2274 *Macromolecules* **1997,** *30,* 2274−2277

Synthesis of Polyenes That Contain Mesogenic Side Chains via the Living Polymerization of 4-(Ferrocenylethynyl)-4′-ethynyltolan[†]

Michael R. Buchmeiser[*]

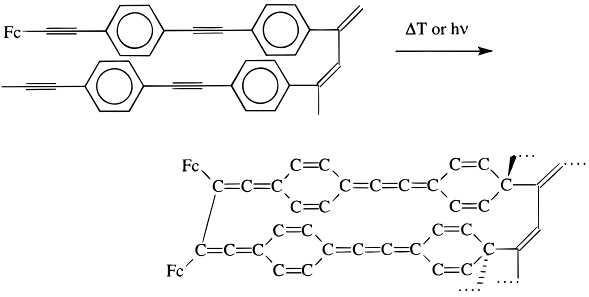
Institut für Analytische Chemie und Radiochemie, Universität Innsbruck, Innrain 52 a, A-6020 Innsbruck, Austria

Received September 5, 1996; Revised Manuscript Received February 18, 1997[⊗]

ABSTRACT: The living polymerization of the metallocenyl-substituted diethynyltolan, 4-(ferrocenylethynyl)-4′-ethynyltolan (**I**), by the well-defined Schrock metathesis catalyst Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$ (**II**) is described. The polymerization starts virtually solely via β-addition of the monomer to the metal−carbon double bond and yields conjugated, surprisingly soluble, main chain polyenes containing mesogenic, rigid side chains. Despite the β-addition, the polymerization proceeds in a controlled, living manner, resulting in the the formation of low polydispersity polymers. The resulting polymers exhibit a remarkable stability against air and thermal treatment.

Introduction

Acetylenes represent important tools in polymer chemistry. Terminal as well as internal systems may serve as unique precursors for conjugated polyenes, which are a widely investigated class of π-systems in the area of nonlinear optics.[1−7] Polyynes, and among them, especially poly(p-phenyleneethynylenes), usually prepared by subsequent coupling and deprotection of terminal acetylenes,[8−12] are additionally of particular interest in the areas of liquid crystals, as well as in those of electronics[13] and electrooptics.[14] Moreover, their potential use as materials with large fluorescence quantum yields[15] has been reported recently. Due to their pronounced linearity and rigidity, poly(p-phenyleneethynylenes) may form in combination with proper functionalization self-assembled monolayers as well as exceptionally stable χ^3 nonlinear optical materials.[16,17] Furthermore, this class of compounds is of great interest in the area of solid state polymerization,[18,19] where both the the monomeric as well as the polymeric forms may act as precursors for chinoid poly(metallocenylallenes) (eq 1).



(1)

Whereas even low molecular weight 1,1′-ferrocendiyl bridged p-(ferrocenylethynyl)tolans suffer from significantly decreased solubility,[16] poly(4-(ferrocenylethynyl)-4′-ethynyltolans) prepared by ROMP exhibit a surprisingly high solubility in common organic solvents such as toluene, benzene, methylene chloride, tetrahydrofuran, etc., allowing the synthesis of highly soluble, rigid poly(4-(ferrocenylethynyl)tolans) bound to a conjugated main chain polyene up to a molecular weight of 25 000.

Results and Discussion

Terminal acetylenes such as ethynylferrocene,[20] ethynylruthenocene,[20] and (o-(trimethylsilyl)phenyl)acetylene (o-TMSPA)[21,22] can be polymerized in a living way using well-defined Schrock catalysts of the type Mo(NAr)($CHCMe_2Ph$)(OR′)$_2$ and Mo(NAd)($CHCMe_2Ph$)(OR′)$_2$·base.[21,22] It has been proposed by Schrock et al.[20,21] that the use of “small”, electron-withdrawing alkoxides favors α-addition, whereas larger alkoxides may give raise to β-addition due to sterical hindrance. This concept prooved to be very useful in the polymerization of o-substituted phenylacetylenes, such as o-TMSPA and related compounds,[21,22] yet other terminal acetylenes (e.g., ethynylferrocene, ethynylruthenocene)[20] behaved in a different way, thus adding α despite of the use of large alkoxides in Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$ and vice versa with metal carbenes containing small alkoxides such as Mo(N-2,6-$Me_2C_6H_3$)($CHCMe_2Ph$)(OC_6F_5)$_2$·quinuclidine. Unfortunately, sterically hindered acetylenes such as *tert*-butylacetylene as well as acetylenes containing electron-withdrawing groups do not react readily even with one of the most reactive molybdenum-based initiators, Mo(N-2,6-i-$Pr_2C_6H_3$)($CHCMe_2Ph$)($OCMe(CF_3)_2$)$_2$ **II**. As the ferrocene moiety exhibits special properties not only with regard to the final possible application of the resulting polymer but also with regard to the reactivity of the monomer itself, the polymerization of **I** using the ROMP technique seemed to be challenging as well as promising. The results of the polymerization of **I**, using **II** as the initiator, are discussed in detail below.

