

# Functionalization and chemical modification of cyclo olefin copolymers (COC)

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Received 26 June 1999; received in revised form 1 September 1999; accepted 4 November 1999

## Abstract

In this paper, we report two simple and effective bromination methods to brominate the cyclo olefin copolymer (COC). A suitable metallic catalyst can accomplish functionalization and chromophorization of the brominated COC. A 2nd NLO dye, Disperse Orange 3 (DO3) containing the  $-NH_2$  functional group, has been grafted onto either the norbornene unit or the PE segment of the COC backbone successfully, by the palladium catalyst,  $Pd_2(dba)_2$  (Bis[dibenzylideneacetone] dipalladium). The observed low dye grafting content can be attributed to the higher hindrance of the norbornene ring.

Based on UV results, the NLO-COC, having dye grafted onto the norbornene unit shows more red shift than that grafted onto the PE unit, probably due to greater shielding on the chromophor. © 2000 Elsevier Science Ltd. All rights reserved.

**Keywords:** Cyclo olefin copolymer (COC); Bromination; 2nd nonlinear optical polymer

## 1. Introduction

Nonlinear optical polymers (NLO polymers) have several advantages over inorganic materials in terms of lower price and better processibility. [1,2] However, NLO polymers also have some disadvantages such as fast dipole decay due to Brownian motion of the amorphous nature, low production yield and difficulty in obtaining the product with high purity. There have been several attempts to chemically bond the NLO group to rigid polymers such as polyimide, IPN polymer or polycarbonate [3–5]. The cyclo olefin copolymer (COC) is amorphous and possesses high  $T_g$  (max. 220°C) [6–10]. The cyclo olefin monomer can undergo addition polymerization by a suitable metallocene catalyst. In addition, the COC also possesses high transparency, high  $T_g$ , low moisture absorption, and a low dielectric constant. It is expected that the 2nd NLO dye grafted COC with the aligned NLO group tends to decay more slowly because of the highly rigid COC structure.

The chemical modification of brominated polyolefins and polystyrene catalyzed by metallic palladium catalysts has been reported. [11–15] In this study we followed a similar

approach in synthesizing NLO-COC by using the same palladium catalyst.

## 2. Experimental

Bromine (reaction grade) was used as received.  $AlCl_3$  and AIBN were used as received and stored under nitrogen atmosphere.

The COC was prepared by following reported literature through metallocene catalyzed polymerization. [6–10] The COC bromination reaction was carried out by *radical bromination* and *cation bromination* by using AIBN/bromine and  $AlCl_3$ /bromine, respectively, as bromination agents.

AIBN was employed in preparing the brominated COC by the free radical reaction at 70°C in chloral free organic solvent under nitrogen atmosphere.

$AlCl_3$ , a Lewis acid catalyst, was employed in preparing the brominated COC by the Friedel–Crafts bromination reaction at room temperature in the nonaromatic solvent under nitrogen atmosphere.

### 2.1. Bromination reaction

A selective bromination of the COC procedure was carried out by the following method. Pre-synthesized COC (0.503 g) was first dissolved or suspended in 50 ml of

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Table 1  
Results of functionalization and NLO grafting

Sample	Yield (%)	Reaction condition	$T_m$ (°C)	$T_g$ (°C)
COC	10	Et(ind.) <sub>2</sub> ZrCl <sub>2</sub> /MAO/toluene	–	81.5
Brcoc-2	90.5	COC/C <sub>7</sub> H <sub>8</sub> /AIBN/70°C	–	135.1
Brcoc-3	92.05	COC/CHCl <sub>3</sub> /AlCl <sub>3</sub>	–	147.1
Brcoc-6	60.1	COC/C <sub>6</sub> H <sub>12</sub> /AlCl <sub>3</sub>	–	137.8
NLOcoc-3	30	Brcoc-2/ DO3/ TEA/CHCl <sub>3</sub>	–	115
NLOcoc-19	31	Brcoc-6/DO3/ (dba) <sub>2</sub> Pd <sub>2</sub> /CHCl <sub>3</sub>	–	118

organic solvent and the free radical initiator AIBN (0.123 g) or cation catalyst AlCl<sub>3</sub> (0.15 g), respectively, was added. The excess amount of liquid bromine (purity >99%), 0.1 g, was added into the solution to proceed the reaction for 30 min at room temperature or higher temperature (50–70°C). The brominated COC product was recovered by precipitating, using the excess methanol nonsolvent. The yield of the brominated COC was determined from a result of the recovery amount divided by the original feeding COC weight.<sup>1</sup> The yield of the radically brominated COC was between 60–92% and the results have been summarized in Table 1. These brominated COCs are also amorphous and have a higher  $T_g$  (>130°C), than the corresponding COCs, because the Br substituent on the polymer main chain tends to increase the chain rigidity of the polymer.

