A New Synthetic Approach for the Incorporation of Highly Efficient Second-order Nonlinear Optical Chromophores containing Tricyanovinyl Electron Acceptors into Methacrylate Polymers

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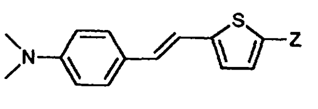
A new synthetic method is developed to incorporate efficient nonlinear optical chromophores containing thiophene conjugating units and tricyanovinyl acceptors into methacrylate polymers; this approach emphasizes the incorporation of tricyanovinyl groups into the pendant side chains after copolymerization of the precursor substituted acrylates with methyl methacrylate.

Some of the major challenges in the development of efficient second-order nonlinear optical (NLO) polymeric materials[1] for electrooptic devices have been (*a*) the design and synthesis of donor–acceptor (D–A) organic molecules[2,5] possessing large molecular nonlinearities (βμ); (*b*) incorporation of a high percentage of efficient D–A molecules in polymeric matrices resulting in thermally stable and processable NLO polymeric materials[3] and (*c*) alignment (a condition for macroscopic non-centrosymmetry) stability of poled NLO polymer thin films.[3,4] In the context of design and synthesis of efficient NLO chromophores, our earlier studies[5] have identified the importance of thiophene conjugating moieties in enhancing the molecular hyperpolarisabilities (βμ) of the charge-transfer compounds. In particular, we have demonstrated that the D–A molecules containing thiophene conjugating units and tricyanovinyl acceptors possess dramatically enhanced βμ values.[5a] In order to transform these impressive molecular nonlinear properties into material nonlinear responses, we have initiated a systematic study to incorporate push–pull thiophenes into polymer matrices. In this communication, we report a new synthetic approach for the incorporation of highly efficient NLO chromophores possessing tricyanovinyl functional groups into methacrylate polymers.

There have been several reports describing synthetic and electro-optic studies on side chain methacrylate copolymers containing well known NLO chromophores such as 4-nitroaniline (PNA), 4-dialkylamino-4′-nitroazobenzene (Disperse Red 1) and 4-dialkylamino-4′-nitrostilbene (DANS).[3b,c,6] The conventional synthetic methodology used in obtaining these side chain polymers involves free-radical initiated copolymerisation of methyl methacrylate and substituted methacrylates containing a NLO chromophore. Our studies (*vide infra*) indicate that this conventional copolymerisation method fails to yield the required copolymers if the methacrylate monomer possesses a NLO chromophore containing a tricyanovinyl acceptor. Tricyanovinyl substituted NLO chromophore **1a** was used as it has a very large molecular hyperpolarisability (βμ = 6200 × 10^{-48} esu) and high thermal stability (>200 °C).[5a]

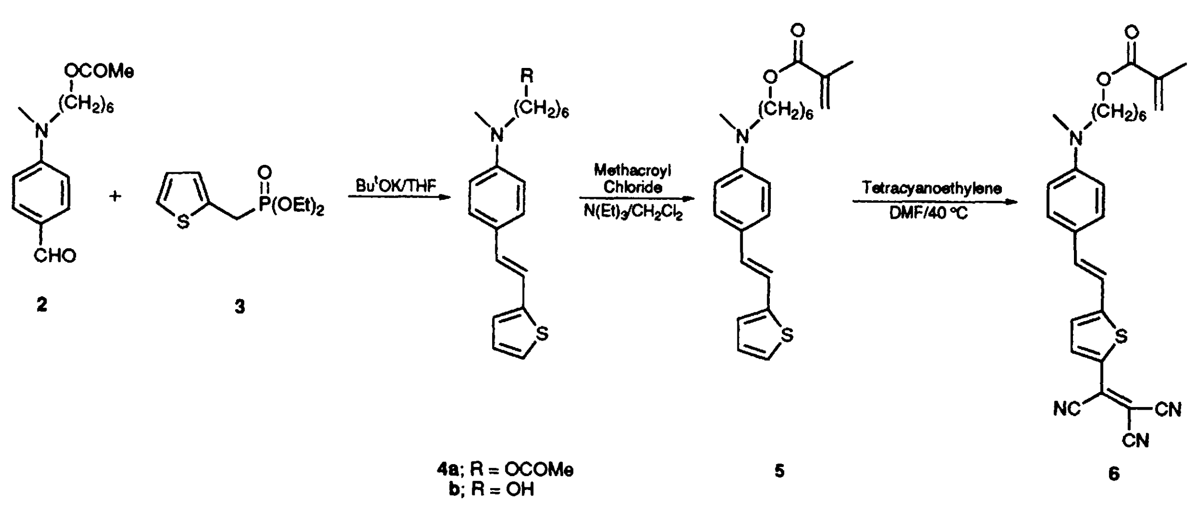
The methacrylate derivative of **1a**, **6**, was synthesized as shown in Scheme 1. Chromophores **2** and **3** were prepared by reported synthetic methods.[3b,5a] Generation of an anion from the phosphonate **3** with Bu^{t}OK in THF and its reaction with aldehyde **2** at 0 °C yielded the stilbene **4a** (R = OCOMe). Treatment of **4a** with 1 equiv. of Bu^{t}OK in THF at room temp. resulted in **4b** (R = OH). Methacrylate **5** was obtained by the reaction of **4b** with methacroyl chloride, catalysed by triethylamine. Tricyanovinylation was carried on methacrylate **5** with tetracyanoethylene in DMF to yield **6**.