There is much evidence that the polymerization of terminal acetylenes proceeds via an alkylidene mechanism[23−26] with an unobservable metallacyclobutene as an intermediate. The present polymerization system is well behaved and living, despite the fact that the monomer adds β to the initiator (eq 2). The evidence for this type of insertion is supported by ^{1}H-NMR. Upon treatment of **II** with 1 equiv of **I**, a sharp singlet for H_γ appears at 5.93 ppm. No coupling can be observed. The signal for the terminal acetylene of **I** at 3.17 ppm

---

[*] Tel: +43-512-507-5184. Fax: +43-512-507-2965. E-mail: michael.r.buchmeiser@uibk.ac.at.

[†] Dedicated to Prof. K.-E. Schwarzhans on the occasion of his 60th birthday.

[⊗] Abstract published in *Advance ACS Abstracts,* April 1, 1997.

S0024-9297(96)01317-4 CCC: $14.00

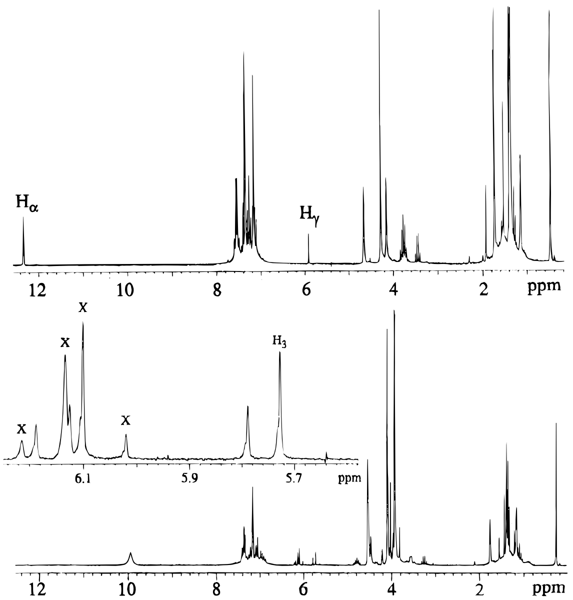
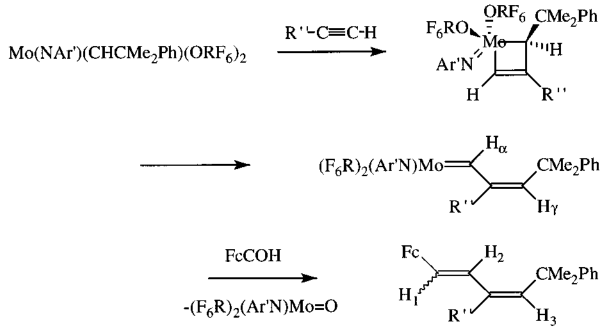


Figure 1. ^{1}H-NMR (C_6D_6) of **I** initiated with **II**: upper spectrum before and lower spectrum after capping with excess of ferrocenecarboxaldehyde. H_α and H_γ of the first insertion product as well as the two doublets (×) and H_3 of the resulting terminal *trans*-alkene ($J = 16.3$ Hz) in the capped product are indicated. Solvent impurity at $\delta = 0.3$ ppm.

disappears and an additional resonance for H_α at 12.37 ppm appears (Figure 1).