## 2.2. Grafting reaction

Grafting of the nonlinear optical dye onto the COC copolymer was carried out by the following methods. The commercially available metallic palladium catalyst, (dba)<sub>2</sub>Pd (Bis[dibenzylideneacetone] palladium), was re-crystallized from warm chloroform solution to yield dark brown crystals of (dba)<sub>3</sub>Pd<sub>2</sub> (Bis[dibenzylideneacetone] dipalladium) (yield >90%). [14,15] The nonlinear optical dye, Disperse Orange 3 (DO3), 310 mg, and the brominated COC (67.5 mg) were dissolved in the chloroform solvent firstly, under an ice bath. Then the 20 mg (dba)<sub>3</sub>Pd<sub>2</sub> in 5 ml chloroform solution for COC with a brominated norbornene unit (Brcoc-6), or the 3 ml triethylamine (TEA) in 20 ml chloroform solution for COC with a brominated PE unit (Brcoc-2), was added slowly over 0.5 h and the reaction proceeded for an additional 8 h at room temperature.

Adding an excessive amount of ethanol nonsolvent into

<sup>1</sup> Degree of functionalization from each polymer chain cannot be obtained, so the bromination percentage is an average value. The product we obtained is mostly the brominated COC because the brominated and the un-brominated COC fractions have difference solubility and we can separate them by re-dissolving in chloroform and re-precipitating in methanol. If the molecular weight of the virgin copolymer is known, we can calculate the bromination percentage by combining with the <sup>1</sup>H NMR data. High temperature GPC is required for measuring the molecular weight of the polymer under 140°C and using chlorobenzene as the eluent solvent. Unfortunately, we did not have the high temperature GPC to conduct the experiment.

the polymer solution, then re-dissolved in pure chloroform and re-precipitated again before additional drying for 8 h at 50°C in vacuum is a procedure for all products' purification and recovery procedures.

## 2.3. Analytical techniques

Product characterizations were conducted on DSC, TGA, NMR and UV–VIS spectrometers. Differential-scanning calorimetry (DSC) and thermo-gravimetric analysis (TGA) were carried out with a Perkin–Elmer analyzer (TGA7) and calorimetry (DSC-7) that calibrated with indium and zinc. Samples of ca. 10 mg were scanned at a heating rate of 10°C/min.  $T_g$  was referred to as the temperature at the maxim transition of the heat flow curve. The <sup>1</sup>H NMR spectra (Bruker RDX-200 liquid NMR) were measured in 10–15% (w/v) CDCl<sub>3</sub> (from Acros) solution at room temperature with tetramethylsilane (TMS) as an inner standard. The scan frequency, spectral width, pulse width and relaxation delays were 200 MHz, 3500 Hz, 3 μs and 4.0 s, respectively. The UV–VIS spectra (Varian Cary-5E UV–VIS–NIR spectrophotometer) were measured in the CDCl<sub>3</sub> solution. The scan range and scan rate were 200–1500 nm and 2 nm/s, respectively.

