Macromolecules 1993, *26,* 695–700

Selective Reaction of Exo-Isomers in Ring-Opening Olefin Metathesis Polymerization (ROMP) of Fluoroalkyl-Substituted Norbornene Derivatives

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Received August 11, 1992; Revised Manuscript Received October 13, 1992

ABSTRACT: Fluoroalkyl-substituted bicyclic and tricyclic olefins were polymerized by ring-opening olefin metathesis polymerization (ROMP). The monomers used were mixtures of exo- and endo-isomers of 5,5,6-trifluoro-6-(trifluoromethyl)spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane), 5,6-difluoro-5-(trifluoromethyl)-6-(heptafluoroisopropyl)bicyclo[2.2.1]hept-2-ene, and 2,3,3,4,4,5,5,6-octafluorotricyclo[2.2.1]hept-2-ene obtained by the Diels–Alder reaction of cyclopentadiene and spiro[2.4]hepta-4,6-diene with perfluorinated olefins. The polymerization reactions were carried out with a conventional catalyst based on tungsten hexachloride. The exo-isomers were found to be more reactive than the corresponding endo-isomers. This difference in reactivity was larger for monomers containing more voluminous substituents. A model based on steric repulsion is proposed to describe the selectivity for polymerization of the exo-isomers.

Introduction

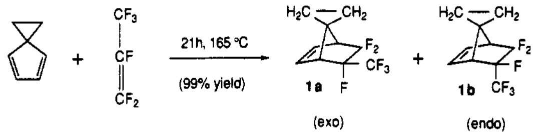
Fluoropolymers find a number of commercial applications within the coating, packaging, lens, seal, textile, and fiber-optic industrial sectors due to their interesting chemical and physical properties.[1] They are characterized by a combination of high thermal stability, excellent chemical inertness, and solvent resistance, very low dielectric constant and refractive index, and interesting surface properties, such as oil, water, and soil repellency. Most industrial processes for fluoropolymer synthesis are based on free-radical chain polymerizations.[1b,d]

Several years ago, Feast et al.[2] demonstrated that ring-opening olefin metathesis polymerization (ROMP) could be used for the preparation of partially fluorinated polymers.[3] In particular, they had been engaged in extensive studies on the influence of different metathesis catalysts on the polymer microstructure.[4] Recently, Schrock, Feast, and Gibson et al.[5] succeeded in the synthesis of a crystalline, highly stereoregular polymer based on 2,3-bis(trifluoromethyl)bicyclo[2.2.1]hepta-2,5-diene by using a well-defined molybdenum alkylidene complex.

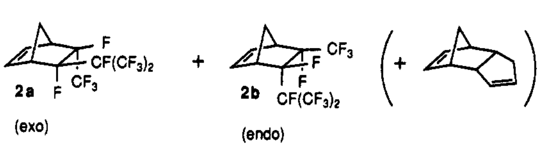
We have been interested in the preparation of amorphous polynorbornene derivatives containing a high proportion of fluorine substituents for potential applications as polymer optical fibers with improved thermal stability (i.e., high glass transition temperatures and high decomposition temperatures).[6a] However, the olefin metathesis reaction of some of the fluoroalkyl-substituted cycloolefin monomers produced only quite moderate polymer yields in the range of 30–60%.[6a,b] The present contribution describes subsequent studies which revealed that monomer conversion is affected by the different reactivity of the exo- and endo-isomers present in the monomer mixtures.

Results and Discussion

Monomer 5,5,6-trifluoro-6-(trifluoromethyl)spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane) (**1a,b**) was obtained in excellent yields by the Diels–Alder reaction of spiro[2.4]hepta-4,6-diene and hexafluoropropene (eq 1). In contrast to monomer syntheses of 5,6-difluoro-5-(trifluoromethyl)-6-(heptafluoroisopropyl)bicyclo[2.2.1]hept-2-ene (**2a,b**; eq 2) and 2,3,3,4,4,5,5,6-octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene (**3a,b**), no dimerization of the diene occurred, thus resulting in a very clean synthesis of **1a,b**. Cycloadducts **2a,b** and **3a,b** required purification by distillation using a spinning band distillation column in order to avoid the formation of cross-linked materials in subsequent metathesis polymerizations with dicyclopentadiene acting as the cross-linking reagent.[7]



(1)



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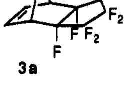
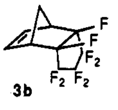


3a



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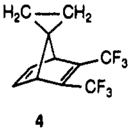

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The cycloaddition reactions produced mixtures of exo- and endo-substituted norbornene derivatives. The ratios of **1a**/**1b**, **2a**/**2b**, and **3a**/**3b** were 48/52, 65/35, and 48/52, respectively (Table I). The exo-isomers were formed in higher proportions than in the synthesis of 5-(tri-

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0024-9297/93/2226-0695$04.00/0

Table I
Synthesis of Fluoroalkyl-Substituted Cycloolefin Monomers

monomer	T/°C[a]	t/h[b]	yield/%	exo/endo[c]
1a/**1b**	165	21	99	48/52
2a/**2b**	155	64	46	65/35
3a/**3b**	150	72	45	48/52
4	110	13	99	*d*

[a] Reaction temperature. [b] Reaction time. [c] Ratio of exo- to endo-isomer, determined by GC and NMR spectroscopy. [d] Exists as a single isomer.

fluoromethyl)bicyclo[2.2.1]hept-2-ene with reported exo/endo ratios below 30/70 for similar reaction conditions.[8,4c]

Isomers **1a** and **1b** were partially separated by distillation (at 21 Torr). However, isomers **2a** and **2b** and isomers **3a** and **3b** could not be separated by distillation. The exo/endo stereochemistry of these partially fluorinated cycloolefins was established by ^{13}C and ^{19}F NMR spectroscopy. Figure 1 shows the ^{19}F NMR spectrum of a cycloolefin mixture (first fraction obtained by distillation of the crude reaction product) containing 28% of exo-isomer **1a** and 72% of endo-isomer **1b**. Both isomers are distinguished on the basis of the following features:

