

## THERMALLY AND PHOTOCHEMICALLY ACTIVE POLYMERS BY CLICK CHEMISTRY

Burcin Gacal<sup>1</sup>, Hakan Akat, Baris Kiskan<sup>1</sup>, Mihrace Ergin<sup>1</sup>, Demet Balta<sup>2</sup>, Nergis Arsu<sup>2</sup> and Yusuf Yagci<sup>1</sup>

<sup>1</sup>Istanbul Technical University, Department of Chemistry, Maslak, Istanbul 34469, Turkey

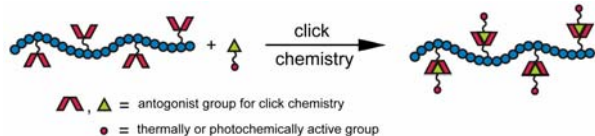
<sup>2</sup>Yildiz Technical University, Department of Chemistry, Davutpasa Campus, Istanbul 34210, Turkey

### Introduction

Recently, 1,3-dipolar cycloadditions, from the reactions between azides and alkynes or nitriles, known as “click reaction”<sup>1,2</sup> have been recognized as a useful synthetic methodology and applied to macromolecular chemistry offering materials ranging from the block copolymers to the complex macromolecular structures<sup>3-5</sup>. These cycloaddition reactions enabled the C-C bond formation in a quantitative yield without side reactions and requirement for additional purification steps. The click reactions are particularly important in preparative methods, in which high conversion of functional groups is desirable. Numerous applications of Click chemistry in polymer science as well as molecular biology and nanoelectronics have recently been reviewed<sup>6-7</sup>. Two other click reactions based on Diels-Alder<sup>8</sup> and thiol-ene reactions<sup>9</sup> were also reported.

Polymers possessing side-chain thermally and photochemically active groups capable of inducing crosslinking reactions receive continuous interest due to their application in the preparation of thermoset polymers. Among various photoactive groups, thioxanthone and derivatives of particular interest because of their excellent optical absorption properties in the near-UV spectral region and capability of producing initiating radicals and consequently forming insoluble networks in the presence of multifunctional monomers. Benzoxazines<sup>10</sup> are a new class of thermally active phenolic resin precursors which undergo ring-opening reaction without any catalyst. The aim of this paper is to prepare new kind of thioxanthone and benzoxazine functional polymers that have potentiality in initiating light induced radical polymerization and thermally activated ring-opening crosslinking reactions, respectively.

The synthetic strategy followed in this study is depicted in Scheme 1



Scheme 1

### Experimental

**Materials.** Detailed description of purification and preparation of the compounds used in this study were reported elsewhere<sup>11-12</sup>.

**Instrumentation** <sup>1</sup>H-NMR spectra were recorded on a Bruker 250 MHz spectrometer with CDCl<sub>3</sub> as the solvent and tetramethylsilane as the internal standard. IR spectra were recorded on a Jasco FT/IR-3 spectrometer. UV-vis spectra were recorded on a Perkin-Elmer Lambda 2 spectrophotometer. Fluorescence spectra were recorded on a F-4500 Fluorescence spectrophotometer. Gel permeation chromatography (g.p.c) analyses were performed with a set up consisting of an Agilent 1100 RI apparatus equipped with three Waters ultrastayragel columns (HR series 4, 3, 2 narrow bore), with THF as the eluent at a flow rate of 0.3 mL/min and a refractive index detector. Molecular weights were calculated with the aid of polystyrene standards.

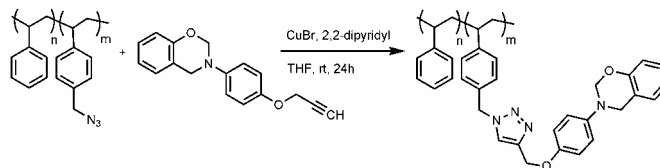
### Results and Discussion

#### Benzoxazine Functional Polymers.

Novel side-chain benzoxazine functional polystyrene was synthesized<sup>11</sup> by using “Click Chemistry” strategy based on 1, 3-dipolar cycloaddition reactions between azides and alkynes. First, a random copolymer of styrene (S) and chloromethyl styrene (CMS) with 39.8 mol% CMS content was

prepared by Nitroxide Mediated Radical Polymerization (NMP) process. Then, the chloromethyl groups were converted to azido groups by using NaN<sub>3</sub> in DMF. Propargyl benzoxazine was prepared independently by a ring closure reaction between *p*-propargyloxy aniline, paraformaldehyde and phenol. Finally, azidofunctionalized polystyrene was coupled to propargyl benzoxazine with high efficiency by click chemistry. The spectral and thermal analysis confirmed the presence of benzoxazine functionality in the resulting polymer. The overall process is presented in Scheme 2.

It is shown that polystyrene containing benzoxazine undergoes thermal



Scheme 2

curing in the absence of any catalyst forming polystyrene thermoset with high thermal stability. The TGA profiles presented in Figure 1 indicate that the temperature for 10% weight loss temperature is (*T*<sub>10</sub>) is 358 °C which much higher than that of the initial polymer. Moreover, the char yield of the thermally cured polystyrene was 36.5%.