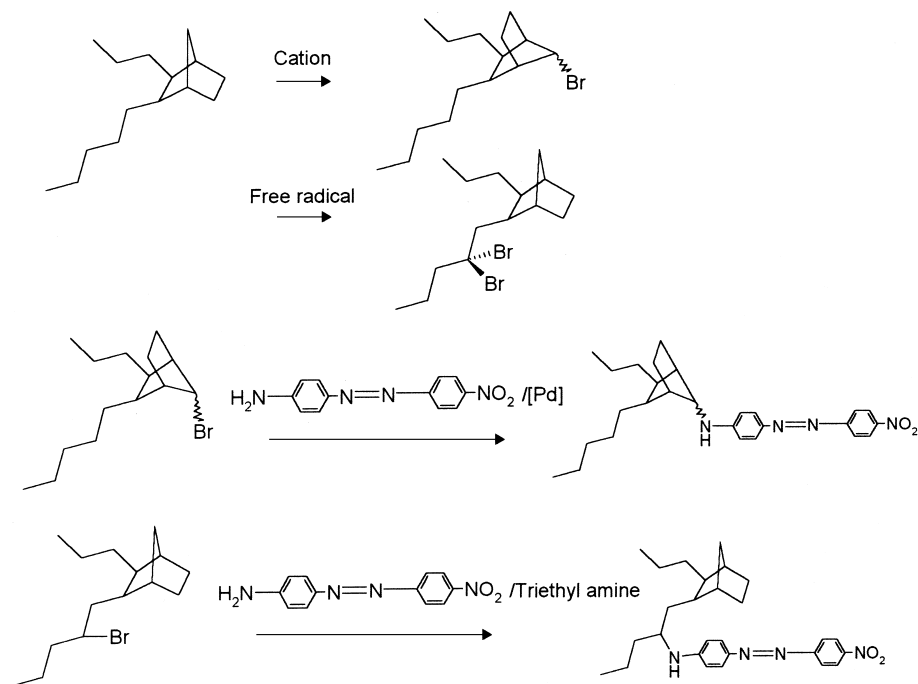
## 3. Results and discussion

A simple method has currently been developed to brominate and graft the NLO group selectively onto either the PE segment or the norbornene unit of the COC copolymers (shown in Scheme 1).

### 3.1. <sup>1</sup>H NMR and FTIR analyses

Bromination either on the norbornene ring or the polyethylene segment in the COC can be controlled by adjusting reaction conditions. <sup>1</sup>H NMR and FTIR have been used to analyze the molecular structure of these brominated COCs. Brcoc-2 is the COC where the polyethylene segment is brominated dominantly, while in Brcoc-6 the norbornene ring segment is brominated dominantly as shown in Table 1. Detailed experimental data will be discussed in the following section.

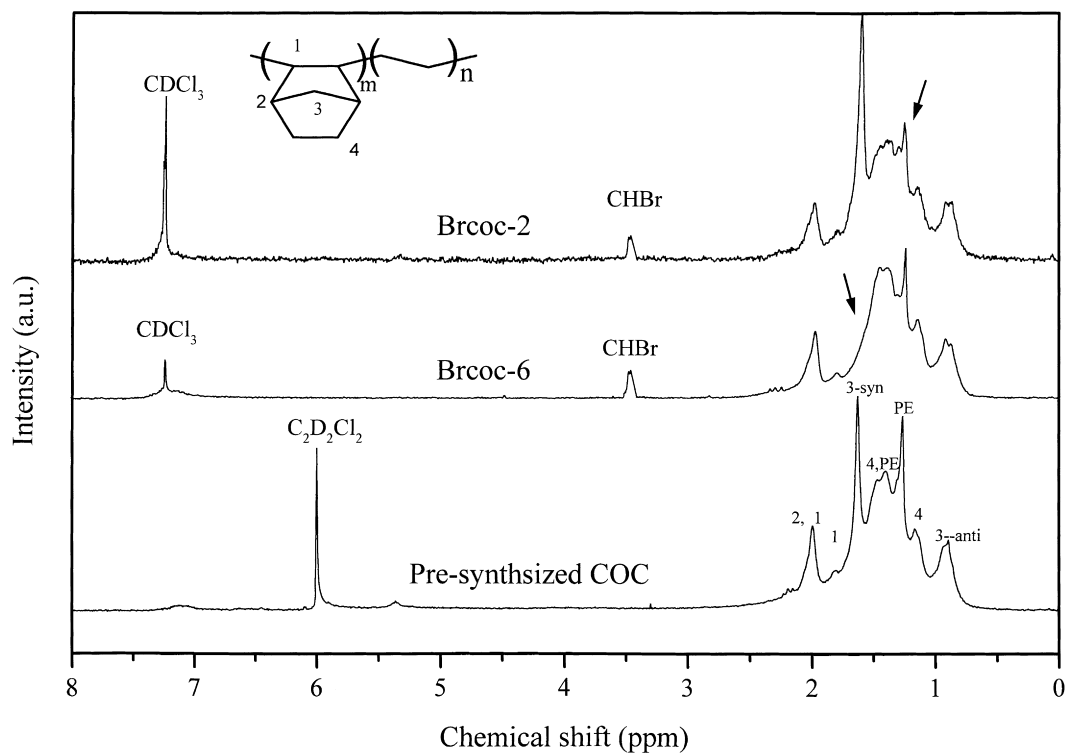
The <sup>1</sup>H NMR spectrum of the brominated COC has a characteristic peak at the chemical shift of 3.46–3.73 ppm