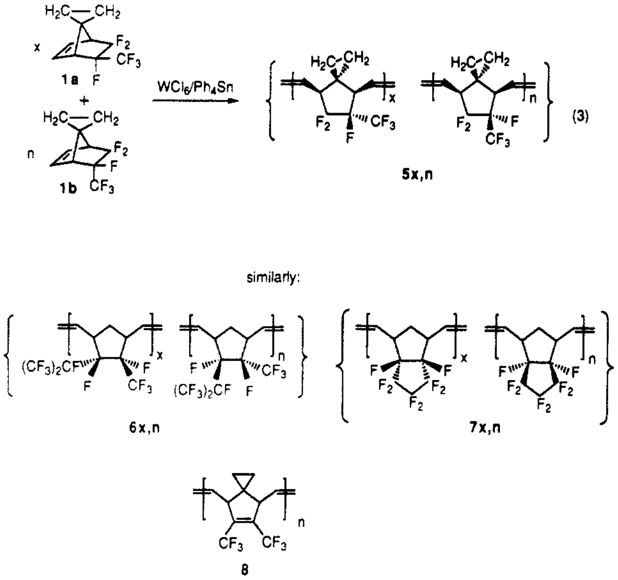
The equatorial fluorine in the 6-position, F_{6e} at $\delta = -171.2$, gives rise to a vicinal coupling to bridgehead proton H_1 with ^3J ($F_{6e}H_1$) = 6 Hz (Figure 1).[9] No coupling $^3J(F_{6a}H_1)$ was observed for the axial fluorine F_{6a} of **1a** at $\delta = -164.3$ due to a dihedral angle ($F_{6a}CCH_1$) close to 90° (the dihedral angle ($F_{6e}CCH_1$) in **1b** is approximately 30°).[10]

A coupling constant $J(F_{6e}F_{5e})$ of 13 Hz was recorded for compound **1b**. The coupling of F_{6a} to F_{5a} in **1a** is so small that it cannot be resolved in Figure 1.[9]

The ^{13}C NMR signal of the *exo*-CF_3 substituent of **1a** at $\delta = 123.5$ appears at a lower field than the *endo*-CF_3 group of **1b** ($\delta = 123.0$).[11]

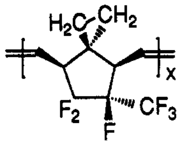
The assignment of exo and endo for the isomer mixture of 2,3,3,4,4,5,5,6-octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene (**3a,b**) was established by a two-dimensional J-resolved ^1H NMR spectrum. Figure 2 shows the chemical shift dimension of this spectrum. A doublet at $\delta = 3.19$ with a heteronuclear coupling constant $^3J(H_{1,4}F_{5,6}) = 5$ Hz was recorded for the bridgehead protons H_1 and H_4 of the endo-isomer. No coupling was observed for the bridgehead protons of the exo-isomer at $\delta = 3.34$. In addition, the exo-isomer **3a** is characterized by coupling of the bridge carbon (C-7) to the two axial fluorines of C-5 and C-6 with $^3J(C_7,F_{5,6}) = 6.5$ Hz, thus giving rise to a triplet at $\delta = 41.2$ in the ^{13}C NMR spectrum. In contrast, the signal corresponding to the bridge carbon (C-7) of the endo-substituted cycloolefin **3b** appears as a singlet at $\delta = 48.9$.

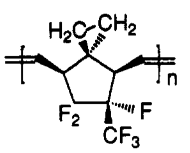
The fluoroalkyl-substituted monomers of Table I were subjected to ring-opening olefin metathesis polymerization (ROMP) with a conventional catalyst system based on WCl_6 and tetraphenyltin (mole ratio 1:2). This is normally a highly reactive catalyst which is known to polymerize 10^2–10^3 equiv of norbornene within a minute.[3b] However, more severe reaction conditions were required to obtain at least moderate yields of fluoroalkyl-substituted polymers **5–8** (Table II). With the exception of the synthesis of polymer **8**, reaction times were between 18 and 72 h at reaction temperatures of 70 to 82 °C. These reaction conditions reflect a drastically decreased monomer reactivity as a result of a reduced electron density of the carbon–carbon double bond caused by fluoro and fluoroalkyl substitution. (The electron-withdrawing influence of the fluoroalkyl groups on the carbon–carbon double bond -HC=CH- affected by the metathesis reaction is moderated by the second double bond in monomer **4**, thus making this monomer slightly more reactive than monomers **1a,b–3a,b**.) Equation 3 outlines the metathesis polymerization of 5,5,6-trifluoro-6-(trifluoromethyl)spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane) (**1a,b**) which leads to polymer ***5x,n***.[12] The steric bulk of the cyclopropane ring of monomer **1a,b** was not sufficient to prevent the approach of the catalytically active transition-metal carbene species to the exo-face of the monomer.[13]



After 65 h at 77 °C, 85% of the initial amount of exo-compound **1a** and 45% of the initial *endo*-cycloolefin **1b** had been consumed (determined by GC analysis),[14] which indicates that the exo-isomer is moderately more reactive than the endo-isomer. This result is in agreement with the NMR analysis of the product obtained from polymerization P1 of Table II. The ratio ***x*/*n*** in polymer (i.e., the ratio of structural units based on the exo-isomer to structural units based on the endo-isomer in polymer ***5x,n***, Table II) is 70/30 for the polymer of reaction P1. Slightly more severe reaction conditions, 72 h at 82 °C in polymerization P2 (Table II), resulted in a higher yield but nearly unchanged composition of polymer ***5x,n***: ***x*/*n*** in polymer = 67/33.

