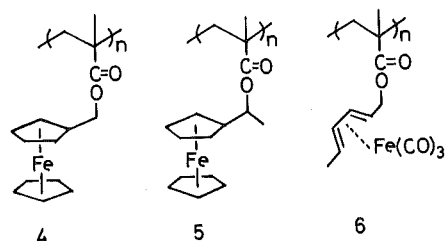


Figure 2. Direct-current conductivity of complex 7 (O) and complex 8 (□) as a function of dopant concentration.

proceeded and the initial polymer 2 could be recovered in >90% conversion as revealed by ¹³C NMR analysis (67.5 MHz). A similar reversible reaction has been observed when polymer 2, oxidized with anhydrous HCl, was treated with AgBF₄ or AgPF₆.

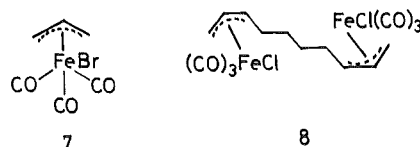
Poly[Fe(CO)₃(η⁴-2,4-hexadienyl methacrylate)] (6)



prepared according to Pittman's procedure⁹ also showed an enhanced conductivity in the semiconductor region ($\sigma = 10^{-4} \text{ S cm}^{-1}$) when sublimation of iodine was conducted on the film (thickness 0.15 mm) in a molar ratio of I₂/Fe = 0.03–0.2. Especially noteworthy is that 1:1.2 and 1:5.8 random copolymers of 2 with methyl methacrylate (polymerized with AIBN) still retain good conductivity ($\sigma = 10^{-5} \text{ S cm}^{-1}$, I₂/Fe = 0.4). This fact suggests the possibility that semiconducting materials may be obtained even by blending or mixing the M(CO)₃(η⁴-diene) with conventional organic polymers. Actually, complex 1 (5–6 wt %) dispersed in polystyrene or poly(methyl methacrylate) showed a conductivity of 10⁻⁶ S cm⁻¹ after doping (I₂/Fe = ca. 0.15). This procedure affords a facile method for preparation of novel conducting materials. Its practical utility is, however, limited because of difficulties involved in the homogeneous mixing of large quantities of the complexes (>5 mol %) with organic polymers. Phase separation and precipitation of the complex on the film as microcrystals occur very often. In this sense, homo- and copolymerization of organometallic monomers are superior to the above blending method.

To collect fundamental information on the electron conducting mechanism, chemical change during doping was investigated. The IR CO stretching vibration of 2 (2060, 1987, and 1970 cm⁻¹) shifted to higher wavenumbers (2110 and 2056 cm⁻¹) when 1 equiv of I₂ was added to 2 in CH₂Cl₂. This suggests that the Fe(CO)₃(1,3-pentadiene) group contained in 2 changed to [Fe^{II}(CO)₃(η³-allyl)]⁺X⁻ (X = I₃, I₅, etc.) or Fe^{II}(CO)₃(η³-allyl) since the CO frequencies are very close to those of well-known [Fe(CO)₄(η³-allyl)]⁺X⁻ (X = BF₄, PF₆)¹⁰ or FeX(CO)₃(η³-allyl) (X = Cl, Br) complexes.¹¹ The polymer containing the

FeCl(CO)₃(η³-allyl) species, which was prepared by reaction of 2 with dry HCl, also showed the CO absorption in nearly the same region (2080, 2035, and 2005 cm⁻¹). Thus, the doping of polymer 2 should give rise to the formation of [Fe^{II}]⁺ or Fe^{II} species. However, these species themselves are insulators as evidenced by the low conductivities of FeBr(CO)₃(η³-allyl) (7) ($\sigma_{dc} = 10^{-10} \text{ S cm}^{-1}$), of [FeCl(CO)₃]₂(1,3-η³,8,10-η³-1,9-octadiene-3,8-diyl) (8)¹² ($\sigma_{dc} = 10^{-9} \text{ S cm}^{-1}$), and of [Fe(CO)₄(η³-allyl)]BF₄ ($\sigma_{dc} = 10^{-7} \text{ S cm}^{-1}$). Therefore, it seems most probable that electron conduction takes place through mixed-valence [Fe^IFe^{II}]⁺ and/or [Fe^{II}Fe^{III}]⁺ species generated by the interaction between the [Fe^{II}]⁺ species with Fe^I or Fe^{III} species. Complexes 7 and 8 also showed semiconductivity when the doping was