Scheme 1.

as shown in Fig. 1. The peaks corresponding to the polyethylene–polynorbornene copolymer [16] have been labeled on the bottom curve in Fig. 1. The disappearance of some  $^1\text{H}$  NMR absorption peaks on the virginal pre-synthesized COC

$^1\text{H}$  NMR spectrum is used to identify the specific bromination position. In addition, the brominated COCs characterized by the IR spectra have absorption peaks at 261, 800.5 and 667.5  $\text{cm}^{-1}$  corresponding to the C–Br

Fig. 1.  $^1\text{H}$  NMR spectrum of the pre-synthesized COC, Brcoc-2 and Brcoc-6.

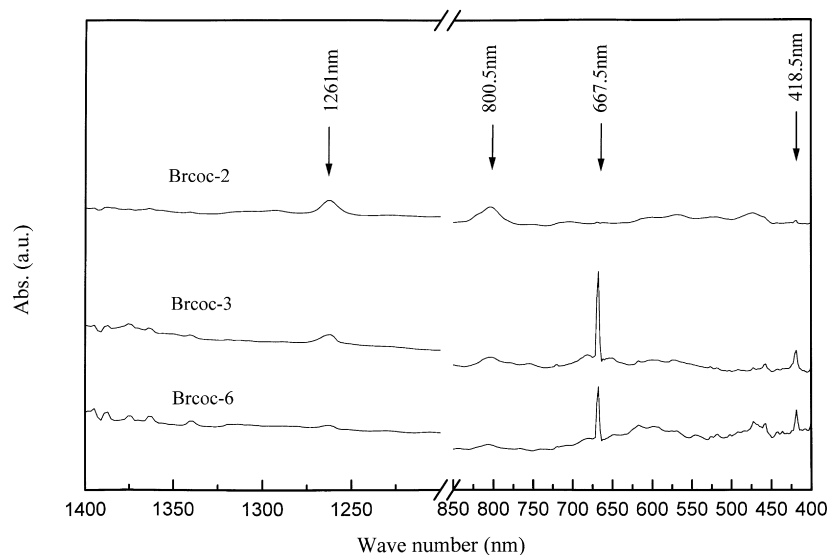


Fig. 2.  $^1\text{H}$  NMR spectrum of Brcoc-2, Brcoc-3 and Brcoc-6.

vibration as shown in Fig. 2. The IR spectra also show large difference between Brcoc-2 and Brcoc-6.

The well-known radical reaction of alkyl bromide with a molecular bromine generally produces a mixture of di-bromide, in which there is vicinal di-bromide predominance (Brcoc-2). The mechanism of the COC cation bromination involves the coordination of the  $\text{AlCl}_3$  onto the norbornene to form the nonclassical cation [17]. The

bromine then undergoes the nucleophilic attachment to the reaction center (Friedel–Crafts reaction) and brominates the norbornene ring (Brcoc-6). Table 1 summarizes the  $T_g$ s of these brominated COC products, as a result of which, essentially all functionalized and the un-functionalized COC are amorphous and without any melting points.

The  $(\text{dba})_3\text{Pd}_2$  chloroform solution was used in grafting the nonlinear optical dye, Disperse Orange 3 (DO3), onto