Figure 3 presents the ^{19}F NMR spectrum of polymer ***5x,n*** obtained from polymerization P1 (Table II). The repeating unit derived from the exo-substituted norbornene derivative **1a** and the repeating unit produced from endo-isomer **1b** are distinguished by chemical shift differences of the trifluoromethyl groups and the fluorine β to CF_3. The signal corresponding to F_{x6a}, formerly the axial fluorine-6 of exo-isomer **1a**, now fluorine-6 on the five-membered ring cis to the olefin substituent of polynorbornene derivative ***5x,n***, is substantially shifted upfield to $\delta = -194.2$ (Figure 3). This marked difference from δ −164.4 (Figure 1) is caused by the change in the





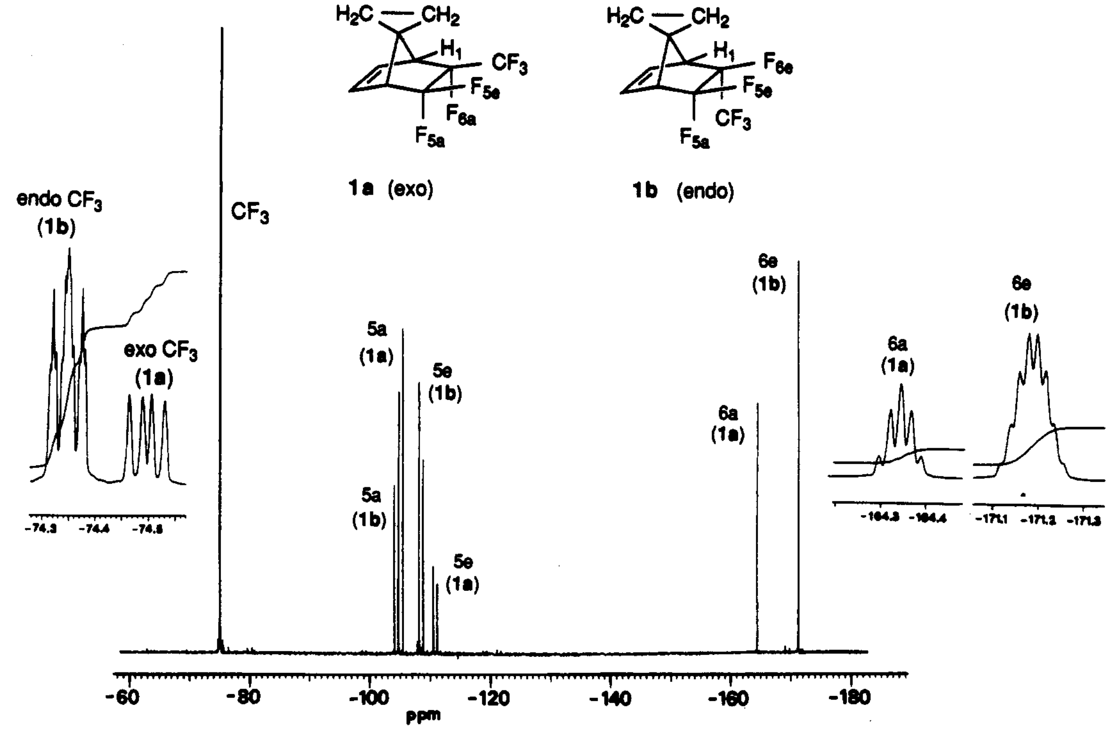


Figure 1. ^{19}F NMR spectrum (338.8 MHz) of 5,5,6-trifluoro-6-(trifluoromethyl)spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane) containing 28% of exo-isomer **1a** and 72% of endo-isomer **1b** (first fraction obtained by distillation of the Diels–Alder reaction product); solvent $CDCl_3$.

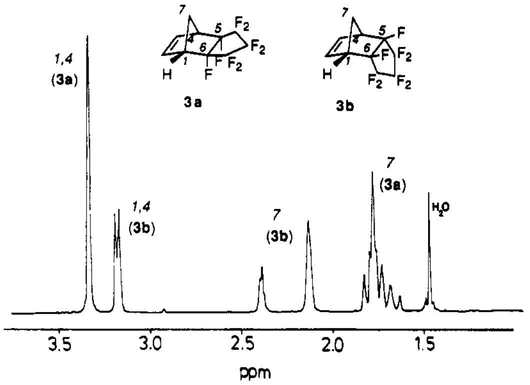


Figure 2. "^{1}H-decoupled" ^{1}H NMR (400-MHz) spectrum obtained from a two-dimensional *J*-resolved spectrum of a mixture of *exo*- and *endo*-2,3,3,4,4,5,5,6-octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene (**3a,b**); solvent $CDCl_3$.

shielding effects (induced by the carbon–carbon double bond) after ring opening of the bicyclic unit.

Both structural units of **5*x*,*n*** are also distinguished by different ^{13}C NMR shifts (Figure 4) for the allylic carbons in the β-position to the trifluoromethyl group and by different shifts assigned to the quaternary carbons: δ = 50.9, 48.2, 24.3, and 23.5 for C_{1n}, C_{1x}, C_{7x} and C_{7n}, respectively.

Considerably more pronounced is the difference in monomer reactivity between the exo- and endo-isomers of 5,6-difluoro-5-(trifluoromethyl)-6-(heptafluoroisopropyl)-bicyclo[2.2.1]hept-2-ene (**2a** and **2b**) and 2,3,3,4,4,5,5,6-octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene (**3a** and **3b**).[15] Only 10–12% of endo-isomer **3b** was incorporated in polynorbornene derivative **7*x*,*n*** (***x***/***n*** in polymer = 88/12 and 90/10 for polymerizations P4 and P5 of Table II, respectively). Exo-isomer **3a** was completely consumed during polymerization P4; the remaining monomer retained after olefin metathesis was exclusively composed of endo-isomer **3b**. The ^{19}F NMR spectrum of **7*x*,*n*** shows a set of signals of δ = −191.6, −191.9, −192.8, −193.1, and −193.6 corresponding to repeating units derived from the exo-derivative **3a** and a group of signals at δ = −165.2, −166.0, and −166.9 assigned to units based on endo-isomer **3b**. In addition, the ^{13}C NMR signals of the allylic carbons allowed us to make a distinction between units obtained from exo- and endo-isomers **3a** and **3b**: δ = 45.9 (d, 18.7 Hz, α to trans –C═C– bonds) and 41.0 (dm, 19.8 Hz, α to cis –C═C– linkages) for structures obtained from the exo-isomer and δ = 48.7 (m, α to trans –C═C–) and 44.6 (m, α to cis –C═C–) for units obtained from endo-compound **3b**.[16]

The polymerization of 5,6-difluoro-5-(heptafluoroisopropyl)-6-(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (**2a,b**) proceeded with a high selectivity for the exo-isomer. An initial exo/endo ratio of 62/38 was used for the synthesis of partially fluorinated polynorbornene derivative **6*x*,*n***. After 52 h at 70 °C, 86% of exo-isomer **2a** and 3% of endo-isomer **2b** had been consumed,[14] thus producing a polymer with ***x***/***n*** in polymer = 98/2 (metathesis polymerization P3 of Table II).