R'' = p-(η^5-C_5H_5-Fe-η^5-C_5H_4)-CC-C_6H_4-CC-C_6H_4- (2)
Ar' = 2,6-Me_2-C_6H_3-
Fc = ferrocenyl, η^5-C_5H_5-Fe-η^5-C_5H_4-

It is worth noting that no signals for a second or third insertion product were observed. Beside the signals for H_α and H_γ, only one characteristic signal group for the ferrocene moiety of the first insertion product at 4.67 ppm (t, $J = 1.82$), 4.28 (s, Cp), 4.16 (t, $J = 1.82$) appeared. As a consequence, it has to be proposed that despite the β-addition, the first insertion product is less reactive toward **I** than is **II**. This finding explains the living character of the polymerization, which usually is not the case in polymerizations with β-addition in comparable systems. As reported earlier,[20] the reaction of ethynylferrocene with initiators exhibiting β-addition results in insoluble polymers, which are formed within a few seconds as the first and presumably also higher insertion products are more reactive than the the initiator itself, resulting in a polymerization system where only a small percentage of the initiator is consumed. An explanation for the present situation is based both on steric as well as electronic arguments. First, the monomer is sterically demanding. As a consequence, β-addition seems favorable for this monomer in the presence of the large alkoxide. This argument is underlined by the fact, that 4-((trimethylsilyl)-ethynyl-4′-ethynyltolan also adds β to **II**. These findings are in accord with the model developed by Schrock et. al. Substitution of the diethynyltolan with the ferrocene moiety results in a more reactive terminal acetylene compared to diethynyltolan due to the pronounced Lewis base character of the metallocene. The fact that the enhanced electron density is transported over the whole system is underlined by the difference of the chemical shifts for the proton of the corresponding terminal acetylene in unsubstituted diethynyltolan (3.72 ppm) and **I** (3.17 ppm). Nevertheless, the monomer is still significantly less reactive than ethynylferrocene, as the additional electron density is distributed over a larger π-system.

In order to be living, a polymerization must fullfill certain requirements,[27−30] the most important ones being that there are low PDI's, a linear plot of M_w vs the number of monomers, is linear and complete consumption of the monomer takes place. Under these conditions, chain transfer or termination are considered to be absent and the polymerization may be regarded as "living". Polymerizations of **I** initiated by **II** proceed within a few hours to yield low PDI polymers. A plot of molecular weight (M_w) vs number of monomers (N) added to the initiator is shown in Figure 2a. Chain termination ("capping") of the living system was performed by the method described earlier,[20] using ferrocenecarboxaldehyde as the capping reagent. No signals for double molecular weight have been observed by GPC (for example see Figure 2b). Upon treatment with ferrocenecarboxaldehyde (eq 2), both capping products may be observed. Signals for the *trans*-configured butadiene ($J = 16.3$ Hz) are indicated in Figure 1. The second set of signals, corresponding to the *cis*-configured butadiene partially overlaps with the *trans* set. The relative ratio of both capping products (*trans*:*cis*) is approximately 6:4.

The resulting materials containing up to 50 metallocene groups are generally obtained in high yields (>95%) except for the 15-mer and shorter chains. Here, precipitation is incomplete. The polyenes exhibit excellent solubility compared to their oligomeric main chain 1,1′-ferrocenediyl analogoues. IR data underline the proposed structure (Figure 3). The signal for a terminal acetylene at 3280 cm^{-1} disappears and a strong band at 740 cm^{-1} for RR′C=CHR″ appears.

The processability of the polymer is significantly enhanced compared to the starting material. While momomeric and oligomeric 1,1′-ferrocenediyltolans have a high tendence toward the formation of amporphous powders, which is the main reason why no crystal structures have been obtained so far, poly-**I** can be processed into thin films on surfaces without any tendency toward crystallization. UV measurements (Figure 4) reveal besides the strong absorptions at 270 nm for the ferrocenyl moiety a pronounced maximum at 335 nm (**I**: 317 nm) for all polymers with unpronounced absorptions up to 550 nm independent from the solvent (toluene, methylene chloride, THF). The low bathochromic shift of the absorption compared to the monomer is explained by a short effective conjugation length in the polyene. The polymers are stable under air for at least several days. Thus, a sample of poly-**I**-10 showed no increase in polydispersity after 5 days. Even in solution upon exposure to air for 5 h, no significant change in the UV−vis spectrum of poly-**I**-10 was observed. These findings are comparable to those

