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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 ¹H NMR spectroscopy and elemental analysis. The polymer (2) was then treated with the sodium salt of *N*-methylaniline¹¹ 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 NaNO₂) 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 ¹H 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, CH₂(OMe)₂, ZnCl₂, SOCl₂, ClCH₂CH₂Cl; ii, PhNHMe, NaH, THF; iii, THF, MeCO₂H, MeCO₂Na, (4).

† Purified by repeated precipitation from CHCl₃ into MeOH.

‡ ¹H 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 λ_{max} . (CHCl₃) 476.7 nm ($\epsilon = 3.15 \times 10^4$ dm³ 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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