According to the results of Table II the exo/endo selectivity for olefin metathesis polymerizations seems to be dependent on the steric bulk of the fluoroalkyl substituents in the 5- and 6-positions of norbornene derivatives **1a,b**–**3a,b**. The biggest difference in reactivity between exo- and endo-substituted cycloolefins was observed for monomer **2a,b** containing the largest substituent, i.e., a perfluoroisopropyl group. Monomer **1a,b** bearing the smallest substituent, a trifluoromethyl group, showed the smallest exo/endo selectivity. Taking into account that chain propagation in metathesis polymerizations proceeds by a transition-metal carbene approaching the exo-face of the monomer, the lower reactivity of the endo-isomer can derive from the steric interference between adjacent groups of cis-substituted five-membered rings obtained upon ring opening of endo-substituted bicyclic structures (Scheme I, path a). Productive cleavage of a metallacyclobutane intermediate is preferred, when the resulting transition-metal carbene and the fluoroalkyl substituent are positioned further apart as in the trans-1,2-substituted cyclopentane structure of Scheme I (path b).[17]

Integration of the ^{13}C NMR signals corresponding to the allylic carbons gave *trans*/*cis*-olefin ratios of 92/8, 80/

Table II
Preparation of Partially Fluorinated Polynorbornene Derivatives by Olefin Metathesis Polymerization

no.[a]	polymer	x/n[b] in polymer	exo/endo[c] in monomer	trans/cis[d]	T/°C[e]	t/h[f]	yield/%
P1	**5x,n**	70/30	55/45[g]	92/8	77	65	64
P2	**5x,n**	67/33	55/45[g]	92/8	82	72	82
P3	**6x,n**	98/2[h]	62/38	[i]	70	52	53
P4	**7x,n**	88/12	48/52	80/20	70	24	55
P5	**7x,n**	90/10	48/52	80/20	70	18	36
P6	8			80/20	70	10	100

[a] Initial molar ratios of monomer:Ph_4Sn:WCl_6 were 200:2:1 for polymerizations P1 and P2, 150:2:1 for polymerizations P4 and P5, and 500:2:1 for polymerizations P3 and P6; solvent = toluene for polymerizations P3–P5 and *p*-xylene for P1, P2, and P6. Inherent viscosities η_{inh} were 0.63, 0.94, 0.59, 0.66, 0.46, and 0.73 dL/g for the products of polymerizations P1–P6, respectively. [b] Ratio of exo- and endo-monomer units incorporated in the corresponding polymer, determined by ^{19}F NMR spectroscopy and GC analysis of initial and residual isomer composition (internal standard = decane). [c] Initial exo- to endo-isomer ratio of the monomer determined by GC and NMR spectroscopy. [d] *trans/cis*-Olefin ratio determined by ^{13}C NMR spectroscopy. [e] Reaction temperature. [f] Reaction time. [g] The third fraction (T = 69 °C at 21 Torr) obtained from distillation of the crude Diels–Alder product, was used for polymer synthesis. [h] Monomer consumption monitored by gas chromatography. [i] Not determined due to very low solubility in common deuterated solvents.

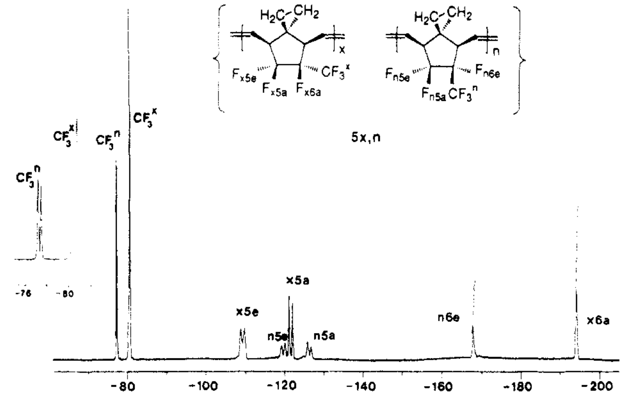


Figure 3. ^{19}F NMR spectrum (282.4 MHz) of poly(spironorbornene) derivative **5x,n**; solvent acetone-d_6.

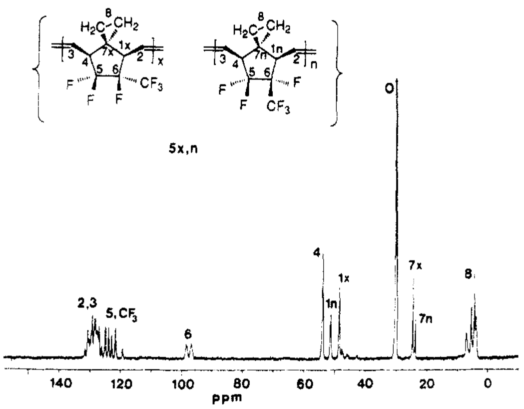
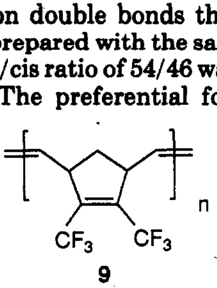


Figure 4. ^{13}C NMR spectrum (100.6 MHz) of poly(spironorbornene) derivative **5x,n**; solvent acetone-d_6. Assignments are made on the basis of data published by Feast et al.[4a] and Ivin and Rooney et al.[16]

20, and 80/20 for polymers **5x,n**, **7x,n**, and 8, respectively (Table II). These polymers contain a larger fraction of trans carbon–carbon double bonds than polynorbornadiene derivative 9 prepared with the same catalyst WCl_6/$(C_6H_5)_4Sn$. A trans/cis ratio of 54/46 was reported for the latter polymer.[4a] The preferential formation of trans