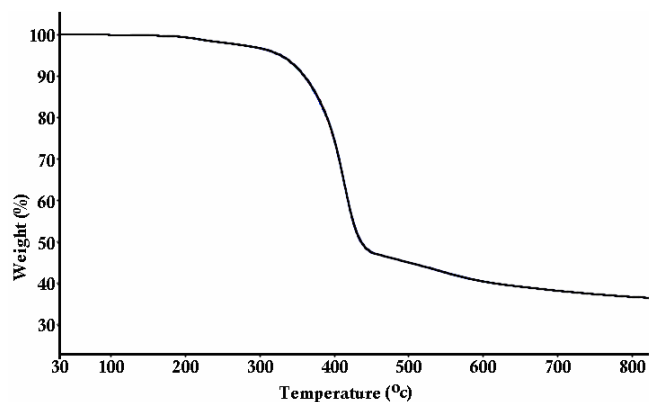
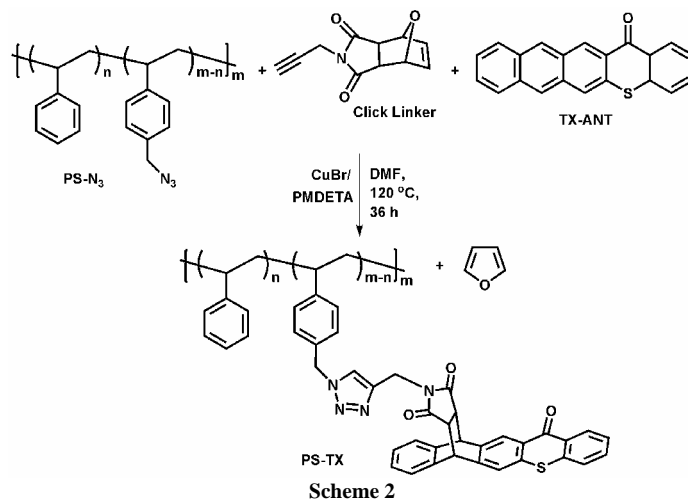


Figure 1. TGA thermogram of thermally cured polystyrene



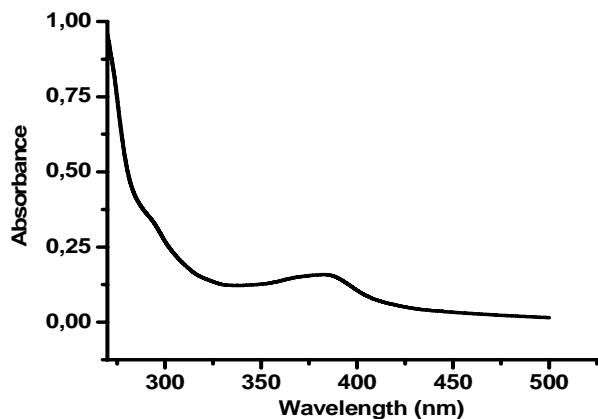
Scheme 2

#### Thioxanthone Functional Polymers

Macrophotoinitiators containing thioxanthone (TX) moieties as side chains were synthesized<sup>12</sup> by using “double click chemistry” strategy; combining *in situ* 1,3-dipolar azide-alkyne [3+2] and thermoreversible Diels-Alder (DA) [4+2] cycloaddition reactions. For this purpose, thioxanthone-

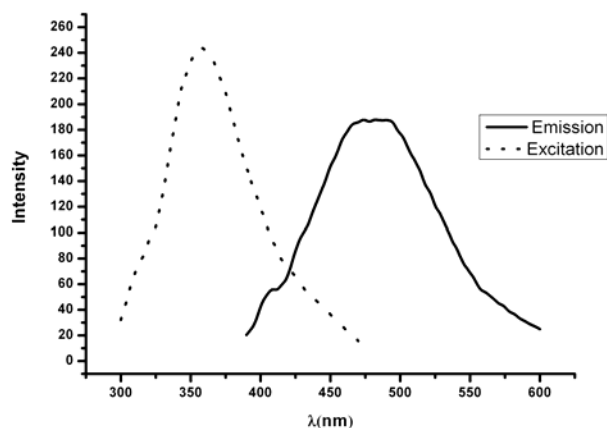
anthracene (TX-A), *N*-propargyl-7-oxynorbornene and polystyrene (PS) with side chain azide moieties were reacted in *N,N*-dimethylformamide (DMF) for 36 h at 120 °C. In this process, *N*-propargyl-7-oxynorbornene acted as a “click linker” since it contains both protected-maleimide and alkyne functional groups suitable for 1,3-dipolar azide-alkyne and Diel-Alder click reactions respectively (Scheme 2). This way, the aromaticity of the central phenyl unit of the anthracene moiety present in TX-A was transformed into TX chromophoric groups.

The resulting polymers possess absorption characteristics similar to the parent TX with absorption maximum at 390 nm (Figure 2). The fluorescence spectrum of PS-TX shows that a nearly mirror-image-like relation exists between excitation and emission again indicating the successful incorporation of thioxanthone moieties (Figure 3).



**Figure 2.** Uv-vis absorption spectrum of polystyrene-thioxanthone (PSt-Tx) obtained by double click chemistry

Their capability to act as photoinitiator for the polymerization of methyl methacrylate (MMA) and styrene (S) was also examined. It was shown that polymeric thioxanthenes readily initiates the polymerization in the presence of hydrogen donors in a manner similar to low molar mass analogous.



**Figure 3:** Excitation-Emission fluorescence spectra of polystyrene-thioxanthone (PSt-Tx) obtained by double click chemistry

In conclusion, simple click reaction route to side-chain thioxanthone and benzoxazine functional polymers is described. This route has the unique feature of being quantitative and at the same time preserving the functional groups.

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