NOTES

Ring-Opening Metathesis Polymerization of Coumarin-Containing Norbornene

Mikhail A. TLENKOPATCHEV, Serguei FOMINE,[†] Lioudmila FOMINA,
Ruben GAVIÑO, and Takeshi OGAWA

*Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México,
Circuito Exterior, Ciudad Universitaria,
Apartado. Postal 70–360, Coyoacán, México DF 04510, México*

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Coumarin-containing polymers have attracted much attention due to their fluorescent properties and physiological activities. Thin films fabricated from such polymers are promising for application, to optoelectronic devices. Polymeric electroluminescence materials have advantages over inorganic compounds, such as easy processability for preparation of thin films with high optical quality by simple casting and color tunability throughout visible spectrum.

The literature shows very few reports on coumarin containing polymers. Coumarin-containing polymers with physiological activities^{1–5} and photoconducting properties were reported by authors.⁶ Novel polyamides with 3,6-disubstituted coumarin units in the main chain have recently been synthesized and characterized.⁷ The polymers show strong photoemission in blue-green region and electroluminescence with turn on voltage of 3–5 V.

In the past several years norbornene monomers have been the subject of intense interest because of their facile functionalization, high reactivity in the ring-opening metathesis polymerization (ROMP) and the ring-preserving polymerization (RPP). Novel light emitting electro- and photoluminescent polynorbornenes have been synthesized by ROMP and RPP of norbornenes containing phenylenevinylene oligomer⁸ and fluorescein⁹ units in the side chain. One easy way to produce coumarin-containing polymers is to synthesize a coumarin-containing monomer followed by its ROMP. Polynorbornenes are amorphous optically transparent materials of importance for optical applications. Moreover, high molecular weight polymers with good mechanical properties can be obtained by ROMP using appropriate catalysts tolerating functional groups.

The present report describes the synthesis of a new light emitting polynorbornene by ring-opening metathesis polymerization of a coumarin-containing norbornene (NBC) using Ru and Os based catalysts. Recent works^{9–12} suggest that RuCl₃ and OsCl₃ hydrates and their complexes are much more tolerant to heteroatoms in the monomer than conventional catalysts containing tungsten halides or molybdenum and metalloorganic co-catalysts.

EXPERIMENTAL

Materials

Polymerization solvents, chlorobenzene, and toluene, were distilled over calcium hydride before use. *N*-Methylpyrrolidone (NMP) and pyridine were distilled over CaH₂. RuCl₃ × H₂O and OsCl₃ × H₂O (Aldrich) were used as received. RuCl₂(PPh₃)₃ was prepared according to the literature.¹³ Other reagents (Aldrich) were used as received (2-Norbornenyl)methyltosylate (**2**) was prepared as described previously.⁹

Monomer Synthesis

7-[(2-Norbornenyl)methoxy]coumarin (NBC)

A mixture of 7-hydroxycoumarin (**3**) (2.9 g, 17.9 mmol), (2-norbornenyl)methyltosylate (**3**) (5 g, 18.1 mmol), K₂CO₃ (2.9 g, 21 mmol) and NMP (25 ml) was stirred overnight at 60°C. The reaction was poured into diluted hydrochloric acid, precipitate formed was filtered off, dried and crystallized from a mixture of hexane–benzene. Yield 64%, *T*_m = 110–111°C, IR (cm^{–1}) 3055 (C–H, arom, vinyl) 2966, 2868 (C–H aliph), 1720 (C=O ester), 1616 (C=C arom). ¹H NMR (ppm) in CDCl₃ 7.60 (d, 1H, *J* = 9.6 Hz, H⁴), 7.32 (d, 1H, *J* = 8.4 Hz, H⁵), 6.79 (d, d, 1H *J*_{ortho} = 8.4 Hz, H⁶), 6.72 (d, 1H, *J* = 2.4 Hz, H⁸), 6.16 (d, 1H, *J* = 9.6 Hz, H³), 6.18–5.92 (m, 2H, olefin), 3.74–3.58 (2H, OCH₃), 3.00–0.62 (m, 7H, aliph). ¹³C NMR (ppm) in CDCl₃: 162.5 (C²), 160.8 (C⁷), 156.0 (C⁹), 143.3 (C⁴), 137.8, 132.1, 128.8 (olefin, C⁵), 112.9, 112.8, 101.6 (C⁶, C³, C⁸), 112.5 (C¹⁰), 72.2 (OCH₂), 49.50, 44.00, 42.35, 38.3, 29.1 (aliph) (Scheme 1).