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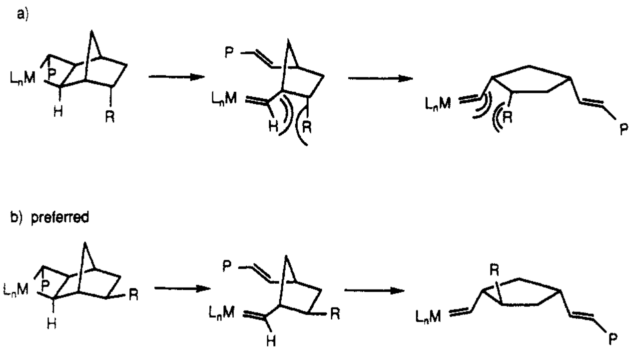
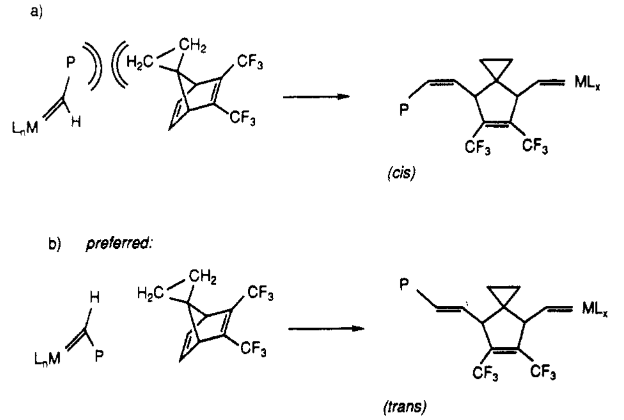
carbon–carbon double bonds in polymer **5x,n** and 8 can be attributed to the steric effect of the three-membered ring. The approach of monomer 4 with the cyclopropane ring pointing away from the α-substituent of the propagating carbene is less hindered (Scheme II, path b).[17]

Scheme I
Ring-Opening Olefin Metathesis of (a) *endo*- and (b) *exo*-Norbornene Derivatives



Scheme II
Preferred Formation of *trans*-Olefin Units due to Steric Hindrance Caused by the Cyclopropane Ring



The high trans/cis ratio for polymer **7x,n** can be caused by the low monomer reactivity of **3a,b** affecting a greater discrimination (than in the synthesis of 8) between two possible transition states: (a) involving the methylene bridge (C-7) of the monomer positioned away from the α-substituent of the transition-metal carbene and (b) involving the methylene bridge directed toward the carbene substituent.

Conclusions

Fluoroalkyl-substituted polynorbornene derivatives were prepared by ring-opening olefin metathesis polymerization. The cyclopropane ring of 5,5,6-trifluoro-6-(trifluoromethyl)-spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane) and 2,3-bis(trifluoromethyl)spiro(bicyclo[2.2.1]hepta-2,5-diene) did not prevent the metathesis reaction. However, the corresponding polymers contained a large proportion of trans carbon–carbon double bonds caused by the steric influence of the three-membered ring. Exo-isomers of fluoroalkyl-substituted norbornene derivatives displayed a higher reactivity than the corresponding endo-isomers, thus resulting in the formation of polymers with a larger proportion of repeating units based on the exo-compound. Larger fluoroalkyl substituents resulted in higher selectivities for exo-isomers. The difference in reactivity is described by a model based on steric repulsion between the fluoroalkyl substituent and the transition-metal carbene unit.

Experimental Section

General Procedures. All work involving air- and/or moisture-sensitive compounds was carried out by using standard high-vacuum, Schlenk or drybox (M. Braun) techniques. NMR spectra were recorded on Bruker AC 300 (300.133-MHz), Bruker WH 400 (400.132-MHz), and Bruker AMX 500 (500.137-MHz) instruments. Inherent viscosities were determined for polymer solutions (0.3 g/dL) in (trifluoromethyl)benzene at 25 °C. Gas chromatographic analysis was carried out on a Chrompack Packard 438 A gas chromatograph equipped with a DB5 glass capillary column (15 m). Differential scanning calorimetry (DSC) was performed on a Mettler DSC 20 (TC 10A processor).

Materials. *trans*-4-(Trifluoromethyl)perfluoropent-2-ene (96.7% by GC) and hexafluoropropene were kindly supplied by Hoechst AG. These fluoroolefins and octafluorocyclopentene (Heraeus) were used without further purification. Cyclopentadiene was freshly prepared by thermal decomposition of dicyclopentadiene. Partially fluorinated monomers **1a,b–4** were dried over calcium hydride, vacuum transferred, and stored under argon. Toluene and *p*-xylene were vacuum transferred from sodium benzophenone ketyl and stored under argon. Tungsten hexachloride (Aldrich, 99.9%) and tetraphenyltin (Aldrich) were used as obtained. We described the synthesis of 2,3-bis(trifluoromethyl)spiro(bicyclo[2.2.1]hepta-2,5-diene-7,1′-cyclopropane) (4) in a recent publication.[6a]

Preparation of 5,5,6-Trifluoro-6-(trifluoromethyl)spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane) (1a,b). A 100-mL steel autoclave was charged with 24.0 g (0.26 mol) of spiro[2.4]hepta-4,6-diene[18] and 100 mg of hydroquinone. A total of 45.0 g (0.30 mol) of hexafluoropropene was transferred from a lecture bottle by cooling the autoclave to −78 °C (with a dry ice/acetone bath). The mixture was heated in an oil bath to 165 °C for 21 h. Yield: 62.2 g (99%) of Diels–Alder adduct containing 48% of **1a** (exo) and 52% of **1b** (endo).

^{1}H NMR ($CDCl_3$): exo-isomer **1a**, δ 6.45 (m, 2 H, H_2 and H_3), 2.91 (m, 1 H, H_1), 2.64 (m, 1 H, H_4), 0.95 (m, 2 H, $H_{8(syn)}$), 0.57 (m, 2 H, $H_{9(anti)}$); endo-isomer **1b**, δ 6.36 (m, 2 H, H_2 and H_3), 2.70 (m, 1 H, H_1), 2.64 (m, 1 H, H_4), 0.94 (m, 2 H, $H_{8(syn)}$), 0.57 (m, 2 H, $H_{9(anti)}$).