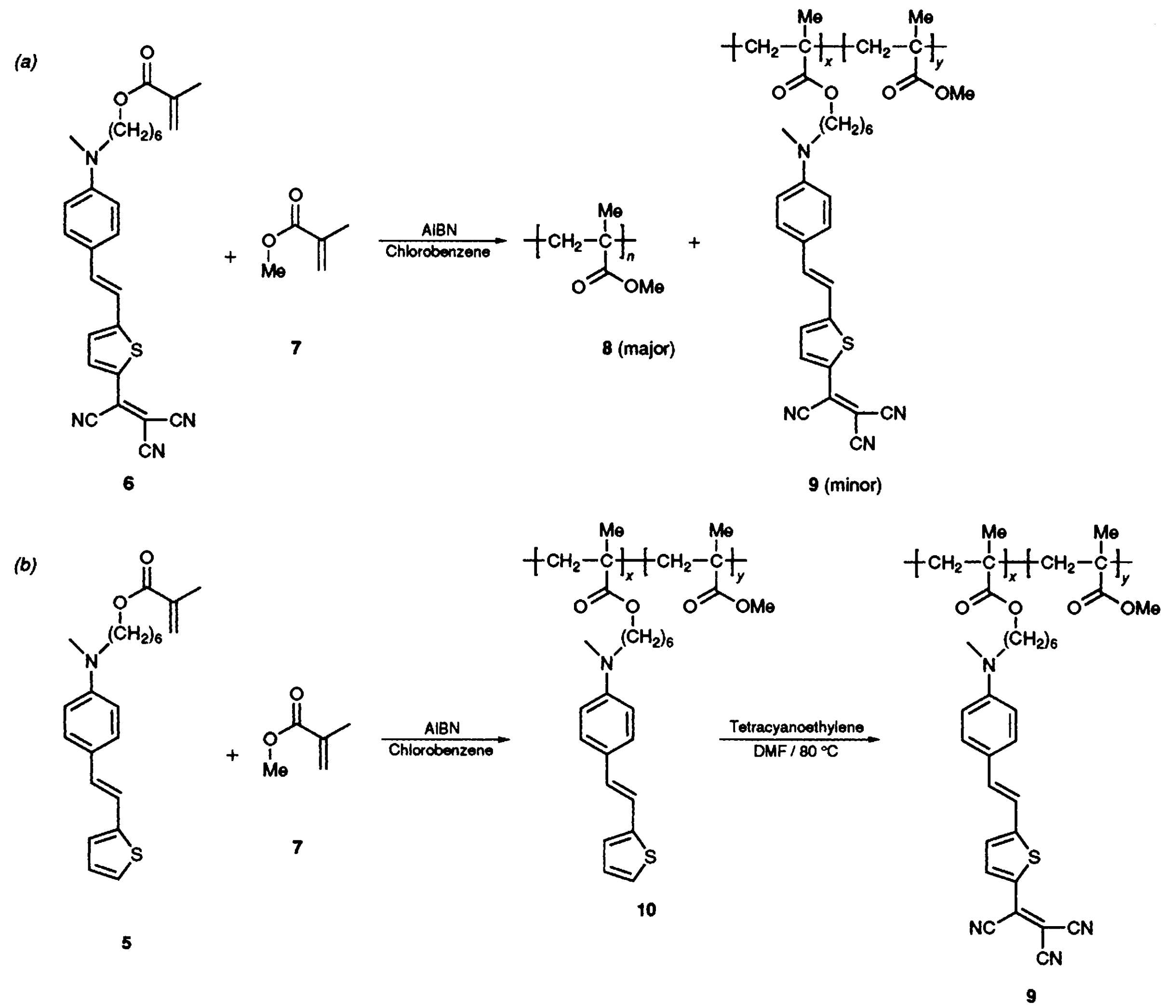
1a (Z = tricyanovinyl)

Table 1 Properties of acrylate copolymers **9** and **10**

	10		**9**	
X:Y	T_g	M_n	T_g	M_n
0:100	110	125000	110	125000
3:97	108	122000	112	126000
6:94	101	86000	110	91000
12:88	91	67000	115	74000
19:81	85	57000	120	65000
21:79	78	40000	124	46000
36:74	55	13000	140	16000



Scheme 1



Scheme 2 (*a*) Attempted method to obtain copolymers of acrylates containing tricyanovinylated NLO chromophores. (*b*) A new approach to incorporate tricyanovinylated NLO chromophres into methacrylate copolymers