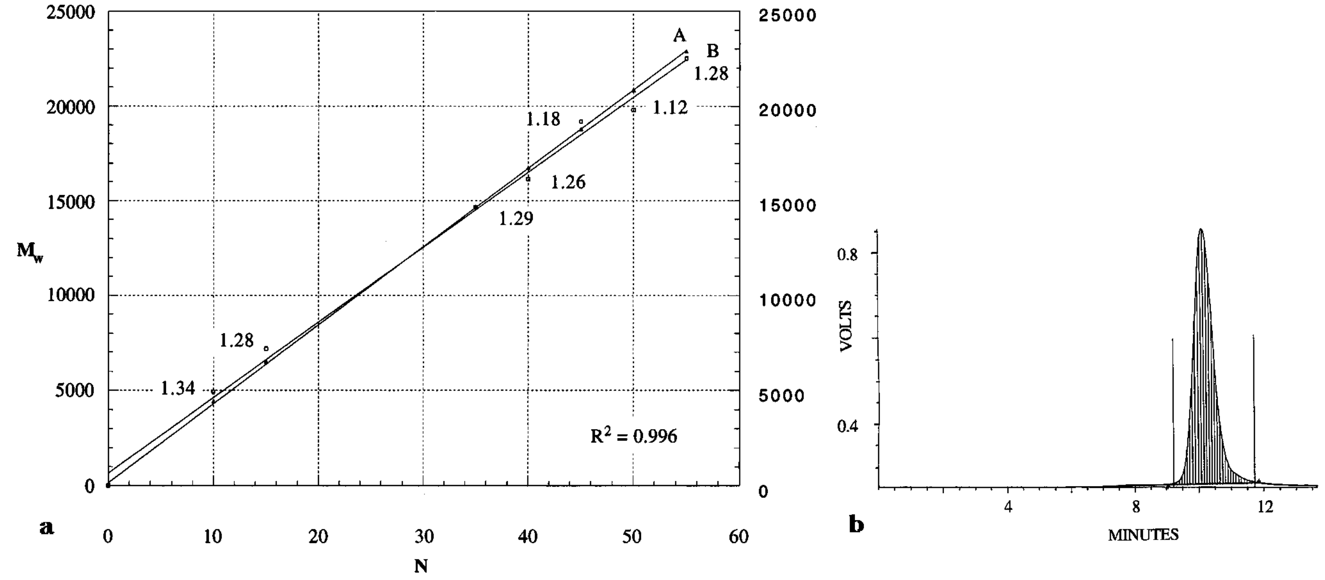


Figure 2. (a) Plot of molecular weight (M_w) determined by GPC vs poly(styrene) for poly-**I** prepared from *N* equivalents of **I** and **II** as the initiator. Solvent: toluene. Key: A, calculated values; B, experimental values. (b) GPC trace of poly-**I**-15 (UV). (For experimental conditions refer to the Experimental Section).

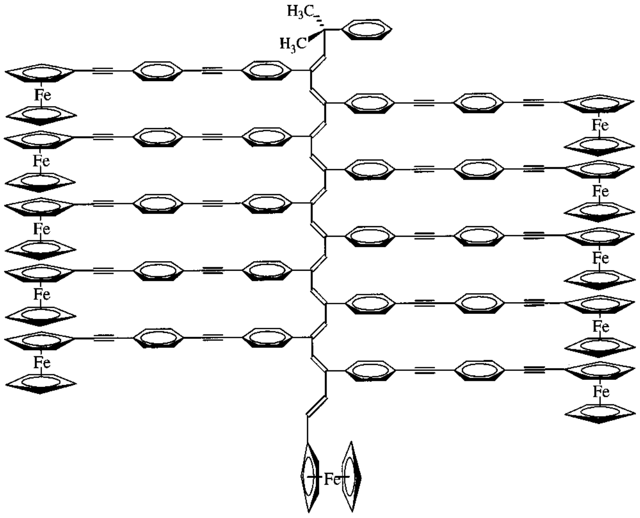


Figure 3. Proposed structure of poly(4-(ferrocenylethynyl)-4′-ethynyl-tolan)$_{10}$.