performed with iodine on compressed disks (Figure 2). Both complexes behaved in a similar manner and no proximity effect was observed for 8. Electron conduction through the [Fe^IFe^{II}]⁺ species is most probable in these cases. Though measurements of EPR, magnetic susceptibility, and temperature dependency of the conductivity are required to ascertain the band gap of these semiconductors, the above findings raise the hope that doping pellets of conventional metal complexes will provide various semiconducting materials. Preliminary experiments have revealed that FeCl₂(PPh₃)₂, CoI₂(dppe), CoCl₂(*t*-BuNC)₄, and PdI₂(PPh₃)₂ have a conductivity of >10⁻⁸ S cm⁻¹ after doping while Fe₂(CO)₉, Mo(CO)₆, W(CO)₆, and FeI(η⁵-C₅H₅)(CO)₂ are insulators even when excess iodine is added. More precise experiments are in progress with single crystals of the Fe(CO)₃(η⁴-diene) and related ML_n(polyene) complexes at various temperatures.

Registry No. 2, 76171-61-4; 2 copolymer with methyl methacrylate, 92346-63-9; 3, 76171-63-6; 4, 35560-97-5; 5, 92346-61-7; 6, 92346-62-8; 7, 12192-46-0; 8, 92346-60-6; I₂, 7553-56-2; SbF₆, 17111-95-4.

References and Notes

- (1) (a) Cowan, D. O.; LeVanda, C. *J. Am. Chem. Soc.* 1972, 94, 9271. (b) Mueller-Westerhoff, U. T.; Eilbracht, P. *J. Am. Chem. Soc.* 1972, 94, 9272.
- (2) Pittman, C. U., Jr.; Suryanarayanan, B. *J. Am. Chem. Soc.* 1974, 96, 7916.
- (3) Noda, I.; Yasuda, H.; Nakamura, A. *J. Organomet. Chem.* 1983, 250, 447.
- (4) Noda, I.; Yasuda, H.; Nakamura, A. *Organometallics* 1983, 2, 1207.
- (5) Yasuda, H.; Morita, Y.; Noda, I.; Sugi, K.; Nakamura, A. *J. Organomet. Chem.* 1981, 205, C9.
- (6) Pittman, C. U., Jr.; Sasaki, Y. *Chem. Lett.* 1975, 383.
- (7) Lai, J. C.; Rousefell, T. D.; Pittman, C. U., Jr. *Macromolecules* 1971, 4, 155.
- (8) Violet, P. F.; Logan, S. R. *J. Chem. Soc., Faraday Trans. 1* 1980, 76, 578.
- (9) Pittman, C. U., Jr.; Ayers, O. E.; McManus, S. P. *J. Macromol. Sci., Chem.* 1973, 1563.
- (10) Brookhart, M.; Whitesides, T. H.; Crockett, J. M. *Inorg. Chem.* 1976, 15, 1550.
- (11) Murdoch, H. D.; Weiss, E. *Helv. Chim. Acta* 1962, 45, 1972.
- (12) Morita, Y.; Yamauchi, M.; Yasuda, H.; Nakamura, A. *Kobunshi Ronbunshu* 1980, 37, 677.

