Ring-Opening Metathesis Polymerization for the Preparation of Surface-Grafted Polymer Supports

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ABSTRACT: A series of norbornene-based, L-valine- and L-phenylalanine-containing chiral monomers have been prepared. Starting from norborn-2-ene-5-carboxylic acid chloride and norborn-2-ene-5,6-dicarboxylic anhydride, *N*-(norborn-2-ene-5-carboxyl)-L-valine **(I)**, *N*-(norborn-2-ene-5-carboxyl)-L-phenylalanine **(II)**, *N*-(norborn-2-ene-5-carboxyl)-L-phenylalanine ethyl ester **(III)**, the *N*,*N*-(norborn-2-ene-5,6-dicarbimid) (NBDCI)-protected amino acid derivatives NBDCI-L-valine **(IV)**, NBDCI-L-phenylalanine **(V)**, NBDCI-L-valine-*tert*-butylamide **(VI)**, NBDCI-L-valine-anilide **(VII)**, NBDCI-L-valine-*m*-nitroanilide **(VIII)**, and NBDCI-L-valine-*p*-chloroanilide **(IX)** have been synthesized. Compounds **I**−**IX** were polymerized via ring-opening metathesis polymerization (ROMP) using initiators based on both molybdenum ($Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$) **(1)** and ruthenium ($Cl_2Ru(CHPh\text{-}p\text{-}F)(PCy_3)_2$, Cy = cyclohexyl) **(2)**. The polymers were characterized in terms of cis/trans structure as well as optical rotation. Bromomethylated, beaded polymer supports based on poly(styrene−divinylbenzene) (PS-DVB) were prepared either via direct bromomethylation or via transhalogenation of chloromethyl-PS-DVB and subsequently surface-derivatized with norborn-2-ene groups by reaction with sodium norborn-2-ene-5-ylmethanolate. Norborn-2-ene-derivatized silica-based supports were prepared by silanization employing norborn-2-ene-5-yltrichlorosilane. Surface grafting of the norbornene-modified supports with monomers **III, VI**, and **VII** was accomplished using ROMP. Both Schrock-type and Grubbs-type initiators were found suitable for that purpose. A poly-**III** surface-grafted, porous 5 μm silica was found suitable for chiral HPLC separations.

Introduction

Polymer grafting represents a well-established and useful procedure for the preparation of certain polymer architectures.[1−3] It may be accomplished by many polymerization techniques, e.g., metathesis polymerization,[4−6] atom-transfer radical polymerization,[7] Ziegler−Natta,[8] or cationic ring-opening polymerization,[9] and carried out either homogeneously, heterogeneously, or from the gas phase.[10] In terms of surface grafting, mainly styrene and acrylate-based resins have been used so far.[1,11] Recently, we reported on the use of ring-opening metathesis polymerization (ROMP) for the preparation of new selective sorbents.[12−17] Designed polymer supports with chelating sites were prepared by precipitation polymerization techniques and used for the selective enrichment of palladium, mercury,[18,19] or lanthanides.[20,21] Due to a rather broad particle size distribution and as a consequence of unfavorable swelling properties of the materials prepared by these techniques, they proved to be unsuitable for their use in high-pressure separation techniques. One approach that circumvents these problems is the use of soluble ROMP prepolymers for spin-coating of monosized carrier materials. Unfortunately, this technique often results in a significant loss of surface area due to pore clogging.[22] Nevertheless, as the synthetic approach based on ROMP offers so many advantages compared to standard procedures, we focused on the development of new synthetic pathways for the preparation of supports applicable for high-pressure separation methods such as HPLC. In this contribution we describe the use of ROMP for the preparation of new graft-type supports. Starting with the synthesis of new chiral monomers, their transformation into linear, soluble polymers was performed in order to obtain information about their reactivity, polymer properties, and optical rotations. Selected monomers were chosen on the basis of their polymerizability for the preparation of surface-grafted supports. To the best of our knowledge, this is the first time that ROMP is used for the controlled surface grafting of organic and inorganic polymer supports. The entire synthetic concept will be presented in detail.

Results and Discussion

Preparation of Chiral Norborn-2-ene-Based Monomers and Their ROMP. To obtain polymerizable chiral molecules, two L-configured amino acids, valine and phenylalanine, were transformed into the corresponding norborn-2-ene-5-carboxylic amides **I** and **II** and norborn-2-ene-5,6-dicarbimides **IV** and **V**, respectively. These two types of compounds were subsequently derivatized into the ester **III** and amides **VI**, **VII**, **VIII**, and **IX**. Scheme 1 gives an illustration of the reaction sequences. Compounds **I, II, III, VI**, and **VII** have additionally been characterized by X-ray analysis. As can be deduced from these X-ray analyses as well as from the NMR spectra of **I** and **II**, the *endo* configuration is selectively formed, despite the fact that the synthesis is conducted with an *exo*/*endo* mixture of norborn-2-ene-5-carboxylic acid chloride. This selective formation of an *endo* isomer has already been observed in the formation of other sterically demanding amides.[18]

Silica as well as PS-DVB-based supports were chosen for surface grafting (vide infra). Because of the different