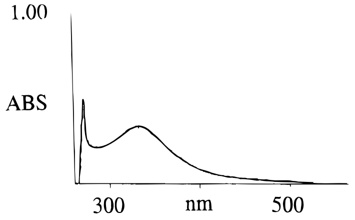


Figure 4. UV−vis spectrum of poly-**I**-20.

for poly(ethynylferrocene) and may be explained in both cases by steric shielding. The remarkable stability of poly-**I** is underlined by the fact, that the system is additionally stable against thermal treatment. DSC-measurements for a sample of poly-**I**-10 reveal no changes up to a temperature of 180°C. At ca. 230°C, an exotherm is observed, and the resulting material is insoluble in any common solvent.

The polymers described in this contribution are comparable to poly(ethynylferrocene) in stability. Despite of their rigid side chains, they possess a higher solublity in organic solvents as well as enhanced processability into thin films. Due to their characteristic properties, these polymers represent in combination with their low PDI values interesting materials for all possible applications mentioned at the beginning.

Experimental Section

General Details. All experiments were performed under an argon atmosphere by standard Schlenk techniques unless stated otherwise. Reaction solvents were purified by standard methods. Purchased starting materials were used without any further purification. Other reagents were prepared according to literature procedures and checked for purity by means of NMR. Reagent grade pentane, diethyl ether, tetrahydrofuran, toluene, and benzene were distilled from sodium benzophenone ketyl under argon. Reagent grade dichloromethane was distilled from calcium hydride under argon. All deuterated NMR solvents were dried by appropriate methods prior to use. $Mo(N\text{-}2,6\text{-}i\text{-}Pr_2C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$,[31] and 4-(ferrocenylethynyl)-4′-ethynyltolan[16] were synthesized as described in the literature.

NMR data were obtained in the indicated solvent at 25 °C on a Bruker AC 200 or Varian EM 360L unless stated otherwise and are listed in parts per million downfield from tetramethylsilane for proton and carbon. Coupling constants are listed in Hertz. IR spectra were recorded on a Midac FT-IR. GPC data were determined in CH_2Cl_2 on a Spectroflow 400 using a Water 484 UV−vis detector and a Biorad 1770 differential refractometer respectively (flow rate 1 mL/min.). Waters Styragel HT 6E columns were used. UV data were obtained on a HP 8452A UV detector (range 190−820 nm) in the solvent indicated and are listed in nanometer. Differential scanning calorimetry was performed on a Perkin-Elmer DSC-4: scan rate 10 K·min^{-1}, 28−250 °C, N_2 atmosphere, $p = 3$ bar.

4-((Trimethylsilyl)ethynyl)-4′-ethynyltolan. Diethynyltolan (220 mg, 0.97 mmol) was dissolved in 30 mL of diethyl ether. *n*-Butyllithium (2.0 M in hexane, 0.5 mL, 1.0 mmol) was added to the solution at −60 °C. The reaction mixture was warmed to 0 °C and cooled again to −60 °C and trimethylsilyl chloride (0.15 mL, 1.4 mmol) was added. The solution was stirred until it had reached room temperature, the solvent was removed in vacuo, and the residue was passed over a column (4 × 30 cm) filled with silica gel G 60 (Fluka, 220-440 mesh) using a mixture of *n*-pentane and diethyl ether (80:20, v/v) as the mobile phase. Recrystallization from diethyl ether yielded 230 mg (79.3%) of pure product. ^{1}H-NMR ($CDCl_3$): δ 7.49−7.46 (m, 8 H, Ar), 3.20 (s, 1 H, CC*H*), 0.28 (s, 9 H, Si*Me*$_3$); ^{13}C-NMR ($CDCl_3$): δ 132.3, 132.1, 131.7, 131.6, 123.2, 122.4,

Table 1. Summary of Polymerization Results for 4-(Ferrocenylethynyl)-4′-ethynyltolan[a]

mol equiv (*N*)	M_w calcd	M_w found	M_w/M_n	time (h)	yield (%)
55	22880	22509	1.28	10	>95
50	20830	19777	1.12	10	>95
45	18780	19191	1.18	10	>95
40	16730	16154	1.26	5	>95
35	14680	14654	1.29	5	>95
15	6480	7186	1.28	3	85
10	4430	4921	1.34	3	70

[a] Solvent: toluene, capped with ferrocenecarboxaldehyde.

104.8, 96.7, 79.3, 0.11 ($Si(CH_3)_3$). Anal. Calcd for $C_{21}H_{18}Si$: C, 84.51; H, 6.08. Found: C, 84.67; H, 6.09.

