Polystyrene Based Azo-dyes for Non-linear Optics; a New Polymer-diazo Coupling Approach

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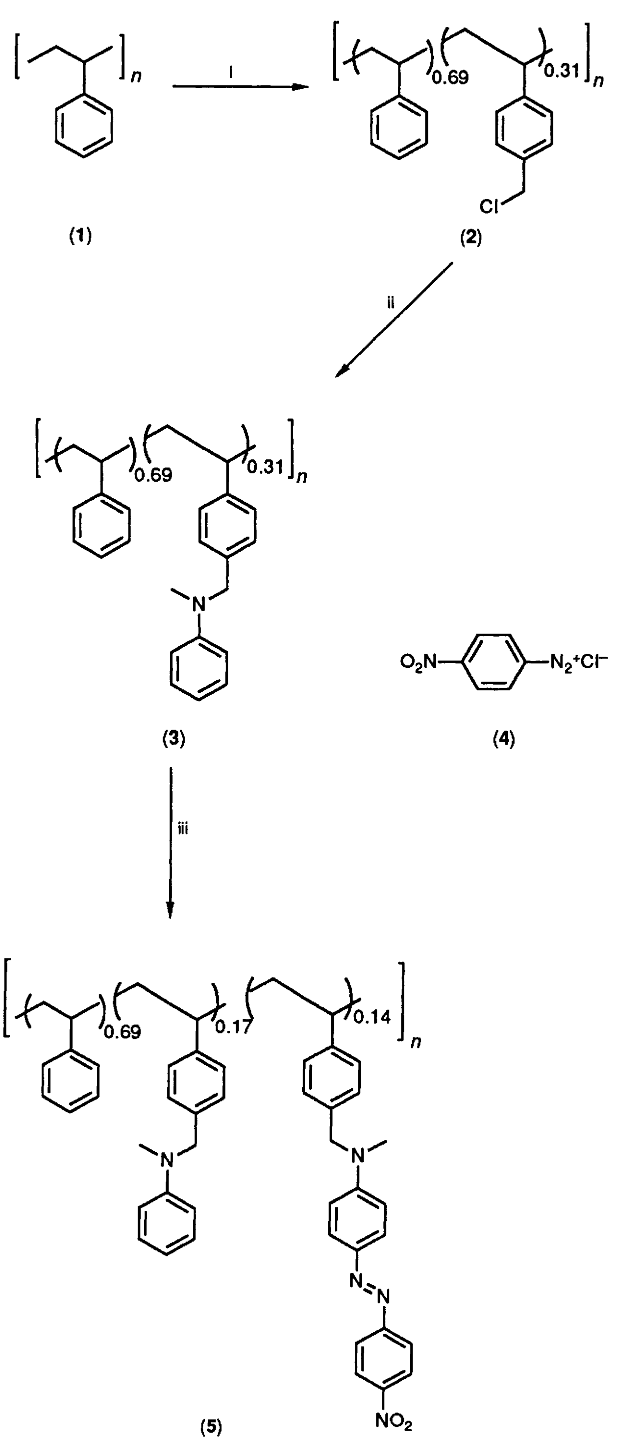
A new direct functionalization of *N*-methylanilino-methylpolystyrene ($\alpha = 0.31$) with *p*-nitrobenzenediazonium chloride yields an azastilbene modified polystyrene with excellent solubility properties.