The methacrylate **6** was subjected to conventional free-radical (AIBN initiator) copolymerisation with methyl methacrylate in chlorobenzene at 60 °C. Unexpectedly, this polymerisation was very inefficient and yielded low molecular weight poly (methyl methacrylate) **8** (PMMA) as the major (95–100%) component, the minor (0–5%) components being the desired copolymers **9**. Attempts to improve the yields of copolymers **9** using different reaction temp. and higher initiator concentrations were quite unsuccessful. The total reluctance of acrylate **6** in the participation of the copolymerisation process with methyl methacrylate may be attributed to the sensitivity of the tricyanovinyl group to the free-radicals such as 1-cyano-1-methylethyl radicals generated from AIBN. To test this concept, **1a** (Z = tricyanovinyl group) was directly treated with AIBN at 60 °C in chlorobenzene to identify if any reaction occurs between the 1-cyano-1-methylethyl radicals and **1a**. Indeed, these free radicals reacted with compound **1a** and yielded a non-specific product mixture. In another experiment, compound **1b** (Z = H) was not reactive towards the free-radicals generated from AIBN. These experiments conclude that the presence of tricyanovinyl group in the chromophore **6** may be inhibiting the polymerisation and affecting the copolymerisation pathway.

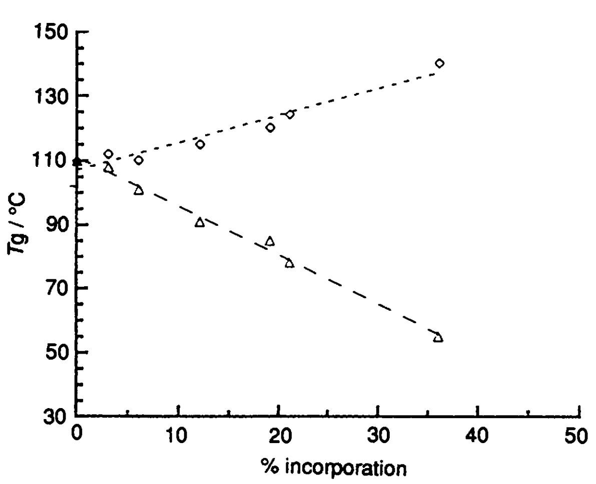


Fig. 1 The relationship between the T_g/°C of polymer **10** (—△—) and **9** (- - ◇ - -) with respect to the percentage incorporation

Since the reluctance of the acrylate **6** to participate in the copolymerisation was due to the tricyanovinyl group, we performed a polymerisation study with the methacrylate **5** (precursor to **6**). We hoped this would allow for the formation of acrylate copolymers of **5** which could be 'post-treated' with tetracyanoethylene to obtain the required methacrylate copolymers of **6**. Methacrylate **5** was copolymerised with methyl methacrylate using AIBN and chlorobenzene. This polymerisation proceeded smoothly and resulted in good quality copolymers (**10**). In order to understand the effect of the number of pendant side chains on the physical properties of the copolymer **10**, the polymerisation was carried out with different initial concentrations of **5** and methyl methacrylate (Table 1), (T_g = glass transition temp., M_n = number average molecular mass). X : Y (percentage of incorporation) was obtained from ^{1}H NMR analysis. Proton integration ratio of N-CH_3 and O-CH_3 was used to determine X : Y. From Table 1, it can be discerned that both M_ns and T_gs of copolymers **10** decrease as the number of side chains increase (X > Y). This decrease in T_g with the increase in incorporation percentage could be attributed to the flexible pendant side chain.

In order to induce second-order NLO activity in the side chains of the copolymers **10**, tricyanovinylation was carried out by dissolving the copolymers **10** in DMF and treating with tetracyanoethylene at 80 °C to yield copolymers **9** in quantitative yield. This tricyanovinylation was monitored by ^{1}H NMR spectroscopy. Comparison of the T_g data obtained with copolymers **8**, **10** and **9** reveals that the presence or absence of tricyanovinyl groups in the pendant side chains has a pronounced effect on the I_g of the copolymers. The T_g's of copolymers **10** decreases with the increasing number of side-chain moieties, while the T_g's of tricyanovinylated copolymer **9** increases with the increasing number of tricyanovinylated side chains. We seek to attribute the increase in T_g with the increase in tricyanovinylated pendant side chains, to the influence of the highly dipolar nature of the NLO chromophore on the molecular motions of the polymer main chains.[†]

Electrooptic studies were carried out with a copolymer of **9** containing 12 mol% (equivalent to 35 wt. %) of NLO chromophore. The electrooptic activity of the parallel plate poled polymer was measured by an experimental setup similar to that described by Teng.[7] We measured the coefficient r_{33} at a wavelength of 1.52 μm using an IR He-Ne laser as the light source. We obtained a r_{33} value of 23 pm V^{-1} by poling at an electric field of 0.5 MV cm^{-1}. The film quality has not been optimised and thus, attempts to pole this polymer at higher electric field has not yet been successful.

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Footnote

[†] Incorporation of **6** into other side-chain polymers such as polyimides also yielded similar enhancement of their T_gs.

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