Investigation of the Type of Insertion. 4-(Ferrocenylethynyl)-4-ethynyltolan. The initiator **II** (20 mg, 26 μmol) was added to a solution of **I** (11 mg, 27 μmol) in C_6D_6 (0.5 mL). The reaction mixture turned deep red immediately. The first insertion product was characterized by the following resonances. ^{1}H-NMR: δ 12.37 (s, H_α, 1H), 7.7−7.0 (m, 16 H), 5.93 (s, H_γ, 1 H). 4.67 (t, J = 1.82, 2 H), 4.28 (s, CpH, 5 H), 4.16 (t, J = 1.82, 2 H), 3.75 (sept, 2 H, J = 4.4, C*H*Me$_2$), 1.73 (s, 6 H, (OC*Me*(CF_3)$_2$)), 1.37 (d, J = 4.4, 12 H, CH*Me$_2$*), 1.36 (s, 6 H, C*Me$_2$*Ph). ^{13}C-NMR: δ 285.3 (C_α), 154.4, 148.3, 147.9, 132.1, 130.0, 129, 127.1, 126.4, 126.3, 125.0, 123.9, 123.2, 122.5, 92.0, 86.7, 81.6, 72.2, 70.2 (CpH), 69.8, 65.9, 55.8 (*C*Me$_2$-Ph), 30.7 (C*Me$_2$*Ph), 29.5 (*C*HMe$_2$), 24.1 (CH*Me$_2$*), 19.1 (OC-*Me*(CF_3)$_2$.

Ferrocenecarboxaldehyde (50 mg, 0.24 mmol) was added to a stirred solution of the first insertion product (30 mg, 25 μmol) in C_6D_6 (0.5 mL). NMR investigations revealed that capping was achieved quantitatively after approximately 15 min. Both products, corresponding to a *cis*- and *trans*- configured butadiene, were observed.

4-((Trimethylsilyl)ethynyl)-4′-ethynyltolan: The initiator (**II**) (20 mg, 26 μmol) was added to a solution of the monomer (10 mg, 34 μmol) in C_6D_6 (0.5 mL). The reaction mixture turned deep red immediately and formation of a gel occured. β-Insertion of the monomer was observed. The first insertion product showed resonances for H_α at δ 12.33 and for H_γ at 5.94 ppm. Additionally, signals for higher insertion products at 12.68 ppm are observed.

Polymerizations. The following procedure is typical. The monomer (30 mg) was dissolved in toluene (10 mL), and the corresponding amount of the initiator was added to the well stirred solution. The color of the reaction mixture changed from yellow-orange to deep red within a few minutes. It was stirred for the time indicated in Table 1, ferrocenecarboxaldehyde was added, and stirring was continued for a further 60 min. Finally, the reaction mixture was poured into pentane, and the precipitate was washed with diethyl ether to remove unreacted ferrocenecarboxaldehyde and dried in vacuo. The polymers form transparent films when cast quickly fromed methylene chloride onto metal or glass surfaces.

Poly(4-(ferrocenylethynyl)-4′-ethynyltolan)$_{10}$. IR (KBr): 2200 m (ν(−CC−)), 1600 w (ν(C=C)), 1516 vs (ar(C−C)), 1280 m, 1105 m (Cp), 1000 w (Cp), 835 vs (δ_{ar}(C−H)), 740 s (δ(C=C)) (monomer IR (KBr): 3280 vs, 3100 w, 2200 m, 1520 s, 1410 s, 1265 s, 1110 s, 840 s, 820 m, 645 m, 625 m, 545 s). ^{1}H-NMR: δ 7.5−7.3 (m, Ar), 4.47 (m), 4.09 (bs, CpH), 4.04 (m), 3.95 (m), 3.90 (s, CpH), 1.48 (C*Me$_2$*Ph). ^{13}C-NMR: δ 137.5,126.2, 125.8, 125.5, 123.3, 84.0, 80.6, 70.0, 69.0, 68.4, 66 5, 31.3 (C*Me$_2$*Ph).

Acknowledgment. The author wishes to thank A. Knöpfler and W. Ritzberger Baumgartner for recording of the NMR data as well as S. Rüdisser for recording of the DSC data.

