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Ring-Opening Metathesis Polymerization of the Bis(methyl carbonate) and Bis(*S*-methyl dithiocarbonate) of Norbornene and Thermal Conversion to Poly(cyclopentadienylenevinylene)

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ABSTRACT: *exo,exo*-Norborn-5-ene-2,3-diyl bis(*S*-methyl dithiocarbonate) (**1**) and *exo,exo*-norborn-5-ene-2,3-diyl bis(methyl carbonate) (**2**) were polymerized by ring-opening metathesis polymerization (ROMP) using $Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$. This is the first time a ROMP of norbornenedixanthate using a molybdenum-carbene initiator was successful. Depending on the bulkiness of the substituents, a higher stereoregularity of the polymer was achieved. Spectroscopic data (IR, NMR) of poly[norborn-5-ene-2,3-diyl bis(*S*-methyl xanthate) (**poly1**) show a complete trans connection of the repeating units, whereas the oxa analogue is not as stereoregular. Thermal properties of **poly1** offer interesting possibilities for application as a precursor polymer to poly(cyclopentadienylenevinylene) (**poly3**). By using the sulfur analogue, the temperature of elimination was reduced to 200 °C (maximum of the DSC plot).

Introduction

Use of precursor polymers is one common way to produce conjugated polymers. Polyacetylene synthesized *via* a precursor polymer was first achieved by an elegant method established by Feast et al.[1-3] A route to poly(*p*-phenylene) (PPP) *via* elimination of acetates was first shown by ICI workers.[4,5] The major disadvantages of these syntheses were the price and short supply of the monomer as well as limited control over the stereochemical outcome. Similar routes were applied for the synthesis of poly(*p*-phenylenevinylene)[6] and poly(cyclopentadienylenevinylene)[7,8] (**poly3**).

All of these procedures used acetates, benzoates, or carbonates. These functional groups usually decompose a temperatures above 300 °C, whereas the glass transition temperature of the precursor polymer is between 50 and 100 °C. Therefore, it is not possible to carry out orientation experiments during elimination. Consequently, we attempted to reduce the temperature of elimination (T_{el}) to the region of the glass transition. From the chemistry of low molecular weight compounds we know that the elimination temperature decreases in the order acetate > benzoate > methyl carbonate > *S*-methyl dithiocarbonate.

The literature indicates little about ring-opening metathesis polymerization (ROMP) of sulfur-containing cycloolefins. Most of the heteroatoms found in the literature are oxygen, halogen, nitrogen, or silicon. 5-Alkylthiocyclooctenes,[9] methyl thioethers of norbornene,[10] and 7-oxanorbornyl sulfones[11] were the only sulfur-containing monomers we found to have been polymerized via ROMP before. Due to the interesting thermal properties, we tried to apply ROMP on norbornenediyl dixanthate. In this paper we compare *exo,exo*-norborn-5-ene-2,3-diyl bis(*S*-methyl dithiocarbonate) (**1**) with its oxa analogue *exo,exo*-norborn-5-ene-2,3-diyl bis(methyl carbonate) (**2**), which are given in Figure 1.

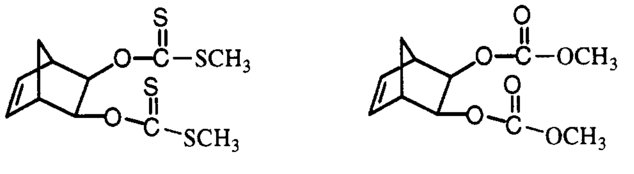

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Figure 1. Monomers 1 and 2.

Experimental Section

Materials and Methods. *exo-exo*-2,3-Dihydroxynorborn-5-ene was prepared from bicyclo[2.2.1]hepta-2,5-diene (norbornadiene) by selective oxidation of one double bond with OsO_4/*N*-methylmorpholine *N*-oxide.[12] Dimethyl sulfoxide, methyl chloroformate, sodium hydroxide, carbon disulfide, and iodomethane were used as obtained from commercial suppliers. Pyridine was dried over molecular sieves. Chlorobenzene and dichloromethane were distilled from calcium hydride in vacuum and transferred into the glovebox when used for ROMP reactions; $(Mo(CH\text{-}t\text{-}Bu)(NAr)(O\text{-}t\text{-}Bu)_2$ was prepared as described in literature.[13] For IR and UV spectroscopy the polymer was dissolved in dichloromethane, spin cast on disks of NaCl or infrasil, and mounted in a Specac high-temperature cell.