Polymerization

The metathesis polymerization of NBC was carried out using RuCl₃ × H₂O and OsCl₃ × H₂O under dry nitrogen atmosphere. The active catalysts was prepared by refluxing of commercial RuCl₃ and OsCl₃ hydrates in ethanol for 3 hours.⁹ A typical polymerization experiment is as follows: 1 g (0.0037 mol) of monomer (NBC) was dissolved in 7 ml of chlorobenzene under dry nitro-

[†] To whom correspondence should be addressed.

gen. To this solution $\text{RuCl}_3(\text{OsCl}_3) \times \text{H}_2\text{O}$ ethanol solution (0.044 mol l^{-1}) (0.4 ml) was added. The reaction was carried out at 70°C for 8 hours. The polymer formed was precipitated into methanol, filtered off and purified by reprecipitation from chloroform into methanol. The polymer was dried in a vacuum oven at 30°C for 24 hours.

Measurements and Sample Preparation

The molecular weights of polymers were determined using a Varian 9012 GPC instrument at 30°C in CHCl_3 with polystyrene standard, universal column and a flow of 1 ml min^{-1} . DSC, TMA, and TGA were performed at a heating rate of $10^\circ\text{C min}^{-1}$ under nitrogen with a du Pont 2100 machine. FT-IR-spectra were taken using a Nicolet 510p spectrometer. UV-visible spectra were taken using a Shimadzu UV-260 spectrometer in thin films spin-coated onto a quartz slide. ^1H NMR and ^{13}C NMR were recorded using a Varian spectrometer at 300 MHz and 75.5 MHz, respectively, in CDCl_3 with trimethylsilane (TMS) as the internal standard. The wide angle X-ray diffractometry was performed on a Siemens D-500 diffractometer. Emission and excitation spectra were measured with a Perkin-Elmer 630-10S fluorimeter using thin films spin-coated onto a quartz slide.

RESULTS AND DISCUSSION

Monomer NBC was polymerized by Ru and Os based metathesis catalysts giving high molecular weight coumarin-containing polynorbornene (Scheme 2). The reaction conditions are listed in Table I. As can be seen from Table I OsCl_3 and RuCl_3 hydrates were effective and show comparable activities in ROMP of NBC. $\text{RuCl}_3 \times \text{H}_2\text{O}$ and $\text{RuCl}_2(\text{PPh}_3)_3$ catalysts produce the polymers with the preferential *trans* configuration of the double bonds (90–95 mol% of *trans* double bonds from ^1H NMR analysis of olefinic protons), whereas $\text{OsCl}_3 \times \text{H}_2\text{O}$ catalyst gives poly-NBC with a mixture of *cis* and

Table I. Polymerization of coumarin-containing norbornene (NBC) using Ru and Os based metathesis catalysts^a

Run	Catalyst	$[\text{M}]/[\text{Cat}]^b$	Polymer yield/% ^c	$M_n/10^5$	M_w/M_n^d
1.	$\text{RuCl}_3 \times \text{H}_2\text{O}$	100	68	1.2	1.95
2.	$\text{RuCl}_3 \times \text{H}_2\text{O}$	300	45	2.4	2.02
3.	$\text{RuCl}_2(\text{PPh}_3)_3$	50	48	2.8	2.13
4.	$\text{OsCl}_3 \times \text{H}_2\text{O}$	100	85	3.75	1.85
5.	$\text{OsCl}_3 \times \text{H}_2\text{O}$	300	74	4.5	1.78