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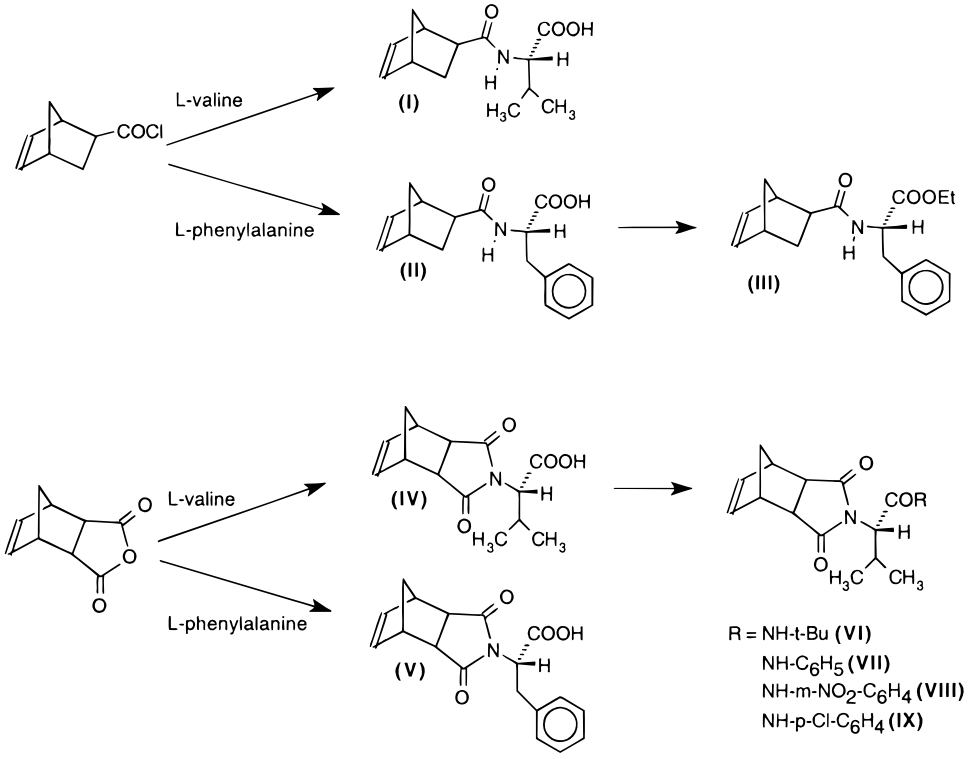
Scheme 1. Synthesis of Compounds I−IX



surface chemistry of these two types of supports in terms of the potential presence of protic functionalities, ROMP of monomers **I**−**XI** was carried out using both Schrock-type and Grubbs-type catalysts. Compounds **III** and **VI**−**IX** may be polymerized by Mo(N-2,6-Me_2-C_6H_3)(CHCMe_2Ph)(OC$Me(CF_3)_2$)$_2$ **(1)**. A stoichiometric initiation was observed for compounds **III**, **VI**, and **VII**, and the living character[23,24] of the polymerization was proven by a linear plot of M_w vs number of monomer equivalents (N) ($R^2 \geq 0.99$) for at least $N \leq 100$. Polydispersities were generally ≤1.4. Within the definitions of livingness suggested by Matyjaszewsky,[23] these systems fulfill at least the criteria of a "class V" living system. Yields are almost quantitative. The polymerization of the *p*-chloroanilide derivative **IX** as well as the 3-nitroanilide analogue **VIII** by the Schrock initiator is characterized by a nonstoichiometric initiation as well as by a nonliving polymerization. Especially in the case of **VIII**, the molybdenum catalyst shows a significant color change upon addition to a well-stirred monomer solution in methylene chloride. Within a few minutes a color change from bright yellow to green, which might be attributed to lower oxidation states of molybdenum, occurs. Consequently, values for M_w of **VIII** were low (6300). In contrast to the polymerization results for compounds **III** and **VI**−**IX** obtained with a Schrock initiator, polymerization yields using Cl_2Ru(=CHPh-*p*-F)(PCy_3)$_2$ **(2)** are generally comparably low (10−20%), and a nonstoichiometric initiation is observed for all the monomers. The polymers derived from **I, II, IV**, and **V** using initiator **2** were found to be insoluble in organic solvents.

Preparation of Polymer Supports Suitable for Surface Grafting. Taking the heterogeneous character of any surface functionalization into consideration, a straightforward yet broadly applicable synthetic route may be accomplished by only two steps. By using a well-defined polymer chemistry, the simple surface derivatization of a support with copolymerizable anchoring groups is followed by the attachment (grafting) of the actual working functionalities. This attachment must be performed in a way that the final derivatization is less or not dependent on the actual amount of anchoring groups, yet the entire synthetic approach provides a high chemical stability of the final material, which is especially of importance in the case of silica-based materials. In other words, the anchoring groups that serve as a linker between the support and the actual functional groups may not be broken mechanically or chemically, e.g., by low or high pH values. To achieve this goal even in the case of silica-based materials, surface grafting has to be carried out in a way that the final graft copolymer forms an impervious layer which prevents any contact of the support with the mobile phase.

To generate stable, covalently bound graft copolymers, a route different to the one reported by Nguyen et al.[25] was elaborated. One of the simplest ways for providing suitable anchoring groups for the preparation of a ROMP graft copolymer lies in the surface attachment of norborn-2-ene-5-yl-groups. This may easily be accomplished in the case of silica materials. Beaded silica was dried and surface derivatized with trichloronorborn-2-ene-5-ylsilane. Subsequent "end-capping" with a mixture of chlorotrimethylsilane and dichlorodimethylsilane leads to a sufficient derivatization of a major part of the surface silanol groups. In the case of PS-DVB-based materials, more sophisticated methods have to be applied. Despite the fact that chloromethylations of PS-DVB resins for the generation of benzylic chloride groups may be carried out with high efficiencies, these groups are not reactive enough to be converted quantitatively into a benzylnorborn-2-ene-5ylmethyl ether by treatment with sodium or lithium norborn-2-ene-5-ylmethanolate. Therefore, bromomethylations using trioxane, tin tetrabromide, and trimethylbromosilane were

Scheme 2. Bromination, Transhalogenation, and Derivatization of PS-DVB Materials: (i) $SnBr_4$, $BrSi(CH_3)_3$, Trioxane, CH_2Cl_2, (ii) NaBr, DMF, $BrCH_2CH_2Br$