Instrumentation. ^{1}H-NMR and ^{13}C-NMR spectra were acquired on a Bruker MSL 300, IR spectra were measured on a Bomem M 100 FTIR spectrometer, and UV-vis spectra were obtained on a Hewlett Packard 8452A diode array spectrophotometer. Elemental analyses were carried out at the Institut für Physikalische Chemie, Universität Wien, Vienna, Austria. Thermal analyses and determination of mp's were performed on a Polymer Laboratories STA 625 simultaneous DSC-thermogravimetric analyzer. Gel permeation chromatographic (GPC) analyses were carried out using columns with pore diameters from 10^3 to 10^6 Å and a Viscotek 200 simultaneous RI-viscosity detector on polymer samples 0.2% w/v in tetrahydrofuran. The GPC columns were calibrated against polystyrene standards, and GPC data were evaluated by means of universal calibration.

Monomer Synthesis. *exo,exo*-Norborn-5-ene-2,3-diyl bis(*S*-methyl dithiocarbonate) (1). A total of 5.5 g of *exo,exo*-norbornenediol was dissolved in 50 mL of dimethyl sulfoxide and 25 mL of carbon disulfide under argon. The solution was cooled to 15 °C, and 50 mL of NaOH (5 M) was added dropwise and kept at 15 °C for 20 min. After addition of 10 mL of iodomethane, the mixture was stirred for another 45 min at 15 °C. Volatile byproducts (CH_3SH, etc.) were removed *in vacuo* at room temperature. The white crystals of NaI were isolated by filtration. The filtrate was concentrated under reduced pressure and purified by column chromatography over silica gel with cyclohexane. Concentration *in vacuo* gave 9.5 g (70% yield) of white yellow crystals of 1. Elem anal. Calcd: C, 43.11; H, 4.60; O, 10.44; S, 41.84. Found: C, 43.18; H, 4.56; O, 10.80; S,

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41.45. MP: 80.86 °C (250 °C dec). ^{1}H-NMR (300 MHz, in $CDCl_3$): δ 6.24 (t, 2H, HC=C), 5.52 (d, 2H, HCO), 3.10 (t, 2H, H-bridgehead), 2.56 (s, 6H, CH_3S), 2.19 (d, 1H, H-bridge), and 1.89 (td, 1H, H-bridge). ^{13}C-NMR (75 MHz, in $CDCl_3$): δ 215.1 (C=S), 136.9 (C=C), 79.5 (CO), 46.2 and 44.9 (bridge and bridgehead carbons), 19.2 (CH_3S–).

***exo,exo*-Norborn-5-ene-2,3-diyl bis(methyl carbonate) 1.** A total of 5.8 g of *exo,exo*-norbornenediol was dissolved in 10 mL of pyridine and 100 mL of dichloromethane and cooled to 0 °C. Under vigorous stirring, 15.4 mL of methyl chloroformate was added slowly over a period of 40 min. After stirring at room temperature for 24 h, the solution was poured into water and extracted with CH_2Cl_2. The organic layer was then washed successively with 1 N HCl, $NaHCO_3$, and finally pure distilled water, dried over Na_2SO_4, and concentrated *in vacuo*. Column chromatography over silica gel yielded 9.5 g (86%) of white crystals of 2. Elem anal. Calcd: C, 54.54; H, 5.82; O, 39.63. Found: C, 54.48; H, 5.82; O, 39.70. Mp: 47.3 °C. ^{1}H-NMR (300 MHz, in $CDCl_3$): δ 6.15 (t, 2H, HC=C), 4.66 (d, 2H, HCO), 3.77 (s, 6H, CH_3S), 2.91 (t, 2H, H-bridgehead), 1.78 (d, 1H, H-bridge) and 1.74 (d, 1H, H-bridge). ^{13}C-NMR (75 MHz, in $CDCl_3$): δ 155.5 (C=O), 135.9 (C=C), 74.5 (CO), 55.1 (CH_3O–), 46.1 and 45.8 (bridge and bridgehead carbons).

Polymer Synthesis. Poly[norborn-5-ene-2,3-diyl bis(*S*-methyl dithiocarbonate)] (poly1). In a typical polymerization experiment, 300 mg of 1 (100 equiv) was dissolved in 3 mL of chlorobenzene under dry nitrogen in the glovebox. To this monomer solution was added 4.7 mg of Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (1 equiv), dissolved in 1 mL chlorobenzene. After stirring for 90 min at room temperature, the polymerization was terminated by the addition of approximately 10 equiv of benzaldehyde. After another 30 min, the polymer was precipitated in MeOH and reprecipitated from CH_2Cl_2/MeOH. After the second precipitation, 270 mg (90%) of white, fibrous **poly1** was afforded. Elem Anal. Calcd: C, 43.11; H, 4.60; O, 10.44; S, 41.84. Found: C, 43.22; H, 4.58; O, 10.86; S, 41.34.