^a Polymerization was carried out in chlorobenzene for 12 h at 70°C , initial monomer (NBC) concentration 0.5 mol l^{-1} . ^b Monomer to Catalyst mole ratio. ^c Methanol insoluble polymer. ^d GPC analysis in chloroform with polystyrene calibration standards.

trans double bonds (50–60 mol% of *cis* double bonds). The polymerization at high monomer concentration (more than 1 mol l^{-1}) rapidly leads to cross-linked polymer, while decrease in the monomer concentration results in a drastic reduction of the polymer yield. To avoid high catalyst concentration in polymer the reaction carried out by adding of small quantities of Ru and Os containing catalysts (0.3–1.0% in relative to the monomer). Our results suggest that the polymer yield is very sensitive to the monomer/catalyst ratio and increasing this ratio in the case of Ru based catalysts leads to more rapid reduction of the polymer yield (Table I). The resulting polymer is soluble in chloroform or chlorobenzene, but insoluble in tetrahydrofuran (THF) and benzene. Coumarin-containing polynorbornene is a rubber like material and can be cast from chloroform to a transparent film.

The results obtained by GPC analysis are presented in Table I. The number average molecular weight (M_n) and the polydispersity of the poly(NBC) were found to be $1.2\text{--}4.5 \times 10^5$ and 1.85–2.1, respectively.

IR spectra of poly(NBC) showed strong absorption of coumarin carbonyl at 1734 cm^{-1} , aliphatic CH stretching in the region of $2950\text{--}2860 \text{ cm}^{-1}$ and the characteristic bands near $870\text{--}970 \text{ cm}^{-1}$ corresponding to the *cis* and

Figure 1. ^1H NMR spectra of monomer (NBC) (a) and poly(NBC) in CDCl_3 obtained using $\text{RuCl}_3 \times \text{H}_2\text{O}$.

trans double bond of the polymer.¹¹ Figure 1 presented ^1H NMR spectra of both the monomer (a) and the polymer (b) prepared by $\text{RuCl}_3 \times \text{H}_2\text{O}$ catalyst. The monomer olefinic signals between 5.98 and 6.2 ppm are replaced by a new signal with a maximum 5.35 ppm corresponding to the linear olefinic protons of the predominant *trans* double bond of the polymer.¹¹ The doublets at 7.62 and 7.35 ppm with $J=9.5$ and 8.5 Hz corresponded to H⁴ and H⁵ of coumarin ring, multiplets at 6.95, 6.80, and 6.23 ppm can be assigned to H⁸, H⁶,

and H³, respectively. The ^{13}C NMR spectrum (Figure 2) also agrees with the fact that the obtained by Ru based catalysts polymer contains predominantly *trans* double bonds and consists of coumarin peaks at 162.5 (C²), 160.8 (C⁷), 156.0 (C⁹), 143.3 (C⁴), 112.9 (C⁶), 112.8 (C³), 101.6 (C⁸), 112.5 (C¹⁰), four different olefinic carbons of polymer chain at 135.0, 135.1, 131.4, and 129.5 corresponding to head to tail and tail to head enhancements along the chain,¹² signals at 72.2, and 49.50, -29.1 correspond to CH₂O and aliphatic carbons, respectively.

Figure 2. ^{13}C NMR spectrum of poly(NBC) in CDCl_3 obtained using $\text{RuCl}_3 \times \text{H}_2\text{O}$.

Figure 3. Absorption (1), emission (2), and excitation (3) spectra of poly(NBC).

The X-ray patterns indicate that prepared polymers are predominantly amorphous. The glass transition temperature (T_g) of the poly(NBC) by DSC and TMA was 67°C . TGA shows that the poly(NBC) is stable up to 340°C in nitrogen atmosphere.

The obtained poly(NBC) showed photoluminescence in solution and films owing to the coumarin fragment. Figure 3 shows absorption and emission and excitation spectra of polymer. Poly(NBC) exhibited long wave absorption maximum at 350 nm and emits at $\lambda_{\text{max}} = 410\text{--}420\text{ nm}$. It is noteworthy that NBS itself shows essentially the same absorption and emission spectra as poly(NBC) thus indicating there is no considerable interaction between coumarin groups in the polymer.

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