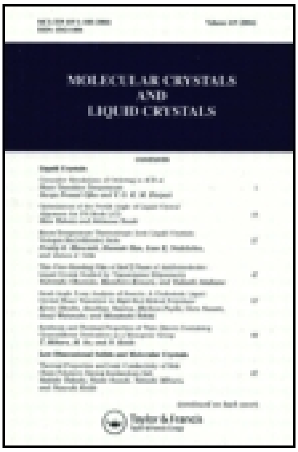

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'Living' Free-Radical Polymerization Process: A New Approach Towards Well-Defined Photochromic (CO) Polymers

Jean-Luc Pozzo [a] , Henri Bouas-Laurent [a] , Alain Deffieux [b] , Daniela Seidler [c] & Heinz Dürr [c]

[a] Laboratoire de Photochimie Organique, URA CNRS 348, Université Bordeaux I, 351.crs de la Libération, F-33405, Talence, FRANCE E-mail:

[b] Laboratoire de Chimie des Polymères Organiques, ENSCPB, BP108, F-33402, Talence, FRANCE

[c] Organische Chemie, Universität des Saarlandes, D-66041, Saarbrücken, 11, Germany

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'LIVING' FREE-RADICAL POLYMERIZATION PROCESS: A NEW APPROACH TOWARDS WELL-DEFINED PHOTOCHROMIC (CO)POLYMERS.

JEAN-LUC POZZO, HENRI BOUAS-LAURENT

Laboratoire de Photochimie Organique, URA CNRS 348, Université Bordeaux I,
351 crs de la Libération, F-33405 Talence, FRANCE, pozzo@cribx1.u-bordeaux.fr

ALAIN DEFFIEUX.

Laboratoire de Chimie des Polymères Organiques, ENSCPB, BP108, F-33402
Talence, FRANCE

AND

DANIELA SEIDLER, HEINZ DÜRR

Organische Chemie, Universität des Saarlandes, D-66041 Saarbrücken 11,
GERMANY

Abstract Different copolymers of styrene and 4-vinylpyridine were prepared using an easy set-up 'living' free-radical polymerization method. After reaction with spiro[cyclopropene-1,9'-fluorenes] on to the pyridine subunits, photochromic coploymers are obtained with controlled weight. Compared to corresponding free dihydroindolizine, a slight bathochromic shift is observed.

INTRODUCTION

Polymers containing photochromic dyes are of great interest, especially those with photoresponsive units chemically incorporated in a macromolecule. [1] The photochromic groups are usually side groups connected to a main chain through a flexible spacer. In such polymers, a very high concentration of a photochrom in a polymer matrix is required for preparing thin films with high optical density of a colored form. In fact, photochromic unit directly linked to macromolecular backbone are quite rare.