References and Notes

(1) Lytel, R.; Lipscomb, G. F.; Thackara, J.; Altman, J.; Elizondo, P.; Stiller, M.; Sullivan, B. In *Nonlinear and Electro-Optic Organic Devices*; Lytel, R., Lipscomb, G. F., Thackara, J., Altman, J., Elizondo, P., Stiller, M., Sullivan, B., Eds.; Plenum Press: New York, 1987; p 415.

(2) Kanis, D. R.; Ratner, M. A.; Marks, T. J. *Chem. Rev.* **1994**, *94*, 195−242.

(3) Prasad, P. N. *Polymer* **1991**, *32*, 1746.

(4) Zyss, J.; Chemla, D. S. In *Nonlinear Optical Properties of Organic Molecules and Crystals*; Zyss, J., Chemla, D. S., Eds.; Academic Press: Orlando, FL, 1987; Vol. 1, p 23.

(5) Brédas, J. L.; Adant, C.; Tackx, P.; Persoons, A.; Pierce, B. M. *Chem. Rev.* **1994**, *94*, 243−278.

(6) Long, N. J. *Angew. Chem.* **1995**, *107*, 37−56.

(7) Marks, T. J.; Ratner, M. A. *Angew. Chem.* **1995**, *107*, 167−187.

(8) Cummis, C. H. *Tetrahedron Lett.* **1994**, *35*, 857.

(9) Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, *50*, 4467.

(10) Sonogashira, K.; Ohga, K.; Takahashi, S.; Hagihara, N. *J. Organomet. Chem.* **1980**, *188*, 237−243.

(11) Altmann, M.; Enkelmann, V.; Lieser, G.; Bunz, U. H. F. *Adv. Mater.* **1995**, *7*, 726−728.

(12) Bunz, U. H. F.; Wiegelmann-Kreiter, J. E. C. *Chem. Ber.* **1996**, *129*, 785−797.

(13) Hsung, R. P.; Chidsey, C. E. D.; Sita, L. R. *Organometallics* **1995**, *14*, 4808−4815.

(14) Levy, D.; Esquivias, L. *Adv. Mat.* **1995**, *7*, 120−129.

(15) Davey, A. P.; Elliott, S.; O'Conner, O.; Blau, W. *J. Chem. Soc., Chem. Commun.* **1995**, 1433−1434.

(16) Nock, H.; Buchmeiser, M.; Polin, H.; Lukasser, J.; Jaitner, P.; Schottenberger, H. *Mol. Cryst. Liq. Cryst.* **1993**, *235*, 237.

(17) Schottenberger, H.; Buchmeiser, M.; Polin, J.; Schwarzhans, K.-E. *Z. Naturforsch.* **1993**, *48B*, 1524.

(18) Takeda, K.; Wegner, G. *Makromol. Chem.* **1972**, *160*, 349−359.

(19) Wegner, G. *Makromol. Chem.* **1972**, *154*, 35−48.

(20) Buchmeiser, M.; Schrock, R. R. *Macromolecules* **1995**, *28*, 6642−6649.

(21) Schrock, R. R.; Luo, S.; Zanetti, N.; Fox, H. H. *Organometallics* **1994**, *13*, 3396.

(22) Schrock, R. R.; Luo, S.; Lee Jr., J. C.; Zanetti, N. C.; Davis, W. M. *J. Am. Chem. Soc.* **1996**, *118*, 3883−3895.

(23) Schlund, R.; Schrock, R. R.; Crowe, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8004.

(24) Fox, H. H.; Schrock, R. S. *Organometallics* **1992**, *11*, 2763−2765.

(25) Wallace, K. C.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 644.

(26) Fox, H. H.; Wolf, M. O.; O'Dell, R.; Lin, B. L.; Schrock, R. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1994**, *116*, 2827.

(27) Szwarc, M. *Macromol. Chem. Rapid Commun.* **1992**, *13*, 141.

(28) Quirk, R. P.; Lee, B. *Polym. Int.* **1992**, *27*, 359.

(29) Penczek, S.; Kubissa, P.; Szymanski, R. *Makromol. Chem. Rapid Commun.* **1991**, *12*, 77.

(30) Matyjaszewski, K. *Macromolecules* **1993**, *26*, 1787−1788.

(31) Oskam, J. H.; Fox, H. H.; Yap, K. B.; McConville, D. H.; O'Dell, R.; Lichtenstein, B. J.; Schrock, R. R. *J. Organomet. Chem.* **1993**, *459*, 185.

MA961317F