^{13}C NMR ($CDCl_3$): exo-isomer **1a**, δ 136.7 (dd, J_1 = 5.2 Hz, J_2 = 0.7 Hz, C_3), 134.6 (ddd, J_1 = 5.7 Hz, J_2 = 2.1 Hz, J_3 = 1.1 Hz, C_2), 125.4 (ddd, $^1J(C_5F_5)$ = 272.4 Hz, $^1J(C_5F_5)$ = 266.4 Hz, $^2J(C_5F_{6a})$ = 16.6 Hz, C_5), 123.5 (qd, $^1J(CF_{CF3})$ = 282.9 Hz, $^2J(CF_{6a})$ = 32.7 Hz, CF_3), 96.7 (dm, $^1J(C_6F_{6a})$ = 208 Hz, C_6), 55.4 (dd, $^2J(C_4F_5)$ = 22.2 Hz, $^2J(C_4F_5)$ = 20.8 Hz, C_4), 52.4 (dd, $^2J(C_1F_{6a})$ = 20.2 Hz, $^3J(C_1F_5)$ = 1.3 Hz, C_1), 39.8 (ddd, $^3J_1$ = 7.0 Hz, $^3J_2$ = 1.3 Hz, J_3 = 0.6 Hz, C_7), 11.2 (dd, $^4J_1$ = 4.1 Hz, $^4J_2$ = 2.3 Hz, $C_{8(syn)}$), 3.9 (s, $C_{9(anti)}$); endo-isomer **1b**, δ 134.7 (dm, J_1 = 4.5 Hz, C_2), 134.4 (d, $^3J(C_3F_5)$ = 5.5 Hz, C_3), 125.5 (dddq, $^1J(C_5F_5)$ = 276.3 Hz, $^1J(C_5F_5)$ = 264.4 Hz, $^2J(C_5F_{6e})$ = 16.2 Hz, $^3J(C_5F_{CF3})$ = 1.6 Hz, C_5), 123.0 (qd, $^1J(CF_{CF3})$ = 282.6 Hz, $^2J(CF_{6e})$ = 31.0 Hz, CF_3), 96.7 (dm, $^1J(C_6F_{6e})$ = 216 Hz, C_6), 55.0 (dd, $^2J(C_4F_5)$ = 22.1 Hz, $^2J(C_4F_5)$ = 21.2 Hz, C_4), 53.6 (ddd, $^2J(C_1F_{6e})$ = 20.2 Hz, $^3J(C_1F_5)$ = 1.6 Hz, $^3J(C_1F_5)$ = 0.5 Hz, C_1), 42.8 (dq, $^3J(C_7F_{5a})$ = 6.7 Hz, $^4J(C_7F_{CF3})$ = 0.8 Hz, C_7), 9.5 (ddd, $^4J(C_8F_{5a})$ = 4.2 Hz, $^4J_2$ = 1.2 Hz, $^4J_3$ = 0.5 Hz, $C_{8(syn)}$), 2.5 (t, ^4J = 1.4 Hz, $C_{9(anti)}$).

^{19}F NMR ($CDCl_3$): exo-isomer **1a**, δ −74.5 (dd, $^4J(CF_3F_{5e})$ = 14 Hz, $^3J(CF_3F_{6a})$ = 8 Hz, CF_3), −104.6 (d, $^2J(F_{5a}F_{5e})$ = 237 Hz, F_{5a}), −110.4 (dqdd, $^2J(F_{5e}F_{5a})$ = 237 Hz, $^4J(F_{5e}CF_3)$ = 14 Hz, $^3J(F_{5e}H_4)$ = 7 Hz, $^5J(F_{5e}H_{9(or\ 8)})$ = 7 Hz, F_{5e}), −164.3 (qd, $^3J(F_{6a}CF_3)$ = 8 Hz, $^5J(F_{6a}H_8)$ = 8 Hz, F_{6a}); endo-isomer **1b** δ −74.4 (ddt, $^4J(CF_3F_{5a})$ = 11 Hz, $^3J(CF_3F_{6e})$ = 8 Hz, J_3 = 1.8 Hz, CF_3), −103.9 (dqm, $^2J(F_{5a}F_{5e})$ = 235 Hz, $^4J(F_{5a}CF_3)$ = 11 Hz, F_{5a}), −108.0 (ddm, $^2J(F_{5e}F_{5a})$ = 235 Hz, $^3J(F_{5e}F_{6e})$ = 13 Hz, F_{5e}), −171.2 (dqdd, $^3J(F_{5e}F_{6e})$ = 13 Hz, $^3J(F_{5e}CF_3)$ = 8 Hz, $^3J(F_{5e}H_1)$ = 7 Hz, $^5J(F_{5e}H_8)$ = 7 Hz, F_{6e}) (atom labeling as for ^{13}C NMR spectrum and Figure 1). Anal. Calcd for $C_{10}H_8F_6$ (242.16): C, 49.60; H, 3.33; F, 47.07. Found: C, 49.65; H, 3.30; F, 47.4.

Isomers **1a** and **1b** were partially separated by distillation at 21 Torr: 6 g of fraction 1 with **1a**/**1b** = 28/72 at 66–67 °C, 1 g of fraction 2 with **1a**/**1b** = 45/55 at 68 °C, and 51 g of fraction 3 with **1a**/**1b** = 55/45 at 69 °C (a small residue remained in the distillation flask). Determination of isomer ratios was carried out by gas chromatography. Retention times: 10.45 min for **1b** and 10.77 min for **1a** (oven: 5 min at 40 °C and then a heating rate of 10 °C/min to 250 °C).

5,6-Difluoro-5-(heptafluoroisopropyl)-6-(trifluoromethyl)bicyclo[2.2.1]hept-2-ene (2a,b) was prepared in a similar fashion: 0.15 mol of *trans*-4-(trifluoromethyl)perfluoropent-2-ene and 0.15 mol of cyclopentadiene were heated for 64 h at 155 °C; distillation with a spinning band distillation column, bp 78 °C at 25 Torr; 46% yield, 62% exo-isomer **2a** and 38% endo-isomer **2b**; gc analysis, 10.16-min retention time for **2a** and 10.30 min for **2b** (oven: 5 min at 40 °C and then 10 °C/min to 250 °C).

^{1}H NMR ($CDCl_3$): exo-isomer **2a**, δ 6.38 (m, H_2), 6.27 (m, H_3), 3.64 (m, H_4), 3.23 (dm, J = 6.8 Hz, H_1), 2.23 (dm, J = 10.9 Hz, H_{7syn}), 1.95 (m, H_{7anti}); endo-isomer **2b**, δ 6.32 (m, H_2 and H_3), 3.41 (m, H_4), 3.30 (m, H_1), 2.29 (dm, J = 10.0 Hz, H_{7syn}), 1.95 (m, H_{7anti}).