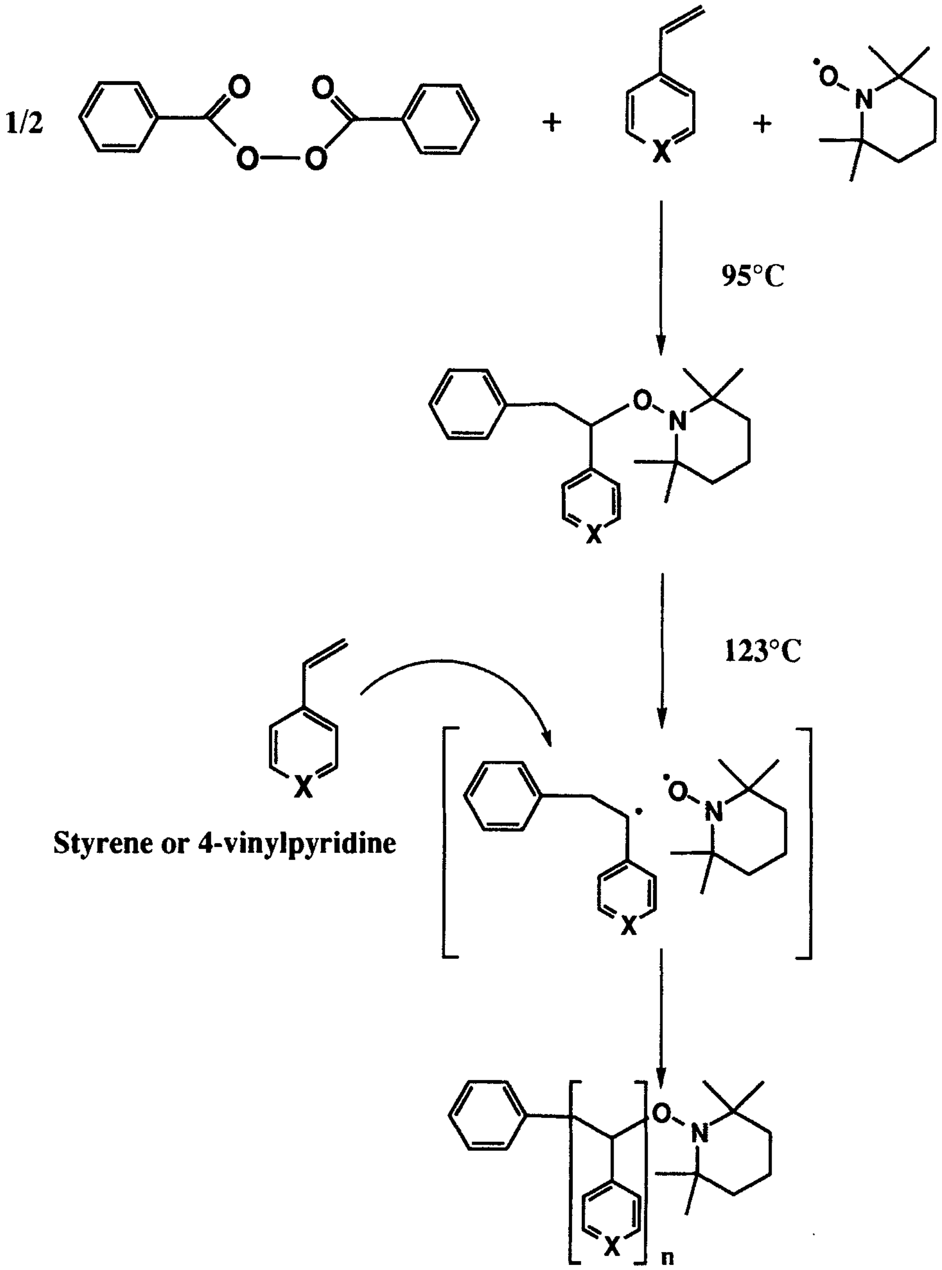
Several photochromes have been included or grafted as a pendant chain or as an optical switch in a variety of polymers. [2]Photochromic properties of dihydroindolizines (DHI) and related compounds, which are an important class among organic photochromes, are well documented. [3] We describe our first attempts to get such photochromic (co)polymers with controlled molecular weights and low polydispersities under mild conditions.

SYNTHESIS

Accurate control of polymerization processes to give well-defined macromolecules is becoming an increasingly important aspect of polymer chemistry. [4]Typically, this could be accomplished using either anionic [5], cationic [6] or ring-opening polymerization techniques. [7]While these procedures are undoubtely sucessful, they do suffer from tedious synthetic requirements and incompatibility with a variety of functional groups.

Free-radical polymerizations are synthetically less rigorous. However, the major drawback of free-radical processes is that they lead to polydisperse products without accurate control over the molecular weight and more importantly the number of chain ends. The latter is due to the competing combination and dispropornation termination steps and in the inefficiency of the initiation step which leads to functionalities less than or greater than theorically expected. Recently, it has been reported that the use of TEMPO (2,2,6,6-tetramethylpiperidinyl-1-oxy) based initiators results in a 'living' process. Especially, the system coupling TEMPO and a radical initiator as the well-known BPO (Benzoyl peroxide) appears to be a very efficient for polymerization of polystyrene. However, the examples cited therein do not ensure the generality of this route, especially concerning 4-vinylpyridine monomer.