Poly[norborn-5-ene-2,3-diyl bis(methyl carbonate)] (poly2). In a typical polymerization experiment 300 mg of 2 (100 equiv) was dissolved in 3 mL of chlorobenzene under dry nitrogen in the glovebox. To this was added 6.0 mg Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$ (1 equiv), dissolved in 1 mL of chlorobenzene. After stirring for 60 min at room temperature, the polymerization was terminated by addition of 3 drops of benzaldehyde. After another 30 min the polymer was precipitated in MeOH and reprecipitated from CH_2Cl_2/MeOH. The yield of white **poly2** after the second precipitation was 282 mg (94%). Elem anal. Calcd: C, 54.54; H, 5.82; O, 39.63. Found: C, 54.60; H, 5.84; O, 39.56.

Results and Discussion

The polymerization process is outlined in Figure 2, which also illustrates the numbering system used in this paper.

Both monomers were readily polymerized with different initiator concentrations to give polymers with different molecular weights. The typical molecular weight distribution was narrower for the oxa analogue (M_w/M_n = 1.09) than for the thia analogue (M_w/M_n = 1.3). Data of GPC analyses are given in Table 1.

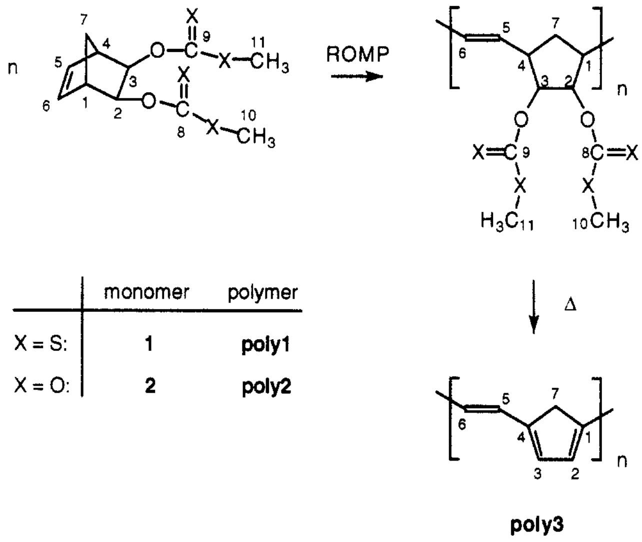

Figure 2. Reaction scheme and numbering system for the ROMP of monomers 1 and 2 to yield polymers **poly1** and **poly2** followed by thermal conversion to **poly3**.

Table 1. GPC Data of Polymers poly1 and poly2

monomer	m/i[a]	yield (%)	M_w/M_n	M_w[b]	M_{corr}[c]	M_{calc}[d]
1	50/1	80	1.3	30 000	45 300	15 300
	100/1	90	1.4	60 000	117 000	30 600
	200/1	93	1.4	114 000	217 000	61 200
2	100/1	94	1.08	80 600	180 000	24 200
	200/1	93	1.09	152 000	610 000	48 400

[a] Molecular ratio of monomer and initiator. [b] Calibrated against polystyrene standards. [c] Corrected molecular weight applying the Viscotek detector. [d] Calculated by m/i.

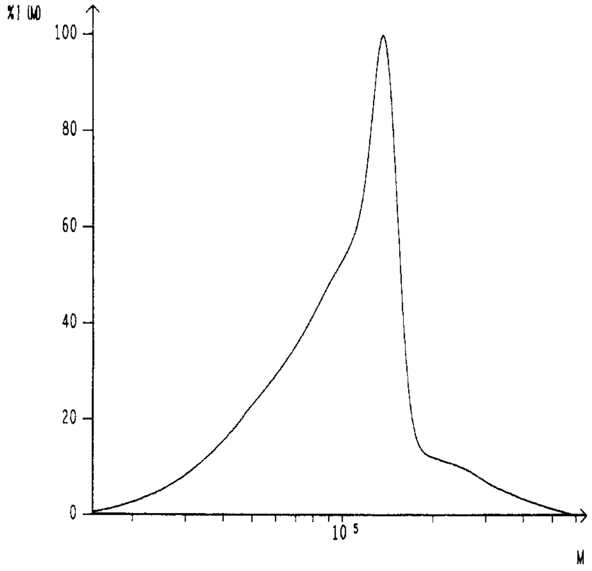

Figure 3. Size-exclusion chromatogram of **poly1**.