Donor–acceptor substituted benzenes, stilbenes, and azo-dyes have gained considerable interest in recent years owing to possible applications in second-order harmonic generation *i.e.*, frequency doubling.[1] The growing importance of organic molecules in new optical materials and devices is based on large non-linear second-order susceptibilities and exquisite design of individual molecules.[2] Disadvantages associated with the use of organic materials are often the stability and the need to grow non-centrosymmetric crystals. The second problem can partly be solved using chiral derivatives [*e.g.*, *N*-(4-nitrophenyl)-1-prolinol],[3] Langmuir–Blodgett techniques,[4] or more recently employing centrosymmetric crystals in host matrices.[5] The use of polymeric materials is considered to be more advantageous owing to mechanical strength, their ability to provide thin films, large areas, and often easy polarization.[6] Several studies have been devoted to doped polymers in which molecular orientation is reached with an applied electric field above the glass transition temperature (T_g).[7] Major problems that remain are the phase separation that might occur at higher dye concentrations and the relaxation after removing the electric field used for poling.[8] A more convenient approach is to link potential non-linear optical (NLO) molecules covalently to a polymer backbone.[9] Here we report the facile synthesis of an azo-dye modified polystyrene *via* diazo coupling directly to a polystyrene functionalized with aniline moieties. The reaction sequence is shown in Scheme 1.

Polystyrene (Dow Styron 666, $M_w = 100000$) was chloromethylated by a modified Galeazzi method.[10] The degree of functionalization ($\alpha = 0.31$) was determined by ^{1}H NMR spectroscopy and elemental analysis. The polymer (**2**) was then treated with the sodium salt of *N*-methylaniline[11] in tetrahydrofuran (THF) for 12 h to provide the *N*-methylanilinopolystyrene derivative (**3**) as a white powder (75% yield).[†‡]

The diazo coupling[§] to the aniline moiety of (**3**) was performed by the addition of a ten-fold excess of an aqueous emulsion of 4-nitrobenzenediazonium salt (**4**) (prepared *in situ* from 4-nitroaniline and NaNO$_2$) to the solution of (**3**) in a mixture of THF and acetic acid (4 : 1) using sodium acetate as buffer.[13] Pure dark-red polymer (**5**) was obtained by precipitation in 70–80% yield.[†] The dye content of (**5**) was determined to be 13.8% by means of UV analysis[¶] and confirmed by ^{1}H NMR spectroscopy and C, H, and N analysis. These results indicate that 45% of the *N*-methylanilino-substituents in (**3**) are functionalized during the diazo coupling. Polymer (**5**) shows excellent solubility properties in various solvents *i.e.*,



Scheme 1. *Reagents and conditions*: i, CH$_2$(OMe)$_2$, ZnCl$_2$, SOCl$_2$, ClCH$_2$CH$_2$Cl; ii, PhNHMe, NaH, THF; iii, THF, MeCO$_2$H, MeCO$_2$Na, (**4**).

[†] Purified by repeated precipitation from CHCl$_3$ into MeOH.

[‡] ^{1}H NMR, IR, and elemental analysis showed that all chlorine atoms had been substituted with *N*-methylanilino-groups.

[§] Recently the first (and so far only) azo coupling on a polymer has been reported.[12]

[¶] UV $\lambda_{max.}$ (CHCl$_3$) 476.7 nm ($\varepsilon = 3.15 \times 10^4$ dm^3 mol^{-1} cm^{-1}); [(4′-nitrophenyl)azo]-*N*,*N*-dimethylaniline was used as reference compound.

chloroform, chlorobenzene, and toluene. This allows facile formation of thin films for application in non-linear optics. To demonstrate the advantages of the new route, linking a dye directly to a polystyrene backbone, as well as the properties of the polymer (**5**), we prepared several films of (**5**) by spincoating (on Pyrex) from a 10% chlorobenzene solution of (**5**). Preliminary studies of the polymer films thus obtained showed excellent stabilities and optical (transparency) properties. In conclusion we have demonstrated for the first time the formation of a new polystyrene based azo-dye employing an unprecedented direct diazo coupling on an appropriately modified polystyrene. The high solubility of (**5**) in various solvents should be emphasized considering the solubility problems associated with other approaches. Furthermore modification of the molar fraction of donor–acceptor substituents is easily conceivable *via* control of the extent of chloromethylation or diazo coupling. Studies along these lines are in progress.

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