We adapted this procedure by varying the monomer/ initiator ratio, so it allows us to prepare different copolymer having polydispersities near 1.5. All starting compounds are mixed and heated without any solvent at *ca* 95°c for 1h in order to lead to the intermediate key after thermal decomposition of the peroxideas depicted in scheme 1 The reaction mixture is then heated for ten additionnal hours.



SCHEME 1: Representation of 'living' free-radical polymerization process

The mixtures of desired polymers were purified by several precipitations in THF, dried under vacuum and were then characterized by electronic spectroscopy and ^1H, NMR. Corresponding yields are listed in table 1.

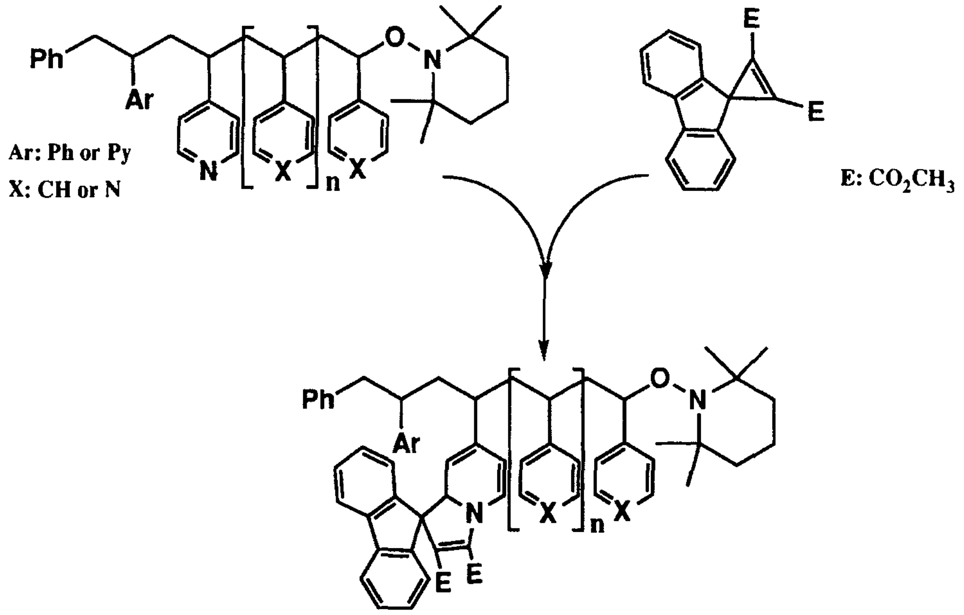
TABLE 1 Reaction conditions and characteristics for polymers.

X= CH/N	Monomer/Initiator Ratio	Yield (%)	Conv (%)	P.D.	Mn	Copolymer Ratio
0/100	288	20	-	-	7500	-
60/40	288	37	13	1.42	3800	55/45
70/30	284	48	43	1.45	13000	66/34
60/40	577	50	8	1.70	4000	52/48
70/30	569	57	32	1.63	19000	66/34

Table 1 clearly shows that chemical yield is directly dependent on structures of starting vinylic compounds. It is estimated that efficiency for polymerization is strictly reliable to viscosity of the reaction mixture. The values of Mn determined by size-exclusion chromatography are in excellent agreement with the theoretical ones and demonstrates the feasibility of this approach. This interesting method will be tested for larger polymer.