Since the calibration against polystyrene standards requires a similar polymer structure, a correction had to be made. This was achieved by simultaneous viscosity and refractive index measurements. These were correlated by means of using the Viscotek simultaneous RI–viscosity detector to give universal calibrated molecular weights (M_{corr}). Data were evaluated using the software from Polymer Standards Service, PSS, and showed that the corrected M_w did not match those expected by m/i. In all done experiments M_{corr} were too high at least by a factor of 3. This might have three reasons: (1) impurities of the initiator, (2) impurities of monomer or solvent, that decrease the concentration of the active initiator, and (3) a slow initiation step followed by a much faster propagation step. In addition, the molecular weight distributions are not as narrow as often found for living ROMP. In most of our experiments we found a more or less trimodal distribution (see Figure 3, an extreme example of a size-exclusion chromatogram): a small peak at high molecular weight, the main peak, and, at half-height of the main peak, a strong tendency toward low molecular mass. The small peak at higher molecular weight can be caused by a combination reaction during the termination of the polymerization which is sometimes observed when oxygen is present. To explain the "tailing" toward lower molecular weights, we can offer three suggestions: (1) again a slow initiation step followed by a faster chain-growth reaction, (2) a chain-transfer reaction or backbiting which, in our

Table 2. ^{1}H-NMR Assignments for poly1 and poly2 in CDCl$_3$

polymer	chemical shift (ppm)	H no. (type)	peak assignment
poly1	5.80	5,6 (olefin)	*trans*
	5.57	2,3	*trans*
	3.06	1,4 (bridgehead)	*trans*
	2.56	10,11 (SCH_3)	
	2.26 and 1.38	7 (methylene)	
poly2	5.50	5,6 (olefin)	*trans*
	5.36	5,6 (olefin)	*cis*
	4.75	2,3	*trans*
	4.62	2,3	*cis*
	3.72	10,11 (OCH_3)	
	3.06	1,4 (bridgehead)	*cis*
	2.76	1,4 (bridgehead)	*trans*
	2.14 and 1.24	7 (methylene)	

opinion, is less probable because of the steric hinderance, or (3) termination through deactivation of the active end of the growing chains. This deactivation might be caused by traces of impurities (not detectable by the NMR spectrum of the monomer) or by coordination of the thiocarbonyl group to the transition metal. Therefore, NMR experiments were applied in order to study the polymerization online. NMR spectra showed that the dithiocarbonate was also polymerized *via* ring-opening methathesis similar to the corresponding oxa analogue. Upon addition of monomer to the initiator solution (toluene-d_8) at 20 °C, the initiator–carbene singlet at δ 11.32 (syn rotamer) disappeared over a period of 15 min and a duplet at δ 11.7 appears. The new signal remains constant during the time necessary for polymerization. Assuming that the resonance at δ 11.7 represents the active site, the polymerization seems to be living.

Polymer Microstructure. The microstructure of polymers from norbornene derivatives depends on the relationship between the adjacent monomer units. Since both of the monomers used in this work are symmetrical, no head–tail, head–head, or tail–tail isomerism exists. Nevertheless, there are few different ways in which the repeating units can be connected in the polymer chain. The double bonds in the diad may have *cis* (c)–*trans* (t) isomerism and the allylic methines on either side of the double bond may have the same chirality, giving racemic (r) diads (i.e., syndiotactic) or, with opposite chirality, giving meso (m) diads (i.e., isotactic).

Besides IR spectroscopy, the cis–*trans* ratio of the double bonds in the polymer can be determined by integration of the ^{1}H-NMR peaks of allylic and olefinic protons. On the basis of ^{1}H-NMR analysis the double bonds in **poly1** are completely *trans* (*cis* signal below detection limits). **Poly2** gives a *trans* content of 93%, the *cis* olefin protons being 0.15 ppm upfield from the *trans* olefin protons. The complete assignments of these spectra are shown in Table 2.

^{13}C-NMR analysis of these polymers provides another method for determining the *cis*–*trans* ratio of the double bonds in the polymers. The spectrum observed is very simple, indicating a very regular, highly tactic polymer. ^{13}C-NMR assignments of **poly1** and **poly2** are given in Table 3.