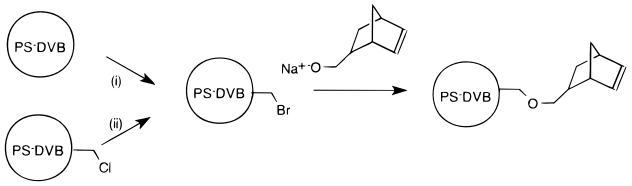


Table 1. Selected Polymerization Results for Monomers I−IX

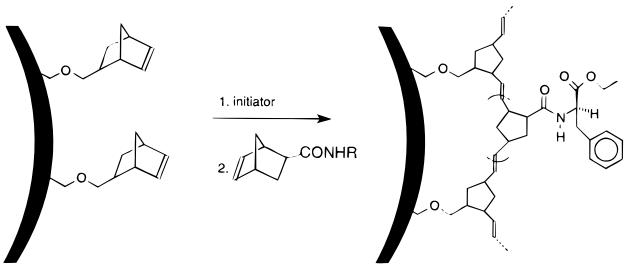
polymer	M_w [D]	M_w/M_n	yield [%]
poly-**I**			11[a,c]
poly-**II**			13[a,c]
poly-**III**	6100	1.31	24[a]
poly-**III**	314300	1.35	>99[b]
poly-**VI**	4400	1.13	12[a]
poly-**VI**	14300	1.26	95[b]
poly-**VII**	2000	1.26	11[a]
poly-**VII**	9800	1.41	>99[b]
poly-**VIII**	200	1.22	22[a]
poly-**VIII**	6300	1.51	15[b]
poly-**IX**	2000	1.25	37[a]
poly-**IX**	21800	2.56	25[b]

[a] $RuCl_2(CHPh\text{-}p\text{-}F)(PCy_3)_2$. [b] $Mo(N\text{-}2,6\text{-}Me_2\text{-}C_6H_3)(CHCMe_2Ph)(OCMe(CF_3)_2)_2$. [c] Insoluble polymer.

performed.[26] Alternatively, conversion of the chloromethyl groups into to the corresponding bromomethyl groups may be accomplished via halogen exchange.[27,28] This reaction proceeds smoothly with yields larger than 80% as determined by elemental analysis and therefore provides a cheap alternative to the rather expensive route based on bromomethylation. In a final step, the bromomethylated PS-DVB resins are easily converted into the norborn-2-ene-5-ylmethyl ethers (Scheme 2). Table 2 gives an overview over the surface-derivatized silica and PS-DVB materials that were used for subsequent grafting reactions.

Surface Grafting. On the basis of the polymerization results for monomers **I**−**IX** with both types of initiators, suitable systems for the surface grafting of silica and PS-DVB were elaborated. Special care had to be taken in the case of silica. Even after excessive treatment with an "end-capping reagent" (chlorotrimethylsilane/dichlorodimethylsilane), small amounts of residual silanol groups still have to be expected at the surface of silica. Because of the rather low tolerance of Schrock initiators vs protic functionalities, we initially decided to carry out surface grafting on norborn-2-ene-derivatized silica with

Scheme 3. Surface Grafting of III on PS-DVB (R = CH(COOEt)CH_2Ph)



the Grubbs initiator **2**. Complementary, due to the enhanced reactivity of the Schrock systems, grafting on norborn-2-ene-derivatized PS-DVB materials was performed with **1** as the initiator (Scheme 3). At this point it should be emphasized that the polymerization order plays a crucial role in the present heterogeneous system. In principle, two different approaches may be performed. Thus, the monomer may be transformed into a living polymer via ROMP and subsequently attached to the support by reaction with the surface norborn-2-ene groups. This approach requires at least a class IV living system[23] and consequently leads to the formation of tentacle-type stationary phases with the linear polymer chains pointing away from the support (method A). Alternatively, the initiator may first be reacted with the support to become heterogenized (method B). A similar system has been reported recently for grafting reactions based on radical polymerization.[29,30] For this approach (method B), heterogenization must be basically quantitative since even small amounts of initiator in solution were found to lead to significantly reduced amounts of grafted polymer. Thus, even less than 2% of homogeneous initiator (as calculated from the experimentally obtained data for M_n) were found to result in the almost exclusive formation of soluble, linear polymer. These findings may be explained by comparing the rates of propagation (k_p) of both the heterogenized and the homogeneous initiator. On the basis of the general knowledge about catalyst activity upon heterogenization,[31−33] it may be assumed that the reaction rate of propagation of a homogeneous initiator is significantly higher than that of a heterogeneous one. In a system were both the homogeneous and the heterogenized initiator are present, only few monomers react with the heterogenized initiator to form a copolymer with the surface norborn-2-ene groups, while the major part is polymerized by the homogeneous one. Thus, after all monomer is consumed, the living polymer chains can hardly find any remaining surface norborn-2-ene groups

Table 2. Surface-Modified and Grafted PS-DVB- and Silica-Based Stationary Phases

stationary phase	functional group/g	initiator	method	yield [%]
bromomethylated PS-DVB, 2% DVB, 4.2 mmol Cl, $d = 74-37\ \mu m$	3.48 mmol **Br**		*c*	82.8
bromomethylated PS-DVB, 55% DVB, $d = 8.0\ \mu m$	0.58 mmol **Br**		*b*	30.0[d]
NOR-SI-Nucleosil, $d = 5\ \mu m$	0.3 mmol **NOR-SI**			6.0[e]
NOR-SI-Silica 60, $d = 40-60\ \mu m$	0.8 mmol **NOR-SI**			15.0[e]
poly-**NBDCA**-grafted NOR-O-PS-DVB, 2% DVB, $d = 37-74\ \mu m$	2 mmol **NBDCA**	1	A, B	70−80[a]
poly-**III** grafted NOR-PS-DVB, nonporous, $d = 8.0\ \mu m$	0.15 mmol **III**	1	B	91.7
poly-**III** grafted Nucleosil-300−5, $d = 5\ \mu m$	0.06 mmol **III**	2	B	21.5
poly-**III** grafted Nucleosil-300−5, $d = 5\ \mu m$	0.04 mmol **III**	1	B	18.9
poly-**III** grafted Nucleosil-300−5, $d = 5\ \mu m$	0.04 mmol **III**	1	A	18.0
poly-**VI** grafted NOR-O-PS-DVB, 2% DVB, $d = 37-74\ \mu m$	0.15 mmol **VI**	1	B	24.4
poly-**VII** grafted NOR-O-PS-DVB, 2% DVB, $d = 37-74\ \mu m$	0.25 mmol **VII**	1	B	25.3