Hajime Yasuda, Ippei Noda, Seiichi Miyayama, and Akira Nakamura*

Department of Macromolecular Science, Faculty of Science, Osaka University, Toyonaka, Osaka 560, Japan

Received May 23, 1984

Butadiene 1,4-Polymerization Initiated by Bis[(η³-allyl)(trifluoroacetato)nickel]: A Perfectly "Living" Coordination System

"Living" chain polymerization reactions have been up to now a nearly exclusive feature of anionic systems,¹ although a few examples of more or less perfectly "living" initiators are known in cationic polymerization^{2,3} and long-lived radicals⁴ have been studied and used in radical homo- and copolymerization. The importance of these systems has been largely demonstrated by their capability to tailor polymer molecular weight and molecular weight distribution, to lead to end-group functionalization (mono and α,ω) of different backbones, and mainly to allow the synthesis of a variety of block copolymers.⁵

More recently, other examples of such behavior have also been found in anionic-coordination polymerization of lactones⁶ and even in coordination polymerization (Ziegler-Natta type) of propene.⁷

That situation prompts us to report now a perfectly "living" coordination initiator, namely, bis[(η³-allyl)(trifluoroacetato)nickel] or [(A)Ni(TFA)]₂, for the selective 1,4-polymerization of butadiene and its further block copolymerization.

(η³-Allyl)nickel Initiator. [(A)Ni(TFA)]₂ is an excellent catalyst for butadiene 1,4-polymerization: it displays a high activity, an excellent regioselectivity (ca. 1% of 1,2 units), and an amazing stereoselectivity controllable from 99% cis to 99% trans units, depending on the choice of proper ligands and kinetic conditions.^{8,9} The rate of initiation is high enough to ensure complete initiator conversion in the early stages of polymerization; moreover, irreversible termination with deactivation of propagation centers does not take place.¹⁰ However, hydride-transfer reactions do occur in these η³-allylic systems (through β-elimination), limiting the chain propagation reaction and the expected molecular weight. We have now found that this [(A)Ni(TFA)]₂ complex, when used under well-defined experimental conditions and in the presence of a certain amount of particular ligands, is able to promote a "living" 1,4-polymerization of butadiene, displaying exactly the same attractive kinetic characteristics as a classical anionic "living" system. Two different types of ligands were used: a typical electron donor, i.e., triphenyl phosphite (TPP) and a strongly electron-withdrawing one, i.e., tetrachlorobenzoquinone (or chloranil (CA)); of course, all manipulations were performed under controlled conditions (dry argon atmosphere or vacuum, perfectly dried solvents, and reagents). It is important to stress that under these conditions, polymers obtained have a unimodal molecular weight distribution with a rather narrow polydispersity (\bar{M}_w/\bar{M}_n between 1.2 and 2.0), a good indication for a single type of catalytic sites.

[(A)Ni(TFA)]₂-TPP System in *n*-Heptane. Experimental data pertaining to this system are gathered in Table

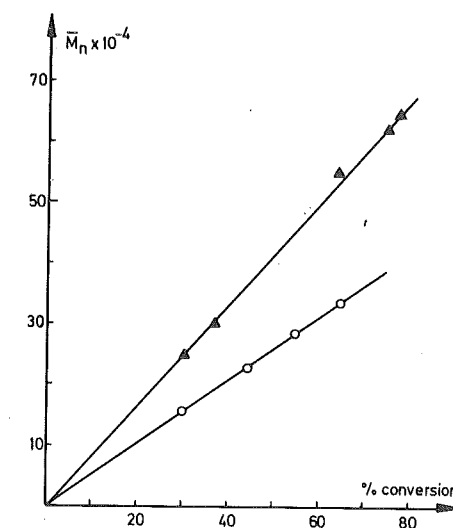


Figure 1. \bar{M}_n as a function of conversion for BD (4.8 mol·L⁻¹) polymerization with [(A)Ni(TFA)]₂: (▲) data for polymerization in heptane at 55 °C ([Ni] = 3 × 10⁻³ mol·L⁻¹, [TPP]/[Ni] = 0.18, cis-1,4 ca. 43%); (○) data for polymerization in toluene at 25 °C ([Ni] = 5 × 10⁻³ mol·L⁻¹, [Ca]/[Ni] = 0.35, cis-1,4 ca. 78%); (—) calculated lines.