The thiocarbonyl carbons give a signal at 214.88 ppm. The presence of a single resonance in the olefinic region of the spectrum of **poly1** suggests that this polymer is completely stereoregular. Due to the obtained IR spectrum, this peak can only be assigned to a *trans* connection. The carbons at positions 2 and 3 give a signal at 84.13 ppm. Allylic carbons adjacent to the *trans* double bond are observed at 45.40 ppm.

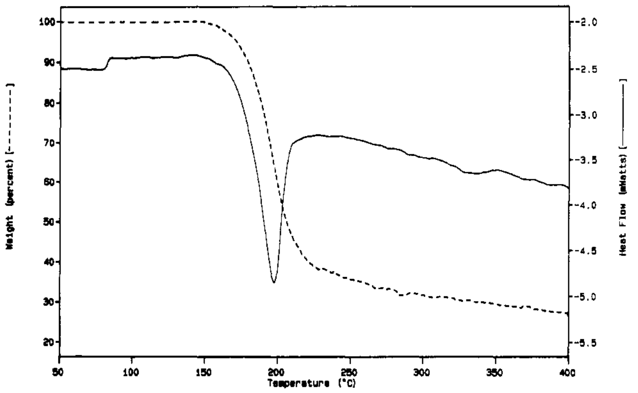

Figure 4. Simultaneous DSC and TGA analysis of **poly1**.

Table 3. ^{13}C-NMR Assignments for Polymers poly1 and poly2 in CDCl$_3$

polymer	chemical shift (ppm)	C no. (type)	peak assignment
poly1	214.88	8,9 (C=S)	
	131.68	5,6 (olefin)	*trans*
	84.13	2,3	*trans*
	45.40	1,4 (bridgehead)	*trans*
	32.90	7 (methylene)	
	19.32	10,11 (SCH_3)	
poly2	155.29	8,9 (C=O)	
	132.62	5,6 (olefin)	*cis*
	132.82	5,6 (olefin)	*trans*
	80.75	2,3 (CO)	*cis*
	80.13	2,3 (CO)	*trans*
	55.12	10,11 (OCH_3)	
	48.48	1,4 (bridgehead)	*cis*
	44.81	1,4 (bridgehead)	*trans*
	40.34	7 (methylene)	*cis*
	33.13	7 (methylene)	*trans*

In contrast to the thio analogue the carbonyl carbon in **poly2** appears at 155.29 ppm. A small double (~7% of the total) downfield to the high *trans* vinylene signal indicates that **poly2** is also a highly stereoregular polymer but only to the extent of ~93%. The results of ^{13}C-NMR analysis are consistent with the assignments from the respective ^{1}H-NMR data. This lower stereoregularity of the oxa analogue could be due to the lower bulkiness of the substituents present in the monomer.

Thermal Elimination. Use of **poly1** and **poly2** for thermal elimination requires intense knowledge about the thermal properties of these polymers. For the DSC measurements we used samples of about the same degree of polymerization (m/i = 100/1). First DSC studies of **poly1** are shown in Figure 4. The DSC plot shows a glass transition *Tg* at 80.3 °C, whereas elimination starts at 176 °C (onset of the peak with its maximum at 198 °C). Simultaneous thermoanalysis (DSC/TGA) shows a calculated weight loss of 69.7% (between the tangents on each side of the elimination) which is close to the theoretical weight loss of about 70.6% for complete elimination of the methyl dithiocarbonate and formation of **poly3**. MS analysis of the pyrolysis products of **poly1** also confirms our hypothesis of elimination as being the main reaction, only fragments of the elimination, and no indication of polymer degradation was observed.

IR spectroscopy of a spin-cast and heated (up to 230 °C) film showed no hydroxylic (~3400 cm^{-1}) absorptions. Due to elimination, the two strong absorptions from the thioesters at 1208 and 1070 cm^{-1} disappear, whereas new peaks at 3021, 1640, 1600, and 864 cm^{-1} appear (see Figure 5). These are attributed to the formation of new double bonds.

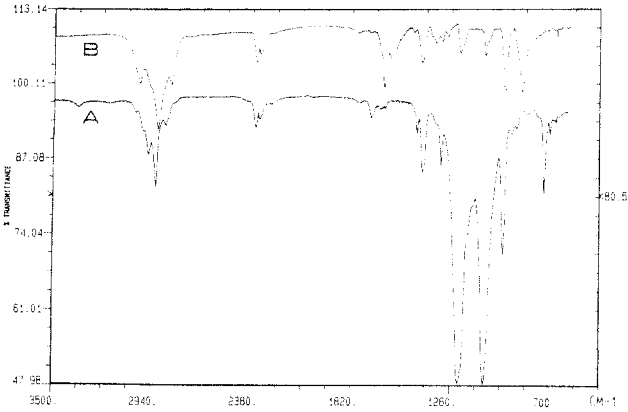

Figure 5. IR spectra of **poly1** (A) before heating and (B) after heating to 230 °C.