^{13}C NMR ($CDCl_3$): δ 135.8 (d, $J(CF)$ = 6.6 Hz, C_2 of **2a**), 135.3 (m, C_3 of **2b**), 134.9 (m, C_2 of **2b**), 134.7 (d, $J(CF)$ = 6.3 Hz, C_3 of **2a**), 122.1 (qd, $^1J(CF)$ = 285.6 Hz, $^2J(CF)$ = 30.7 Hz, C_6–CF_3 of **2b**), 121.8 (qd, $^1J(CF)$ = 284.5 Hz, $^2J(CF)$ = 29.4 Hz, C_6–CF_3 of **2a**), 120.3 (qm, $^1J(CF)$ = 289.7 Hz, $CF(CF_3)_2$), 119.7 (qm, $^1J(CF)$ = 288.7 Hz, $CF(CF_3)_2$), 102.5 (dm, C_5), 99.8 (dm, $^1J(CF)$ = 212 Hz, $CF(CF_3)_2$ of **2a**), 93.5 (dm, C_6), 90.6 (dm, $CF(CF_3)_2$ of **2b**), 51.8 (d, $^2J(C_4F_5)$ = 21.5 Hz, C_4 of **2b**), 49.3 (d, $^2J(CF)$ = 22.0 Hz, C_4 of **2a**), 49.2 (d, $^2J(C_1F_6)$ = 21.1 Hz, C_1 of **2a**), 47.5 (d, $^2J(CF)$ = 20.6 Hz, C_1 of **2b**), 43.8 (s, C_7 of **2a**), 43.7 (s, C_7 of **2b**).

^{19}F NMR ($CDCl_3$): δ −69.8 (m, CF_3), −70.8 (m, CF_3), −71.5 (m, CF_3), −72.1 (m, CF_3), −73.0 (m, CF_3), −161.7 (m, F_5 (or F_6) of **2a**), −167.1 (m, F_6 (or F_5) of **2b**), −167.8 (m, F_6 (or F_5) of **2a**), −168.5 (m, F_5 (or F_6) of **2b**), −178.4 (d, $^3J(FF)$ = 31.9 Hz, $CF(CF_3)_2$ of **2a**), −180.3 (d, $^3J(FF)$ = 32 Hz, $CF(CF_3)_2$ of **2b**).

Anal. Calcd for $C_{11}H_6F_{12}$ (366.14): C, 36.08; H, 1.65; F, 62.27. Found: C, 36.28; H, 1.78; F, 62.5.

2,3,3,4,4,5,5,6-Octafluorotricyclo[5.2.1.0^{2,6}]dec-8-ene (3a,b) was synthesized as previously described.[6b]

^{1}H NMR ($CDCl_3$): exo-isomer **3a**, δ 6.42 (s, H_2 and H_3), 3.34 (m, H_1 and H_4), 1.75 (m, H_7), 1.67 (m, H_7); endo-isomer **3b**, δ 6.07 (m, H_2 and H_3), 3.19 (m, H_1 and H_4), 2.39 (dd, J_1 = 10 Hz, J_2 = 1.1 Hz, H_7), 2.13 (dd, J_1 = 10 Hz, J_2 = 1.4 Hz, H_7).

^{13}C NMR ($CDCl_3$): exo-isomer **3a**, δ 136.6 (s, C_2, C_3), 113.4 (m, C(F)), 111.3 (m, C(F)), 98.4 (dm, C_5, C_6), 44.9 (dm, 2$J(CF)$ = 19.7 Hz, C_1, C_4), 41.2 (t, $^3J(CF)$ = 6.5 Hz, C_7); endo-isomer **3b**, δ 135.1 (C_2, C_3), 113.4 (C(F)), 111.3 (C(F)), 98.4 (C_5, C_6), 48.9 (C_7), 48.3 (dm, $^2J(CF)$ = 22.1 Hz, C_1, C_4).

Preparation of Poly[[3,5-[1,1,2-trifluoro-2-(trifluoromethyl)spiro-4,1′-(cyclopropane)cyclopentylene]]vinylene] 5*x*,*n*. A heavy-walled glass tube equipped with a female NS 14.5 joint and a Teflon valve[19] was charged with 6.0 mg (15.1 μmol) of WCl_6, 12.9 mg (30.2 μmol) of $(C_6H_5)_4Sn$, and 1 mL of *p*-xylene. After stirring at room temperature for 15 min, 731 mg (3.02 mmol) of 5,5,6-trifluoro-6-(trifluoromethyl)spiro(bicyclo[2.2.1]hept-2-ene-7,1′-cyclopropane) (**1a,b**) (55% of **1a** and 45% of **1b**) dissolved in 3 mL of *p*-xylene was added. The mixture was heated to 82 °C for 72 h. The resulting polymer was precipitated with petroleum ether (bp: 40–60 °C). Yield: 600 mg (82%). ***x*/*n*** in polymer = 67/33; η_{inh} = 0.94 dL/g; T_g = 174 °C.

^{1}H NMR (acetone-d_6): δ 5.53 (m, olefinic H), 3.62 (b m, allylic H (of *cis*-olefin unit), 3.47, 3.38, 3.28 (unresolved b m, allylic H (of *trans*-olefin unit)), 0.53 (b m, cyclopropyl H (of *x*)), 0.41 (b m, cyclopropyl H (of *n*)).

^{13}C NMR (acetone-d_6): δ 131.2, 130.4, 129.9, 129.2, 128.9, 128.2, 127.8, 127.2 (unresolved signals, C_2 and C_3), 124.5 (ddt, $^1J(CF)$ = 274 Hz, $^1J(CF)$ = 258 Hz, $^2J(CF)$ and $^3J(CF)$ = 22 Hz, C_5), 122.3 (qt, $^1J(CF)$ = 284 Hz, $^2J(CF)$ and $^3J(CF)$ = 25 Hz, CF_3), 97.3 (dm, $^1J(CF)$ = 200 Hz, C_6), 53.8 and 53.6 (unresolved signals, C_4 α to *trans*-olefin unit), 50.9 (C_{1n} α to *trans*-olefin unit), 48.2 (C_{1x} α to *trans*-olefin unit), 47.4, 47.2, 47.0 (unresolved signals, C_4 α to *cis*-olefin unit), 45.8–45.5 (set of unresolved signals, C_{1n} α to *cis*-olefin unit), 42.5 (C_{1x} α to *cis*-olefin unit), 24.3 (C_{7x}), 23.5 (C_{7n}), 6.7, 5.2, 4.2, 3.5 (C_{8n}, C_{8x}, $C_{8'x}$, $C_{8'n}$) (labeling of atoms identical with the formula of Figure 4).