I and indicate a satisfactory correlation between experimental and calculated \bar{DP} , assuming a "living" process. The fact to be stressed here is obviously that this correlation holds relatively well all over the stereoselectivity scale (i.e., whatever the cis or trans microstructure, leading to very different products). This "living" character has been further ascertained by the linear increase of \bar{M}_n with conversion, the experimental data fitting perfectly the calculated straight line (Figure 1); similar data have been obtained for other [TPP]/[Ni] ratios (0 and 0.8). A final confirmation came from seeding experiments, where after partial consumption of a first crop of monomer ([TPP]/[Ni] = 0.18, 77% conversion, $\bar{M}_n(\text{calcd}) = 66528$, $\bar{M}_n(\text{exptl}) = 65800$), further addition of butadiene ([BD]₀ = 3 mol·L⁻¹ [Ni] = 2.5 × 10⁻³ mol·L⁻¹) caused resumption of polymerization with the expected increase in \bar{MW} (53% conversion, $\bar{M}_n(\text{calcd}) = 34344$, $\bar{M}_n(\text{calcd, total}) = 100872$, $\bar{M}_n(\text{exptl, total}) = 99900$). With all these systems, the possibility exists to obtain high \bar{M}_n 's (over 10⁶) and quantitative conversions although the catalyst is expectedly somewhat less stable in the absence of monomer.

[(A)Ni(TFA)]₂-CA System in Toluene. Exactly the same trends were observed for this system, as illustrated in Table I, which shows furthermore the essential influence of the ligand concentration upon the agreement between experimental and calculated \bar{M}_n values, i.e., on the "living" character, in this toluene medium. Again, \bar{M}_n increases proportionally to conversion at constant microstructure. (See also Figure 1.)

Table I
Butadiene Polymerization with [(A)Ni(TFA)]₂, ([BD]₀ = 4.8 mol·L⁻¹)

[L]/[Ni]	[Ni], mol·L ⁻¹	solvent	T, °C	t, h	% conv	$\bar{M}_n(\text{exptl})^a$	$\bar{M}_n(\text{calcd})^b$	% cis-1,4 ^c
TPP 0.00	3 × 10 ⁻³	<i>n</i> -heptane	55	24.3	60	46.500	51.840	93.5
TPP 0.18	3 × 10 ⁻³	<i>n</i> -heptane	55	20.5	65	57.000	56.592	43.5
TPP 0.27	3 × 10 ⁻³	<i>n</i> -heptane	55	21.3	77	66.500	66.528	30.0
TPP 0.54	3 × 10 ⁻³	<i>n</i> -heptane	55	22.0	69	60.000	59.616	15.5
TPP 0.80	3 × 10 ⁻³	<i>n</i> -heptane	55	95.0	52	49.600	44.928	<2.0
CA 0.00	5 × 10 ⁻³	toluene	25	13.0	65	16.000	33.696	59.0
CA 0.20	5 × 10 ⁻³	toluene	25	3.5	41	22.400	21.254	66.0
CA 0.35	5 × 10 ⁻³	toluene	25	2.0	55	28.700	28.512	78.0
CA 0.50	5 × 10 ⁻³	toluene	25	0.6	72	37.600	37.325	89.5

^a Calculated from GPC curves. ^b Calculated as 54 × [BD]₀ × % conv × [Ni]⁻¹. ^c Calculated from IR spectra.¹⁴

In conclusion, we have now the ability to prepare "living" 1,4-polybutadiene chains over a broad range of stereostructures. Obviously, this unique behavior paves the way for the synthesis of interesting new block copolymers: suffice it to cite the preparation of a stereodiblock poly(*cis*-1,4-butadiene-*b-trans*-1,4-butadiene)¹¹ and of a poly(1,4-butadiene-*b*-styrene) diblock,^{12a} which upon hydrogenation yields an interesting poly(ethylene-*b*-styrene) copolymer useful as an emulsifier for blends of high-density polyethylene and polystyrene.^{12b}

One must realize however that one faces here all of the extremely sensitive features of classical coordination catalysis. In particular, the process is critically dependent on temperature and concentrations, on the presence of a given ligand (L) in a particular L/Ni ratio (probably in order to block coordination positions prone to promote β -elimination¹³ as will be discussed elsewhere), and very much so on the nature of the solvent.