[a] Determined via ion exchange of Na^+ and subsequent FES determination. NBDCA = norborn-2-ene-5,6-dicarboxylic anhydride. NOR-SI- = norborn-2-ene-5-ylmethylsiloxyl. [b] Direct bromomethylation. [c] Transhalogenation, yield based on initial Cl content. [d] Yield based on $SnBr_4$. [e] Yield based on norborn-2-ene-5-yltrichlorosilane.

and are therefore not grafted onto the material. For both grafting methods, preliminary experiments were carried out on PS-DVB resins with norborn-2-ene-5,6-dicarboxylic anhydride (NBDCA) using **1** as an initiator. This monomer was chosen for various reasons. On one hand it is cheap, and polymer yields of this monomer with **1** are known to be quantitative.[13] On the other hand, any surface-bound NBDCA may easily be detected by IR spectroscopy and may further be quantified by simple titration methods. Finally, any unreacted monomer or noncovalently bound polymer adsorbed onto the carrier may easily be removed by treatment with diluted sodium carbonate solution. Following the synthetic approaches described above, NBDCA was grafted onto PS-DVB materials up to a total amount of 2 mmol/g (Table 2). It should be emphasized that such high degrees of functionalization may usually only be obtained for example via sulfonation reactions of PS-DVB under rigorous conditions.

For the system silica/initiator **2**, method B was found suitable. The first step of the synthetic protocol entailed the reaction of **2** with the norborn-2-ene-derivatized silica. Small amounts of initiator (1−2% with respect to the support) were required. Usually 15 min was sufficient in order to allow the entire initiator to react with the surface-bound norborn-2-ene groups. As at least a 10-fold excess of norborn-2-ene groups with respect to the initiator was present, enough norbornene groups were incorporated into the growing polymer chain upon addition of the functional monomer. The resulting graft polymer is therefore believed to be multiply attached to the support via the norborn-2-ene groups and consequently provides a quite inert protective layer. This is supported by the fact that silica modified by this procedure may be used within a pH range of 2−10 and therefore exhibits an enhanced stability compared to standard surface-modified silica. On the basis of these data, we therefore tentatively describe the chemical structure of a grafted polymer prepared by this route to be as shown in Scheme 3. Interestingly, both grafting methods were found applicable with both types of carriers using initiator **1**. The fact that the Schrock initiator does *not* react with any surface silanol groups suggests a high surface coverage with norborn-2-ene and methylsilane groups. The reaction of **1** with norborn-2-ene-derivatized silica may easily be monitored. Upon addition of a solution of **1** to a suspension of silica in methylene chloride, the solution becomes colorless within a few minutes while the support shows a deep yellow color. Addition of a monomer after approximately 15 min yields surface-derivatized supports. Alternatively to this procedure, the first step may consist of the preparation of a living polymer that is subsequently attached to the surface (method A). Typical loadings of compound **III** that may be achieved by this approach are ca. 0.04 mmol/g. Nevertheless, to contribute to a maximum pH stability of the final grafted carrier and in light of the similar amounts of graft polymer that may be attached by either of the two methods, method B was used throughout.

For further surface grafting, monomers **III**, **VI**, and **VII** were chosen on the basis of their polymerizability. Grafting was started by reaction of the norborn-2-ene-derivatized support with the corresponding initiator. The actual loading of a support with any functional monomer was determined by elemental (nitrogen) analysis. Table 2 gives a summary of the loadings and

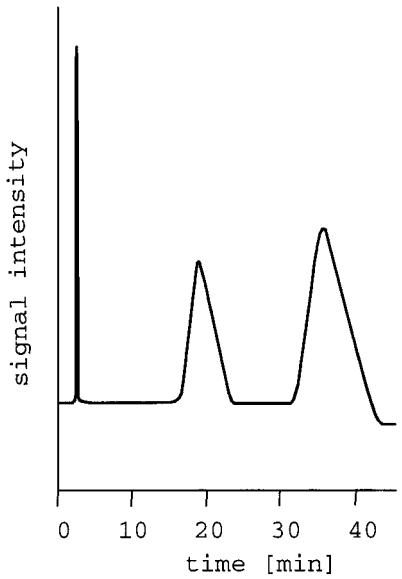


Figure 1. Separation of DNB-phenylalanine on a poly-**III**-grafted Nucleosil 300-5. $\alpha = 2.0$, $R_s = 1.91$. First peak: L-enantiomer.

properties of the materials obtained. Generally speaking, larger amounts of polymer may be grafted onto PS-DVB-based supports than onto silica supports. This may be due to the rigid pore structure of silica, which leads to a kind of restricted access after a certain amount of polymer has been grafted into these pores. Measuring the specific surface areas (σ) via BET experiments (N_2 adsorption) prior to and after grafting further supports this assumption. These investigations revealed that changes in σ were less than 10% over the course of the grafting procedure using nonporous PS-DVB- as well as porous silica-based materials, indicating that the pores are not filled with graft polymer. The general quality of the grafting as well as the applicability of these materials in separation sciences was finally demonstrated by using these materials as sorbents in chiral HPLC. Such a chiral separation of a dinitrobenzoyl-protected amino acid (DNB-phenylalanine) has been carried out on a poly-**III** grafted silica support and is shown in Figure 1.