^{19}F NMR (acetone-d_6): δ −77.2, −77.5 (CF_{3n}, HH and HT diads), −80.7 (CF_{3x}), −109.5 (dm, ^2J(FF) = 261 Hz, F_{x5e}), −119.7 (dm, ^2J(FF) = 232 Hz, F_{n5e}), −121.5 (d, ^2J(FF) = 250 Hz) and −121.7 (d, ^2J(FF) = 251 Hz) (F_{x5a}, HH and HT diads), −126.3 (dm, ^2J(FF) = 230 Hz, F_{n5a}), −168.0 (F_{n6e}), −194.2 (F_{x6e}) (labeling of atoms identical with the formula of Figure 3).

Anal. Calcd for $(C_{19}H_8F_6)_n$ [$(242.16)_n$]: C, 49.60; H, 3.33; F, 47.07. Found: C, 49.64; H, 3.45; F, 47.1.

Fluoroalkyl-substituted polynorbornene derivatives **6*x*,*n*** and **7*x*,*n*** were prepared similarly; the preparation of poly[[3,5-[1,2-bis(trifluoromethyl)spiro-4,1′-(cyclopropane)cyclopentenylene]]-vinylene] (8) was described in a recent publication.[6a]

Poly[[3,5-[1,2-difluoro-1-(trifluoromethyl)-2-(heptafluoroisopropyl)cyclopentylene]]vinylene] 6*x*,*n*: 6.81 mmol of monomer **2a,b** (62% of exo-isomer **2a**, 38% of endo-isomer **2b**), 13.6 μmol of WCl_6, and 27.2 μmol of $(C_6H_5)_4Sn$ in 5 mL of toluene; 52 h at 70 °C; 53% yield; 86% of exo-isomer **2a** and 3% of endo-isomer **2b** was consumed during the polymerization (by GC), i.e., ***x*/*n*** in polymer = 98/2; η_{inh} = 0.59 dL/g; T_g = 182 °C.

^{1}H NMR (30 vol % $CDCl_3$, 70 vol % octafluorotoluene): 5.8 (b m, 2 H, olefinic), 3.7, 3.5, and 3.2 (3 unresolved b m, 2 H, allylic), 2.1 (b m, 2 H, β to olefin).

Anal. Calcd for $(C_{11}H_6F_{12})_n$ [$(366.14)_n$]: C, 36.08; H, 1.65; F, 62.27. Found: C, 36.13; H, 1.66; F, 62.3.

Poly[[6,8-(1,2,2,3,3,4,4,5-octafluoro)bicyclo[3.3.0]octylene]-vinylene] 7*x*,*n*: 3.7 mmol of **3a,b** (48% of exo-isomer **3a**, 52% of endo-isomer **3b**), 26 μmol of WCl_6, and 52 μmol of $(C_6H_5)_4Sn$ in 5 mL of toluene; 24 h at 70 °C; 55% yield; ***x*/*n*** in polymer = 88/12; η_{inh} = 0.66 dL/g; T_g = 193 °C.

^{1}H NMR (acetone-d_6): 6.03 (b m, 2 H, olefin derived from **3b** (endo)), 5.87 (b m, 2 H, olefin derived from **3a** (exo)), 3.55 (b m, 2 H, allylic α to *cis*-olefin), 3.30 (b m, 2 H, allylic α to *trans*-olefin), 2.22 (m, 2 H, β to olefin derived from **3a** (exo)), 1.76 (m, 2 H, β to olefin derived from **3b** (endo)). ***x*/*n*** in polymer = 88/12; trans/cis = 80/20.

^{13}C NMR (acetone-d_6): 130.0 (m, trans −C=C− derived from **3b** (endo)), 128.8 (m, trans −C=C− derived from **3a** (exo)), 127.1 (m, cis −C=C− derived from **3a**), 114.1 (tm, ^{1}J (CF) = 270 Hz, 2 C, >CF*C*F$_2$−), 112.6 (tm, ^{1}J (CF) = 280 Hz, 1 C, −CF$_2$*C*F$_2$CF$_2$−), 99.9 (dm, ^1J(CF) = 230 Hz, 2 C, >*C*FCF$_2$−, derived from **3a**), 98.7 (dm, 2 C, >*C*FCF$_2$− derived from **3b**), 48.7 (m, 2 C, α to trans −C=C−, derived from **3b**), 45.9 (d, ^2J(CF) = 18.7 Hz, 2 C, α to trans −C=C−, derived from **3a**), 44.6 (m, 2 C, α to cis −C=C− derived from **3b**), 41.0 (dm, ^2J(CF) = 19.8 Hz, 2 C, α to cis −C=C−, derived from **3a**), 37.4 (m, 1 C, β to cis −C=C−), 36.3 (m, 1 C, β to cis −C=C−).

Anal. Calcd for $(C_{10}H_6F_8)_n$ [$(278.14)_n$]: C, 43.29; H, 2.17; F, 54.65. Found: C, 43.29; H, 2.16; F, 54.3.

Acknowledgment. The authors thank Prof. R. H. Grubbs and Prof. W. Heitz for many helpful discussions and Prof. S. Berger (Marburg University), Dr. H. Kluge, G. Schwarz (Hoechst AG), and Dr. A. Rous (University College Dublin) for providing the NMR spectra. We are very grateful to Prof. W. J. Feast for many valuable comments. We gratefully acknowledge financial support by BMFT, in collaboration with Hoechst Co. (Dr. Karl-Heinz Stahl, Dr. Wieners, Dr. Schütze, Dr. Fritsch, Dr. Osan, Dr. Dittmer, and Dr. Brekner), by DFG and Fonds der Chemische Industrie.

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