Acknowledgment. We are indebted to FRFC (Contract 100 70) and SPPS (Contract 82/87-33) for financial support as well as to IRSIA for a fellowship to P.H.

Registry No. [(A)Ni(TFA)]₂, 32823-77-1.

References and Notes

- (1) M. Szwarc, "Carbanions, Living Polymers and Electron Transfer Processes", Wiley-Interscience, New York, 1968.
- (2) G. Berger, M. Levy, and D. Vofsi, *J. Polym. Sci.*, **34**, 183 (1966). Y. Yamashita and K. Chiba, *Polym. J.*, **4**, 200 (1973).
- (3) J. P. Kennedy, *Makromol. Chem., Suppl.*, **3**, 1 (1979); *J. Macromol. Sci., Chem.*, **A14**, 1 (1980); Lal, J. "Elastomers and Rubber Elasticity"; Mark, J. E., Ed.; American Chemical So-

- ciety: Washington, D.C., 1982; ACS Symp. Ser. No. 193, pp 214-227.
- (4) Seymour, R. B.; Stahl, G. A.; Owen, D. R.; Wood, H. "Copolymers, Polyblends and Composites"; Platzer, N. A., Ed.; American Chemical Society: Washington, D.C., 1975; Adv. Chem. Ser. No. 142, p 309.
 - (5) D. H. Richards, Symposium on Anionic Polymerization, J. McGrath, Ed., ACS 179th Meeting, Houston, 1980.
 - (6) A. Hamitou, R. Jérôme, A. J. Hubert, and Ph. Teyssié, *Macromolecules*, **6**, 651 (1973); J. Heuschen, R. Jérôme, and Ph. Teyssié, *ibid.*, **14**, 242 (1981).
 - (7) Y. Doi, S. Veki, and T. Keii, *Macromolecules*, **12**, 814 (1979); *Makromol. Chem.*, **180**, 1359 (1979); Y. Doi and R. Evens, in "Transition Metal Catalyzed Polymerizations", P. Quirck, Ed., Harwood Academic Publishers, New York, 1983.
 - (8) J. P. Durand, F. Dawans, and Ph. Teyssié, *J. Polym. Sci., Part A-1*, **8**, 979 (1970).
 - (9) J. C. Maréchal, F. Dawans, and Ph. Teyssié, *J. Polym. Sci., Part A-1*, **8**, 1993 (1970).
 - (10) J. M. Thomassin, E. Walckiers, R. Warin, and Ph. Teyssié, *J. Polym. Sci., Polym. Chem. Ed.*, **13**, 1147 (1975).
 - (11) P. Hadjiandreou, Reprints of IUPAC International Symposium on Macromolecules, Bucharest, 1983; *J. Polym. Sci., Polym. Chem. Ed.*, in press.
 - (12) (a) P. Hadjiandreou, Ph.D. Thesis, Liège, 1980; (b) R. Fayt, P. Hadjiandreou, and Ph. Teyssié, *J. Polym. Sci., Polym. Chem. Ed.*, in press.
 - (13) G. Wilke, oral communication.
 - (14) D. Morero, A. Santambrogio, L. Porri, and F. Ciampelli, *Chim. Ind. (Milan)*, **41**, 758 (1959).
 - (15) Present address: Raychem Ltd., Dorean, Swindon, Wiltshire, United Kingdom, SN3 5HH.

Pavlos Hadjiandreou,¹⁵ Michel Julémont, and Philippe Teyssié*

Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège Sart-Tilman, 4000 Liège, Belgium

Received May 25, 1984

Macromolecules

Volume 17, Number 12 December 1984

© Copyright 1984 by the American Chemical Society

Synthesis and Polymerization of Racemic and Optically Active β -Monosubstituted β -Propiolactones

Claude Lavallée,[†] Gilles Lemay,[†] Alain Leborgne,[†] Nicolas Spassky,[†] and Robert E. Prud'homme*[†]