Experimental Section

All experiments were performed in a nitrogen-mediated drybox (BRAUN, Garching, Germany) or by standard Schlenk techniques. DMF was dried over molecular sieve (3 Å) and distilled in vacuo. General statements on standard procedures or on equipment and methods have been made previously.[13,18] Flame emission experiments (FES) were carried out on a Phillips PU-7000. Molecular weights and polydispersities were determined by means of GPC in THF using a 717 Autosampler, a column heater (35 °C), a 510 HPLC pump, a 490E UV detector, a 410 RI detector, and a Millenium work package (all Waters). GPC columns (Ultrastyragel 10^5 Å, 10^4 Å, and 10^3 Å, all 7.8 × 300 mm, Waters) were calibrated vs polystyrene (PS). Column packing was carried out in methanol at $p = 400$ bar using a Knaur high-pressure HPLC packing pump. HPLC experiments were carried out on a Waters 600 S controller system (484 UV detector). Values for the specific rotation were determined on a Perkin-Elmer model 141 polarimeter using a 10 cm ORD (Q) cell at $\lambda = 589$ nm.

Materials, Monomers, Polymers, and Catalysts. Silica materials (Silica 60, 40−63 μm and Nucleosil 300−5, 5 μm, 300 Å, specific surface = 100 m^2) were purchased from Merck (Darmstadt, Germany) and Macherey & Nagel, (Düren, Germany). Bicyclohept-2-ene-5-ylmethyldichlorosilane and bicyclohept-2-ene-5-yltrichlorosilane were purchased from

ABCR (Karlsruhe, Germany). Bicyclohept-2-ene-5-ylcarboxylic acid chloride (**I**),[18] bicyclohept-2-ene-5,6-dicarboxylic anhydride,[34] and the initiators Mo(N-2,6-Me_2-C_6H_3)($CHCMe_2Ph$)-($OCMe(CF_3)_2)_2$)[35] and $Cl_2Ru(PCy_3)_2(CHC_6H_5$-p-F) (Ph = phenyl, Cy = cyclohexyl)[36] were prepared according to literature procedures and checked for purity by means of NMR. Purchased starting materials, HPLC solvents, and the investigated chiral compounds were used without any further purification. Norborn-2-ene-5-methyl alcohol[37] was prepared form norborn-2-ene-5-carbaldehyde[34] (30 g, 0.246 mol) and lithium aluminum hydride (LAH, 2.64 g, 69.6 mmol) in THF (100 mL) at 0 °C. Yield 78%; bp = 103 °C/1.3 Torr. The synthesis and polymer properties of poly(norborn-2-ene-5,6-dicarboxylic anhydride) have been described previously.[13]

***N*-(Norborn-2-ene-5-ylcarboxy)-L-valine (I)**. To a solution of L-valine (1.0 g, 8.54 mmol) and sodium hydroxide (0.683 g, 17.1 mmol) in 10 mL of water was gradually added norborn-2-ene-carbonyl chloride (1.474 g, 9.45 mmol). The reaction mixture was stirred for 30 min at room temperature, diluted with 10 mL of water, and then acidified with 2 N hydrochloric acid. The solution was immediately extracted with methylene chloride (2 × 100 mL). The methylene chloride solution was dried over anhydrous sodium sulfate, concentrated, and recrystallized from methylene chloride/diethyl ether (1:4). Yield 1.03 g (51%). IR (KBr, cm^{-1}): 3359 $bs_{\nu(OH)}$, 2971 $vs_{\nu(C=O)}$, 1717 $vs_{\nu(N-C=O)}$, 1630$s_{\nu(C-O)}$, 1213. ^1H NMR ($CDCl_3$) δ: 9.51 (s, 1H, O*H*), 6.26 (m, 1H, H_2), 6.01 (m, 2H, H_3HN), 4.59 (dxd, J_1 = 13.1 Hz, J_2 = 4.6 Hz, 1H, H_{10}), 3.15 (m, 1H, H_6), 2.98 (m, 3H, $H_{1,4,5}$), 2.11 (m, 1H, H_{11}), 0.94 (m, 3H, $H_{7,12,13}$). ^{13}C NMR ($CDCl_3$) δ: 175.96 $C_{9,8}$, 138.45, 138.1 C_2, 132.6, 132.3 C_3, 57.2, 57.1 C_{10}, 50.4,50.2 C_6, 46.6, 46.4 C_1, 45.1, 45.0 C_4, 43.0, 42.9 C_{11}, 31.3, 31.2 C_7, 19.3 C_{12}, 17.9, 17.8 C_{13}. Elemental analysis calcd for $C_{13}H_{19}NO_3$ (M_w = 237.29): C, 65.8; H, 8.07; N, 5.9. Found: C, 66.04; H, 8.09; N, 5.9.

***N*-(Norborn-2-ene-5-carbonyl)-L-phenylalanine (II)**. Norborn-2-ene-5-carbonyl-L-phenylalanine was synthesized according to the procedure described for **I**. Yield 58%. IR (KBr, cm^{-1}): 3330 $bs_{\nu(OH)}$, 2965, 1720$_{\nu(C=O)}$, 1620$_{\nu(N-C=O)}$,1227$_{\nu(C-O)}$. ^1H NMR ($CDCl_3$) δ: 9.40 (s, 1H, H_{OH}), 7.28 (m (broad), 4H, $H_{14,\ 15,\ NH}$), 7.18 (m, 2H, H_{13}), 6.14 (dxd, 2H, J_1 = 8.5 Hz, J_2 = 3.1 Hz, $H_{2,\ 3}$), 5.78 (dxd, 1H, J_1 = 8.6 Hz, J_2 = 2.7 Hz, H_2), 5.68 (dxd, 1H, J_1 = 8.5 Hz, J_2 = 3.1 Hz, H_3), 4.81 (m, 1H, H_9), 3.18 (m (broad), 3H, $H_{1,\ 4,\ 6}$), 2.87 (m (broad), 2H, H_5), 1.87 (m, 2H, $H_{7a,\ b}$), 1.2−1.21 (m, 2H, H_{11}). ^{13}C NMR ($CDCl_3$) δ: 175.6 C_{10}, 175.1 C_8, 138.3, 139.1 C_2, 132.6, 132.1 C_3, 129.5 C_{12}, 128.9 C_{13}, 128.8 C_{14}, 128.4 C_{15}, 53.4, 53.3 C_9, 50.3, 50.1 C_6, 46.6, 46.2 C_1, 45.0, 44.8 C_4, 42.9, 42.8 C_5, 37.4, 47.2 C_7, 30.4, 30.1 C_{11}. Elemental analysis calcd for $C_{17}H_{19}NO_3$ (M_w = 285.32 g/mol): C, 71.56; H, 6.71; N, 4.91. Found: C, 71.67; H, 6.86; N, 4.8.