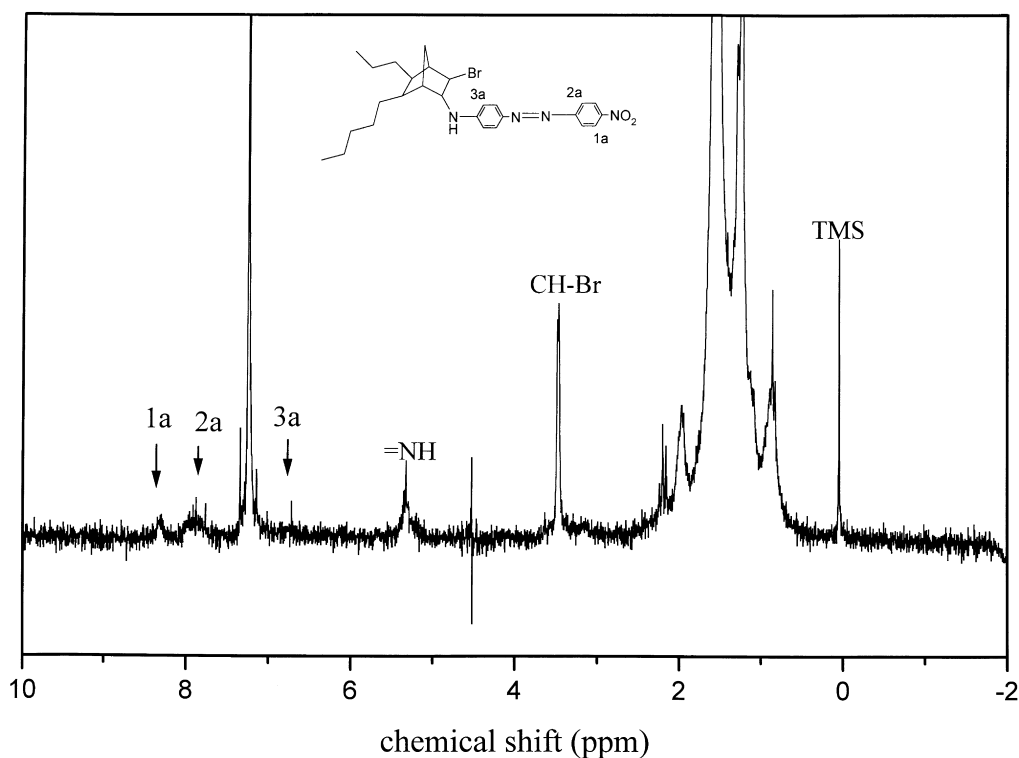


Fig. 3.  $^1\text{H}$  NMR spectrum of NLOcoc-19.

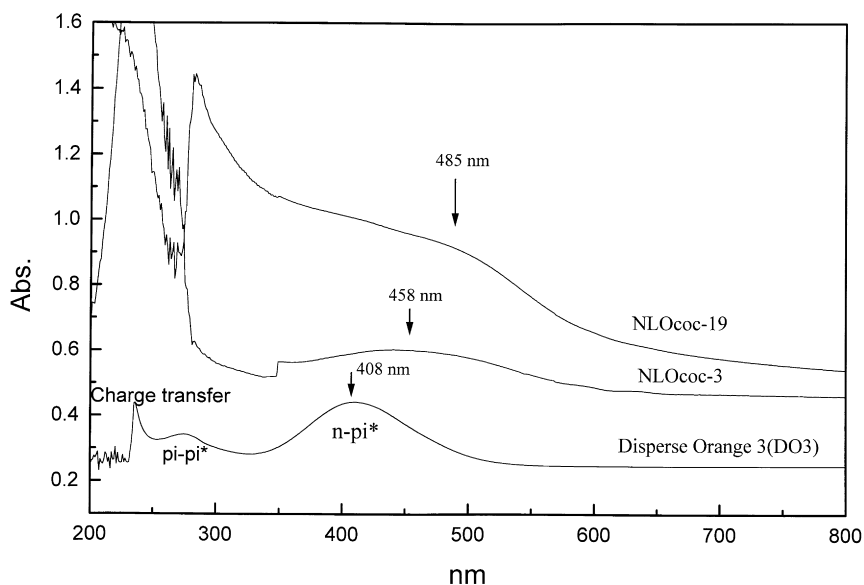


Fig. 4. UV absorption of NLOcoc-3, NLOcoc-19 and pure DO3 dye.

the COC with the brominated norbornene unit (Brcoc-6) and produced the NLOcoc-3 product. On the contrary, the TEA chloroform solution was employed to graft the nonlinear optical dye, Disperse Orange 3 (DO3), on the COC with the brominated PE unit (Brcoc-2) and produced the NLOcoc-19 product. After grafting Brcoc-6 with the DO3 dye (Table 1, NLOcoc-19), the aromatic ring's characteristic peaks of the azo dye with chemical shifts 6.71 ppm (3a), 7.75–7.91 ppm (2a) and 8.31 ppm (1a) that can be, are shown in Fig. 3. The calculation of the  $^1\text{H}$  NMR integral value reveals that about 4.7 mol% of the norbornene rings are grafted with NLO group (indirectly calculated by assuming the polymer molecular weight to be about 10 K).<sup>1</sup> The apparent difference exists in the  $^1\text{H}$  NMR

spectra between 0.6–2.0 ppm for Brcoc-6 and Nlococ-19 but we are still unable to explain this observation. We further feel that bromination on the norbornene unit may occur during the grafting reaction.