Département de Chimie, Université Laval, Québec, Canada G1K 7P4, and Laboratoire de Chimie Macromoléculaire, Université Pierre et Marie Curie, 75230 Paris, France. Received February 7, 1984

ABSTRACT: The reaction of ketene with chloral and 2,2-dichloropropanal leads, respectively, to the synthesis of β -(trichloromethyl)- β -propiolactone (CCl₃-PL) and β -(1,1-dichloroethyl)- β -propiolactone (CH₃CCl₂-PL). Both monomers were prepared in the optically active form with enantiomeric excesses of 100% and 95% for CCl₃-PL and CH₃CCl₂-PL, respectively, using quinidine as a catalyst, and an enantiomeric excess of 100% for CH₃CCl₂-PL using brucine as a catalyst. Both monomers were also prepared in the racemic form. Enantiomeric excesses were determined from optical rotation (CCl₃-PL) or ¹H NMR spectroscopy (CH₃CCl₂-PL and CCl₃-PL) after complexation of the lactone with a europium chiral shift reagent. Polymerization was carried out in bulk and toluene solution, under vacuum, using mainly triethylaluminum as initiator. Solution characterization of the polymers was conducted by viscometry, osmometry, and gel permeation chromatography. The polymers prepared from optically active monomers are less soluble in organic solvents than those prepared from racemic monomers. In addition, the former polymers are crystalline and exhibit a high-temperature melting peak ($T_m = 275$ °C for poly(CCl₃-PL) and 235 °C for poly(CH₃CCl₂-PL)) whereas the latter polymers are amorphous and decompose at about 200 °C.

Introduction

The synthesis of high optical purity β -lactones and poly(lactones) is a difficult task. However, interesting results have been obtained with α -substituted β -propiolactones. For example, D'Hondt and Lenz¹ and Carrière and Eisenbach² prepared α -phenyl- α -ethyl- β -propiolactones having enantiomeric excesses of 80% and 95%, respectively. They showed that the polymers synthesized from these optically active monomers have a melting point of about 130 °C higher than the melting point of the polymer prepared from the corresponding racemic monomer.

More recently, Grenier et al. have prepared optically active poly(α -methyl- α -ethyl- β -propiolactones) from monomers having enantiomeric excesses of 97% and 99%.³ They have shown that these polymers have higher equilibrium melting points, enthalpies of fusion, and crystallization rates than those of the corresponding racemic polymers.⁴ Moreover, the change in properties is not a linear function of the enantiomeric excess of the polymer: most properties remain almost constant for enantiomeric excesses between 0% and 60%; between 60% and 100%, they increase linearly. This general behavior of the optically active α -substituted poly(β -propiolactones) is

therefore similar to that of the optically active polyamides, prepared by Schmidt⁵ from β -lactams containing one or two asymmetric centers.

With β -substituted β -propiolactones, the results obtained so far are less convincing. An interesting^{6,7} attempt was reported by Agostini et al., who prepared D-(+)- β -butyrolactone from β -bromobutyric acid having an enantiomeric excess of 90%. Unfortunately, some racemization occurred during the closure of the lactone whose enantiomeric excess dropped to 73%. From this lactone, poly(β -methyl- β -propiolactone), also called poly(β -hydroxybutyrate) (PHB), was synthesized and compared with the naturally occurring, high optical purity PHB. The enantiomeric excess of the PHB could not be measured but it is presumably low. An attempt to prepare optically active PHB's, using stereoselective⁸ initiators, led to polymers with moderate enantiomeric enrichments.

A series of β -monosubstituted poly(β -propiolactones) was prepared from the corresponding racemic monomers by using achiral organoaluminum or organozinc initiators (substituents = methyl, ethyl, isopropyl, *tert*-butyl, chloromethyl, dichloromethyl, trichloromethyl),⁹⁻¹¹ solid-state polymerization upon γ - and X-ray irradiation (substituents = dichloromethyl and trichloromethyl),¹² and cationic polymerization (substituent = trichloromethyl).¹³ After fractionation, a crystalline and tactic fraction is usually obtained.¹⁴

[†] Université Laval.

* Université Pierre et Marie Curie.