***N*-Norborn-2-ene-5-carboxy-L-phenylalanine Ethylester (III).** A mixture of **II** (0.578 g, 2 mmol) and *p*-toluenesulfonic acid (16 mg, 0.084 mmol) was dissolved in 30 mL dry ethanol and refluxed for 6 h. The ethanol was evaporated, and the white residue was dissolved in diethyl ether. The ether solution was subsequently washed with water, aqueous sodium hydrogen carbonate solution, and water. The ether solution was concentrated and flash-chromatographed over silica gel 60 with diethyl ether:pentane (5:1) as the mobile phase. The ester was isolated in 74% yield. ^1H NMR ($CDCl_3$) δ: 7.22 (m (broad), 5H, $H_{aryl,\ NH}$), 7.09 (m (broad), 2H, H_{15}), 6.18 (dxd, 1H, J_1 = 8.8 Hz, J_2 = 3.1 Hz, H_2), 5.86 (dxd, 1H, J_1 = 8.4 Hz, J_2 = 2.7, H_3), 4.81 (m, 1H, H_9), 4.17 (q, 2H, J_1 = 21.7 Hz, J_2 = 4.6 Hz, H_{11}), 3.09 (m, 3H, $H_{1,\ 2,\ 6}$), 2.89 (m, 2H, H_5), 1.89 (m, 2H, $H_{7a,\ b}$), 1.25 (m, 5H, $H_{12,\ 13}$). ^{13}C NMR ($CDCl_3$) δ: 211.5 C_{12}, 172.1 C_8, 138.1, 137.8 C_2, 132.7, 132.1 C_3, 129.5 C_{14}, 128.7 C $_{16,17}$, 127.2 C_{17}, 61.6 C_9, 53.1, 53.0 C_{11}, 50.3, 50.1 C_6, 46.5, 46.1 C_1, 45.0, 44.8 C_4, 42.9, 42.8 C_5, 38.2, 37.9 C_{13}, 30.1, 29.9 C_7, 14.3 C_{12}. Elemental analysis calcd for $C_{19}H_{23}NO_3$ (M_w = 313.84 g/mol): C, 72.81; H, 7.4; N, 4.47. Found: C, 72.67; H, 7.52; N, 4.44. $\alpha(30/\lambda) = +15.3°$ (c = 0.04 in $CHCl_3$).

L-Valine-*N,N*-(norborn-2-ene-5,6-dicarbimide) (NBDCI-L-valine) (IV). Norborn-2-ene-5,6-dicarbanhydride (1.67 g, 10.2 mmol) and L-valine (1.14 g, 9.73 mmol) were placed in a two-necked flask with a water separator and suspended in dry toluene. To this solution was added triethylamine (1.5 mL). The reaction mixture was refluxed for 2 h until no further water collected in the water separator. The toluene was removed under reduced pressure to yield a white residue. Both 30 mL of water and 0.5 mL of concentrated hydrochloric acid were added. The aqueous acid solution was shaken with 3 × 30 mL of diethyl ether, and the combined ether extracts were dried over sodium sulfate. The solution was concentrated in vacuo and placed in a deep freezer overnight. Yield: 2.4 g (94%). IR (KBr, cm^{-1}): 2940 vs (broad), 1745 s 1700 vs, 1673 s, 720 m. ^1H NMR(DMSO-d_6) δ: 6.08 (m, H_2, H_3), 4.05 (d, H_8, J = 18 Hz), 3.4 (m, 2 H, $H_{5,6}$), 3.31 (m, 2 H, $H_{4,1}$), 2.32 (m, 1 H, H_9), 1.52 (m 2 H, $H_{7a,\ 7b}$), 0.90 (d, J = 6.8 Hz, H_{10}), 0.69 (d, J = 6.6 Hz, H_{11}). ^{13}C NMR ($CDCl_3$) δ: 177.3, 173.2, 135.0, 134.4, 128.3, 57.8, 52.4, 45.9, 45.1, 44.9, 27.7, 20.7, 19.4. Elemental analysis calcd for $C_{14}H_{17}NO_4$ (M_w = 263.29 g/mol): C, 63.51; H, 6.51; N, 5.3. Found: C, 63.87; H, 6.43; N, 5.20.

L-Phenylalanine *N,N*-(norborn-2-ene-5,6-dicarbimide) (NBDCI-L-phenylalanine) (V). The compound was synthesized according to the procedure for **IV**. Yield 60%. IR (KBr, cm^{-1}): 3253 $bm_{\nu(OH)}$, 2950 s, 1752 $s_{\nu(C=O)}$, 1686 $s_{\nu(C=O)}$, 1190 $s_{\nu(C-O)}$. ^1H NMR (DMSO-d_6) δ: 7.31−7.09 (m, $H_{aromatic}$), 5.66 (dxd, J_1 = 2.4, Hz J_2 = 8.2 Hz, H_2), 5.22 (dxd, J_1 = 2.4 Hz, J_2 = 8.2 Hz, H_3), 4.89 (d, J = 4.9, H_5), 4.22 (d, J = 4.9 Hz, H_6), 3.36−3.07 (m, $H_{1,4,7,11}$), 1.42 (s, H_{12}). ^{13}C NMR (DMSO-d_6) δ: 176.7 C_{10}, 169.8 $C_{8,9}$, 134.23 C_2, 133.7 C_3, 129.0 C_{13}, 128.1 C_{14}, 126.0 C_{15}, 52.3 $C_{5,6}$, 51.53 C_{11}, 44.2 C_1, 44.1 C_4, 33.3 C_{12}. Elemental analysis calcd for $C_{18}H_{17}NO_4$ (M_w = 311.33 g/mol): C, 69.44; H, 5.5; N, 4.5. Found: C, 69.48; H, 5.75; N, 4.45.