### 3.2. UV absorption spectra of NLOCOCs

Fig. 4 shows the UV absorption spectra of NLOCOCs in the D-chloroform solution. For NLOcoc-3, the NLO dye is grafted on the PE segment due to the brominated position, only on the PE segment, while NLOcoc-19, the NLO dye is grafted on the norbornene ring (see the discussion in Section 3.1). By comparing the  $n-\pi^*$  transitions of pure DO3, NLOcoc-3 and NLOcoc-19, that are 408, 458 and 485  $\text{nm}^{-1}$ ,

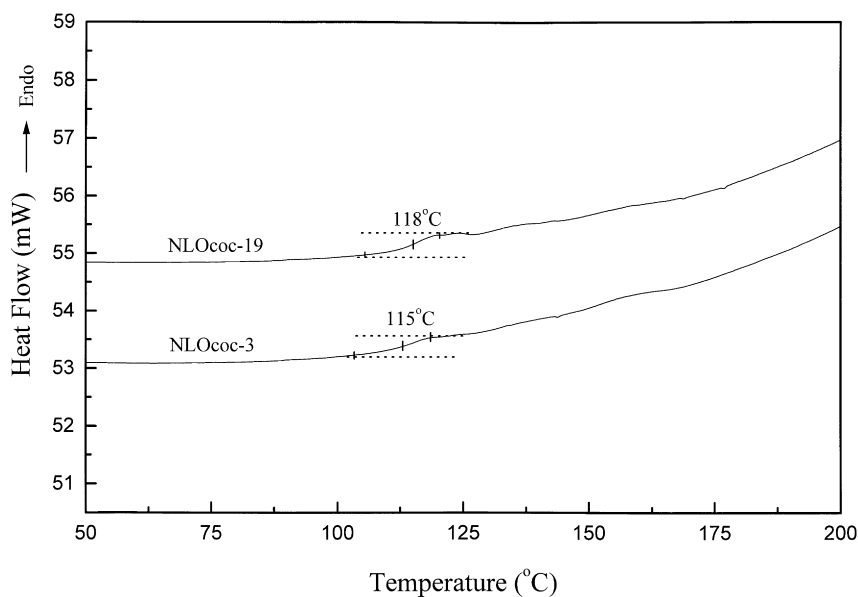


Fig. 5. DSC scans of NLOcoc-3 and NLOcoc-19.

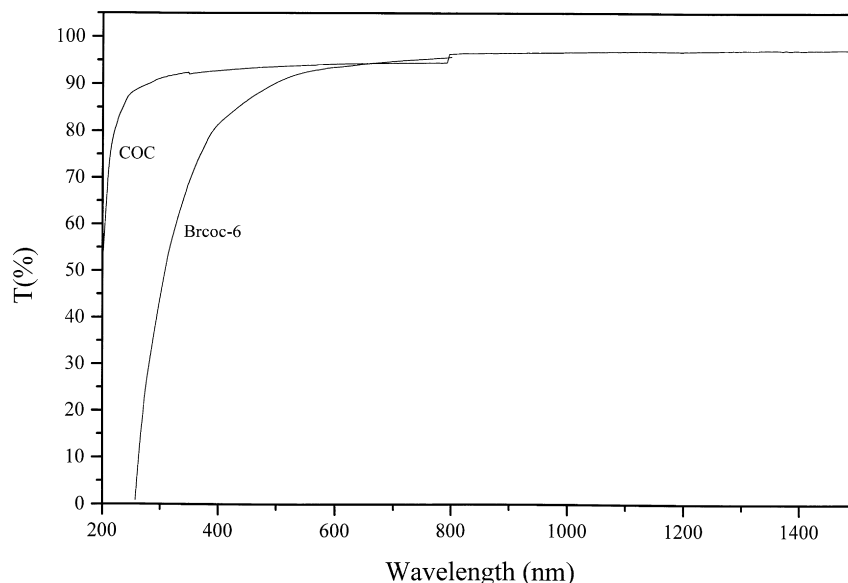


Fig. 6. UV-VIS absorption spectra of the pre-synthesized COC and Brcoc-6 thin film.

respectively, a red shift is observed. This is a common phenomenon, which occurs for NLO dye grafted polymers [1–5]. After grafting on the polymer, the original wavelength of the dye's  $n-\pi^*$  transition will shift to a lower energy. The NLO dye grafting on PE segment results in a less red shift than that grafting on norbornene. This may be due to the bulky norbornene unit with greater shielding effect.