In situ synthesis of photochromic polymer

The aforementionned (co)polymers and adequately substituted spiro[fluorene-cyclopropene] were stirred for several days in the dark. Cooling of deep-green solution with ice-water gave a powder which is further washed with petroleum ether. The grafting rate of pyridine subunits could be controlled by time reaction and amount of cyclopropene derivatives. Several cycles of this reaction is required to high concentration of photochromic dyes for keeping the advantages of the polymerization techniques, namely controlled molecular weights and low polydispersities. The amount of dihydroindolizine moities is determined by ^{1}H NMR.



SCHEME 2: Representation of synthetic pathway for photochromic (co)polymers.

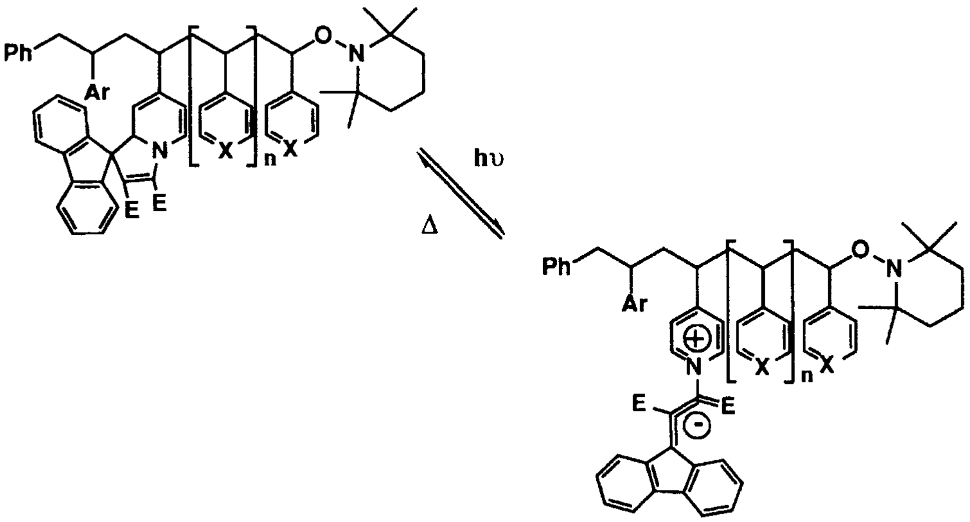
PHOTOCHROMIC PROPERTIES

Upon activation by ultra-violet light or by sunlight, Dihydroindolizines are known to undergo a reversible 1,5-electrocyclization. The resulting chromophoric species or betaines are responsible for the photo-generated colors.

TABLE 2 Reaction conditions and characteristics for polymers.

Sample	P.D.	Styrene/4-vinylpyridine ratio	Solvent	λ_{max} CF (nm)	λ_{max} OF (nm)	Mn	$t_{1/2}$ (s)
free DHI			CH_2Cl_2	384	586		14.2
	1.60	55/45	CH_2Cl_2	392	604	10000	119
	1.86	66/34	CH_2Cl_2	391	599	24000	165
			THF	388	600		93

The spectra of the betaines in matrice/solvent host were determined using flash photolysis. All the described grafted polymers exhibit photochromic behavior at room temperature in dichloromethane solution. The given spectral data of the synthezised polymers along with those of related free dihydroindolizine, clearly indicate that photochromic behavior is poorly dependent on macromolecular backone. No solvatochromic and a slight bathochromic effects are observed. Furthermore, the shape of the absorption spectra is weakly modified. On the other hand, those polymers show significative variations of stabilization of colored forms which are ten-time increased.



SCHEME 3: Photochromic equilibrium of copolymers containing dihydroindolizine subunits.

CONCLUSION

Polyvinylpyridines and copolymers of styrene and 4-vinylpyridine of controlled molecular weight and low polydispersity can be prepared by a TEMPO based initiator The 'living' free-radical methodology involves an easy setup. The photochromic (co)polymers were then obtained by reaction with adequately substituted spiro[cyclopropene-1,9'-fluorenes] on to the pyridine subunits leading to dihydroindolizine moities. This approach opens new prospects for the preparation of well-defined photoresponsive devices.

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