L-Valine-norborn-2-ene-5,6-dicarbimide-*tert*-butylamide (VI). To **IV** (5.0 g, 1.9 mmol) dissolved in acetonitrile was added dicyclohexyldicarbodiimide (DCC)[38] (1.96 g, 0.95 mmol). Soon after addition of DCC, dicyclohexylurea (DCU) precipitated, and the reaction mixture was stirred for a further 6 h. DCU was filtered off, *tert*-butylamine (2.0 mL, 1.9 mmol) was added to the filtrate, and the reaction mixture was stirred for 12 h. Finally, the ammonium salt was filtered off. Acetonitrile was evaporated under reduced pressure until an oily residue remained which was dissolved in diethyl ether. The ether solution was subsequently washed with 0.1 M hydrochloric acid and saturated aqueous sodium hydrogen carbonate and finally dried over sodium sulfate. The solution was concentrated, and about the same amount of pentane was added. Crystallization was performed at −18 °C. Yield: 2.6 g (43%). Unreacted **IV** may be recovered from its ammonium salt and used for further synthesis. IR (KBr, cm^{-1}): 3300 m, 2940 s, 1760 s, 1770 vs, 1515 s, 1450 m, 722 s, 620 s. ^1H NMR ($CDCl_3$) δ: 6.58 (bs, 1H, H_{NH}), 6.08 (m, 2H, $H_{2,3}$), 3.91 (d, 1H, J = 11.6, H_{11}), 3.38 (m, 2H, $H_{5,6}$), 3.25 (m, 2H, $H_{1,4}$), 2.60 (dxtxt, 1H, J_1 = 6.7 Hz, J_2 = 13.1 Hz, H_{11}), 1.63 (dxt, J_1 = 1.8 Hz, J_2 = 39.6 Hz, 1H, H_{7a}), 1.58 (d, broad, J_1 = 39.6 Hz, 1H, H_{7a}), 1.26 (s, 9H, $H_{t-butyl}$), 0.95 (d, 1H, J = 6.7 Hz, H_{13}), 0.72 (d, 1H, J = 6.7 Hz, H_{14}). ^{13}C NMR ($CDCl_3$) δ: 178.5, 167.7, 135.1, 134.8, 65.2, 52.7, 51.3, 45.8, 45.6, 45.3, 28.8, 26.7, 19.8, 19.7. Elemental analysis calcd for $C_{18}H_{26}N_2O_3$ (M_w = 315.18 g/mol): C, 67.9; H, 8.23; N, 8.8. Found: C, 67.98; H, 8.29; N, 8.86. $\alpha(30/\lambda) = +0.57°$ (c = 0.05 in $CHCl_3$).

L-Valine-*N,N*−(norborn-2-ene-5,6-dicarboimide)anilide (VII). The anilide was prepared according to the procedure described for **VI**. Recrystallization was performed in a mixture of diethyl ether and methylene chloride. Yield: 40%. The amide may also be prepared from nornorn-2-ene-5-carboxylic acid chloride methods in 56% yield. IR (KBr, cm^{-1}): 3272 bs $_{\nu(OH)}$, 2988 s $_{\nu(C=O)}$, 1696 s $_{\nu(C-O)}$, 1242 s. ^1H NMR ($CDCl_3$) δ: 8.82 (s, 1H, H_{NH}), 7.50 (dxd, 1H, J_1 = 1.2 Hz, J_2 = 8.8 Hz, $H_{17,19}$), 7.34 (d, 2H, J = 7.3 Hz, H $_{16,20}$), 7.11 (dxt, 1H, J_1 = 1.2, J_2 = 7.3 Hz, H_{18}), 6.12 (m, 1H, H_2), 6.06 (m, 1H, H_3), 4.22 (d, 1H, J_1 = 11.6 Hz, H_{11}), 3.4 (m, 2H, $H_{5,6}$), 3.35 (m, 2H, $H_{1,4}$), 2.79 (m, 1H, J_1 = 6.4 Hz, H_{12}), 1.68 (m, 1H, J_1 = 37.5 Hz, H_{7a}), 1.63 (m, 1H, J_1 = 37.5 Hz, H_{7b}), 1.06 (d, 1H, J = 6.7 Hz, H_{13}), 0.85 (d, 1H, J = 6.4 Hz, H_{14}). ^{13}C NMR ($CDCl_3$) δ: 178.5 $C_{9,8}$, 166.7 C_{10}, 135.0 C_2, 134.99 C_3, 129.2 C $_{17,19}$, 124.5 C_{18}, 119.9 $C_{16,20}$, 65.4 C_{11}, 52.6 $C_{5,6}$, 45.9 C_1, 45.7 C_4, 45.4 C_{12}, 25.8 C_7, 19.9 C_{13}, 19,8 C_{14}. Elemental analysis calcd for $C_{20}H_{22}N_2O_3$ (M_w = 337.4 g/mol): C, 70.99; H, 6.55; N, 8.28. Found: C, 71.02; H, 6.81; N, 8.32. $\alpha(30/\lambda) = -21.62°$ (c = 0.05 in $CHCl_3$).