In order to follow the course of the elimination reaction of **poly1**, UV spectroscopy was applied on thin films cast on an infrasil disk. They were heated to 200 °C (heating rate = 20 °C/min) *in vacuo* followed by an isothermal period for 120 min. The UV spectra recorded after 1, 5, 20, and 60 min at 200 °C are shown in Figure 6. Upon heating, the peak at 4.3 eV (≈285 nm) completely disappears, indicating a loss of the *S*-methyl dithiocarbonate group. Instead of the peak at 4.3 eV, a new peak is formed at about 3.3 eV (≈375 nm). This peak is assigned to the formation of a conjugated π-bonding system (see Figure 3; **poly3**). Elemental analysis of a sample that was heated *in vacuo* to 240 °C for 2 h gives 92.5% C, 6.4% H, and 0.9% S. The calculated values are 92.3% C and 6.7% H.

As expected, **poly2** eliminates at higher temperatures (270 °C), whereas a glass transition is observed at 96.0 °C. Theoretical weight loss for elimination of the ester functions is 62.8%. The weight loss determined by simultaneous TGA is 60% at 350 °C. IR spectroscopy of heated **poly2** (350 °C) also shows a small amount of functional groups remaining in the dark and red insoluble film. Due to insolubility (often found with conjugated polymers), no NMR measurements could be carried out; solid-state MAS experiments are under way but require a larger sample.

Conclusions

We have shown, for the first time, that *exo,exo*-norborn-5-ene-2,3-diyl bis(*S*-methyl carbonate) can be polymerized via ring-opening metathesis. We have therefore widened the range of functionalities tolerated by the well-defined catalyst Mo(CH-*t*-Bu)(NAr)(O-*t*-Bu)$_2$. It not only tolerates halogen, silicon, or oxygen but is also able to polymerize sulfur-containing norbornene derivatives. However, it is not completely clear that it is a living ring-opening metathesis polymerization. Although NMR experiments show that the assumed active site is present during polymerization, the molecular weight distribution is not as narrow as often found for living ROMP. Furthermore, the broad, sometimes multimodal molecular weight distribution indicates a side reaction which might deactivate the catalyst or enable chain transfer but could not be observed by NMR spectroscopy. The small amount of higher mass polymer may originate from a termination of the polymerization by combination.

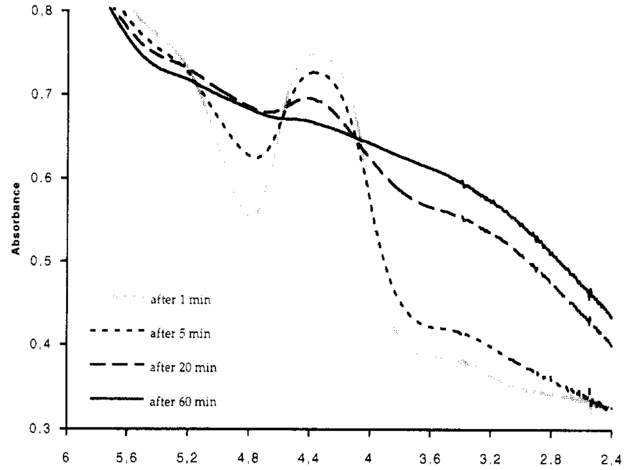

Figure 6. UV spectra of **poly1** heated to 200 °C *in vacuo*.

We have also illustrated that it is possible to reduce the temperature of elimination by use of *S*-methyl dithiocarbonates as leaving groups instead of methyl carbonate. This substitution may not only be restricted to norbornene derivatives. It could even be more successful for precursors to poly(*p*-phenylene) and poly(*p*-phenylenevinylene). Reduction of the temperature of elimination below the glass transition temperature was not accomplished. With respect to this goal the acid-catalyzed elimination with an onset at ~70 °C is still the better method. We were unable to obtain an NMR analysis of **poly3** [poly(cyclopentadienylenevinylene)] due to its insolubility. Nevertheless, we are convinced of its polyconjugated structure on the basis of the obtained UV spectra.

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