NLO polymers with high  $T_g$  ( $>200^\circ\text{C}$ ) have a slower decay rate for the aligned dye's dipole moment. However they are difficult to poling because the thermal decomposition may occur at the poling temperature ( $>T_g + 50^\circ\text{C}$ ). Usually, the NLO polymers with  $T_g$  between  $80-130^\circ\text{C}$  are easier for the conduction of corona poling or contact poling [1–5].

### 3.3. Thermal and optical properties of the pre-synthesized COC

In this paper, we have synthesized NLO-COC successfully. DSC traces show that show these NLO-COC copolymers possess a suitable  $T_g$  (Fig. 5) for NLO polymer applications. The pre-synthesized COC has excellent thermal and optical properties, in terms of high  $T_g$ , high transparency ( $>95\%$ ) (Fig. 6), high thermal degradation temperature ( $T_d > 450^\circ\text{C}$ ) (Fig. 5) and high viscosity above  $T_g$ . [10].

Fig. 6 shows the UV absorption spectra of the brominated COC (Brcoc-6) and pre-synthesized COC thin films. In the

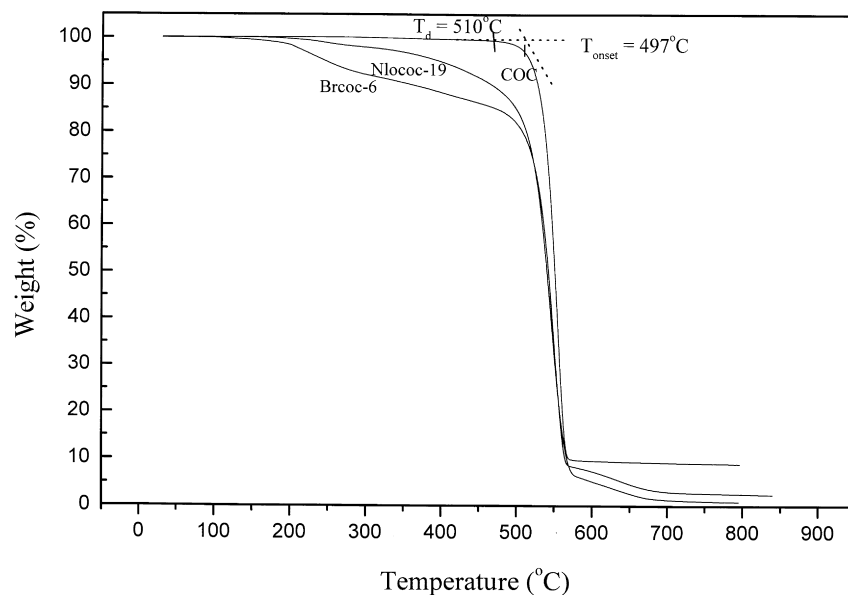


Fig. 7. TGA curves of the pre-synthesized COC, Brcoc-6 and NLOcoc-19.

range of 380–800 nm, the pre-synthesized COC thin film does not show any absorption, while the brominated COC (Brcoc-6) shows strong absorption above 500 nm, which is because of the photo-degradation of C–Br bonding.

The comparison of the thermal properties of pre-synthesized COC, brominated COC and NLOCOC is given in Fig. 7. The brominated COC (Brcoc-6) shows a two step degradation transition. The first step should correspond to the C–Br degradation reaction and the second transition is due to the COC chain degradation. NLOCOC (NLOcoc-19) also shows good heat resistance ( $T_d$  ca. 200°C).

#### 4. Conclusions

We have demonstrated that a simple method has been developed to brominate and graft the NLO group selectively, on either the PE segment, or the norbornene unit of the COC copolymers. This new chemical modification methodology has the potential to manufacture novel NLOCOC polymers of high quality. In addition, this brominated COC is able to convert the –Br group to –OH, –CO<sub>2</sub>H or –OR (R: alkyl, alkene group) by changing the nucleophile agent and offers a simple and economic way to synthesize numerous functionalized COCs. This may expand future applications of COC materials in the areas of electro-optical, medical and optical fibers.

#### Acknowledgements

Financial support for this research was provided by the National Science Council of the Republic of China under contract number NSC88-2216-E-009-007.

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