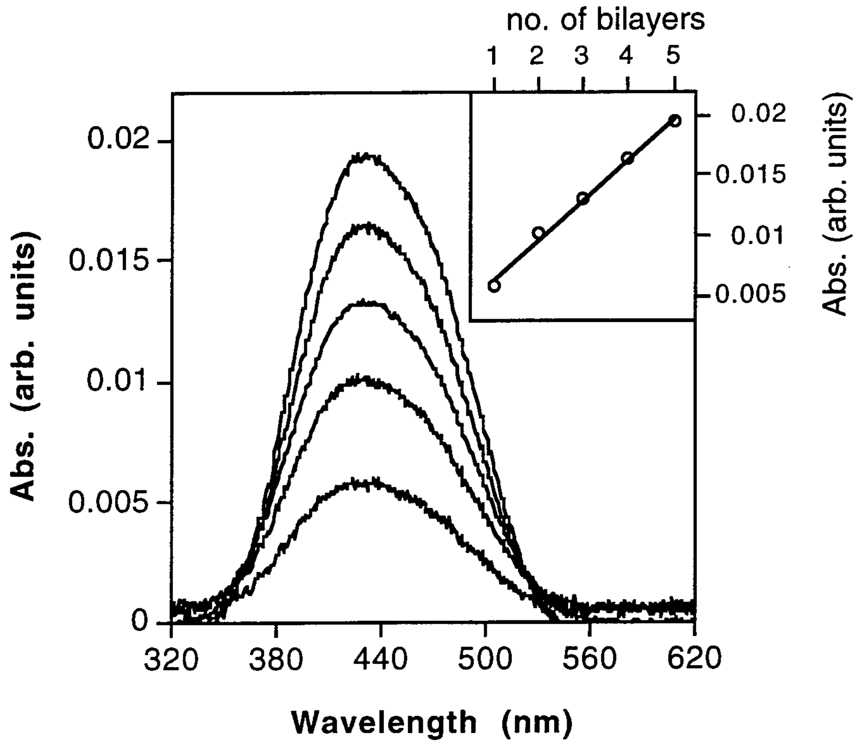

Figure 4. UV-vis spectra of PDAC/CH-AZ-Ca multilayer films; Inset shows increase in absorption with increase in number of bilayers.

We have recently synthesized a new series of diacetylenes, 9-(N-methyl-N-phenylamino)-5,7-nonadiynyl-N-(alkoxycarbonylmethyl)carbamate (MNRC; R = alkyl), whose structures are shown in Figure 5. The diacetylenes contain a functionalizable aniline group and various urethane chains. The presence of the aniline group allows modifications either in the monomer or in the polymer stage. We have carried out one-pot post azo-coupling on the poly(MNRC) [PMNRC such as PMNBC and PMNMC] with different chromophores as shown in Figure 5. Tricyanovinylation reactions can also be carried out on these polydiacetylene derivatives to obtain tricyanovinylated polydiacetylenes (from PMNBC and PMNMC). The tricyanovinylation occurs at the para position of the aniline groups as inferred from visible absorption and ^{1}H-NMR spectra. Relatively large second-order NLO activity was achieved upon corona poling of the tricyanovinylated polymer films at 1.136 μm. The poling was performed at 130 °C for 30 min. A d_{33} value of 33 pm/V was determined from the poled polymer thin films. The unpoled spin-coated films of PMNBC and PMNMC did not show second harmonic generation (SHG) signals.

IV. CONCLUSIONS

We have successfully employed one-pot post modification reactions such as post azo-coupling and post tricyanovinylation reactions to prepare NLO chromophore and ionophore functionalized polymers, with various backbone structures including epoxy and conjugated polydiacetylenes. Epoxy polymers containing 2-(4-aminophenyl)-(5-tricyanovinyl)thiophene chromophores, exhibited highest optical nonlinearity with good thermal and temporal stabilities among the series of polymers with variety of heteroaromatic chromophores. Synthesized ionic polymers were fabricated as second order NLO active thin films using electrostatic self assembling technique. NLO chromophore functionalized polydiacetylene derivatives were developed using post azo-coupling and post tricyanovinylation, for studying photorefractive characteristics.

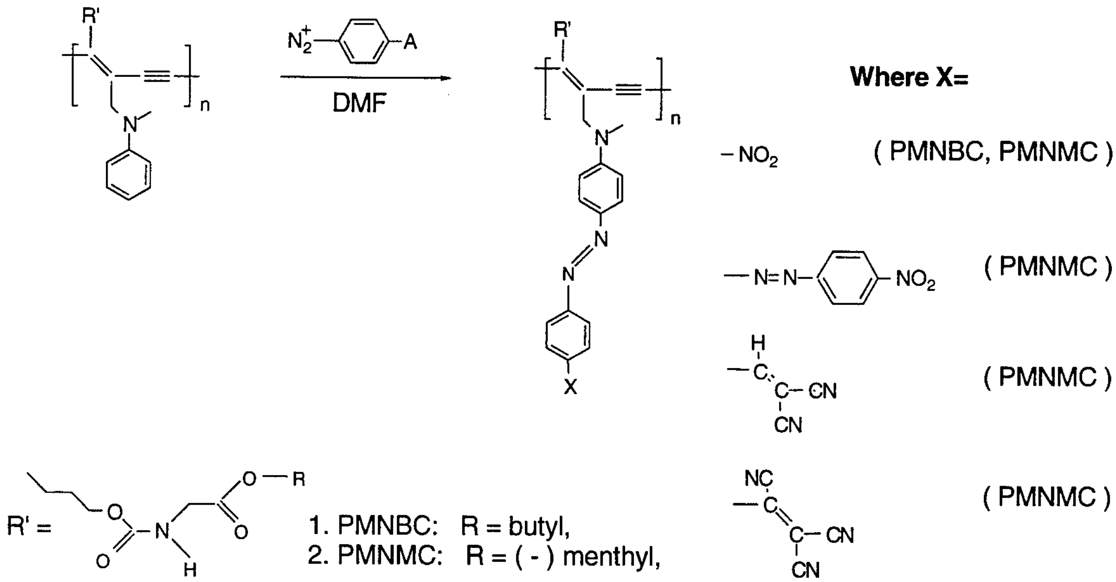

Figure 5. Synthesis of polydiacetylene based photorefractive polymer by post azo-coupling reaction.

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