Amides of L-Valine-norborn-2-ene-5,6-dicarbimide via Carboxylic Acid Chlorides: General Method. Dry pyridine (0.5 mL) was added to a solution of **IV** (1.0 g, 3.8 mmol) in methylene chloride (80 mL). To this solution was added thionyl chloride (3.16 g, 26.6 mmol) diluted with methylene chloride (20 mL) over a period of 5 min. The reaction mixture was stirred at room temperature for 30 min and refluxed for 8 h. Excess thionyl chloride and methylene chloride were removed to yield a yellow and in some cases light brown residue. It was dissolved in methylene chloride and cooled to −90 °C. A mixture of dry triethylamine (0.53 mL, 3.8 mmol) and an appropriate amine (3.8 mmol) were added to this solution over a period of 10 min. The reaction temperature was gradually allowed to rise to room temperature, and stirring was continued overnight. The reaction mixture was neutralized with 0.1 mol of hydrochloric acid and extracted with 3 × 30 mL of methylene chloride. The combined organic phases were dried over sodium sulfate and evaporated in a rotator until a light brown residue remained. The residue was dissolved in diethyl ether or a solvent mixture of diethyl ether and methylene chloride and filtered through silica gel-60. Recrystallization was performed as explained for the individual compounds.

L-Valine-(norborn-2-ene-5,6-dicarbimide)-*m*-nitroanilide (VIII). The amide was prepared according to the carboxylic acid chloride method and recrystallized from a mixture of diethyl ether and methylene chloride. Yield: 59%. IR (KBr, cm^{-1}): 3359 bm $\nu_{(OH)}$, 2963, 1771s $\nu_{(C=O)}$, 1694s $\nu_{(C-O)}$, 1202. ^{1}H NMR ($CDCl_3$) δ: 9.28 (s, 1H, N*H*), 8.37 (m, 1H, H_{16}), 7.93 (m, 2H, $H_{18/20}$), 7.48 (t, 1H, J = 8.2 Hz, H_{19}), 6.14 (m, 1H, H_2), 6.04 (m, 1H, H_3), 4.27 (d, 1H, J = 11.3 Hz, H_{11}), 3.46 (s(broad), 2H, $H_{5/6}$), 3.39 (s(broad), 2H, $H_{1/4}$), 2.77 (m, 1H, J_1 = 6.7 Hz, H_{12}), 1.70 (d, 1H, J = 37.5 Hz, H_{7a}), 1.66 (d, 1H, J = 10.4, H_{7b}), 1.06 (d, 3H, J = 6.7 Hz, H_{13}), 0.86 (d, 3H, J = 6.4 Hz, H_{14}). ^{13}C NMR ($CDCl_3$) δ: 178.8 C_9, 178.6 C_8, 167.2 C_{10}, 135.1 $C_{17/15}$, 130.1 C_{19}, 125.6 C_{20}, 119.2$C_{16,18}$, 114.7 $C_{2/3}$, 65.3 C_5, 52.7 C_6, 46.0 C_{11}, 45.8 C_4, 45.5 C_1, 45.4 C_{12}, 26.8 C_7, 19.8 C_{13}, 19.7 C_{14}. Elemental analysis calcd for $C_{20}H_{21}N_3O_5$ (M_w = 383.4 g/mol): C, 62.65; H, 5.53; N, 10.96. Found: C, 62.43; H, 5.52; N, 10.74. $\alpha(30/\lambda) = -23.4°$ (c = 0.05 in $CHCl_3$).

L-Valine-(norborn-2-ene-5,6-dicarbimide)-*p*-chloroanilide (IX). The amide was prepared according to the carboxylic acid chloride method and was recrystallized from a solvent mixture of diethyl ether and methylene chloride. Yield: 69%. IR (KBr, cm^{-1}): 3372 bm ν(NH), ν(C=O) 1765s$_{\nu(C=O)}$, 1697$_{\nu(C-O)}$, 1242. ^{1}H NMR (DMSO-d_6) δ: 9.28 (s, 1H, N*H*), 7.55 (d(broad), 2H, J = 9.1 Hz, H $_{16,20}$), 7.33 (d, 2H, J = 8.9 Hz, H $_{17,19}$), 6.09 (m, 1H, H_2), 6.02 (m, 1H, H_3), 4.17 (d, 1H, J = 8.5 Hz, H_{11}), 3.36 (m, 2H, $H_{5,6}$), 3.26 (m, 2H, $H_{1,4}$), 2.68 (sept, 1H, J_1 = 7.0 Hz, H_{11}), 1.55 (s, 2H, H $_{7a,b}$), 0.89 (d, 3H, J = 6.7 Hz, H_{13}), 0.78 (d, 3H, J = 6.7 Hz, H_{14}). ^{13}C NMR (DMSO-d_6) δ: 177.3 ($C_{8,9}$), 166.4 (C_{10}), 137.5 (C_{15}), 134.8(C_{18}), 134.7 ($C_{17,19}$), 128.5 ($C_{16,20}$), 121.4 ($C_{2,3}$), 60.4 (C_5), 52.0 (C_6), 45.5 (C_{11}), 45.1 (C_4), 44.5 (C_1), 44.4 (C_{12}), 26.7 (C_7), 20.1 (C_{13}), 19.3 (C_{14}). Elemental analysis calcd for $C_{20}H_{21}N_3O_3Cl$ (M_w = 372.84 g/mol): C, 64.42; H, 5.68; N, 7.52. Found: C, 64.15; H, 5.64; N, 7.43. $\alpha(30/\lambda) = -25.3°$ (c = 0.05 in $CHCl_3$).

Preparation of Linear Polymers. Mo(N-2,6-Me_2-C_6H_3)-($CHCMe_2Ph$)($OCMe(CF_3)_2)_2$)-based polymerizations were carried out in methylene chloride at room temperature and terminated by adding ferrocene aldehyde as described previously.[39] $Cl_2Ru(PCy_3)_2$(CHC_6H_5-p-F)-based polymerizations were performed at 60 °C in dry 1,2-dichloroethane and terminated by adding 1-hexene.

Poly-*cis*-III (using **1**): M_w = 20 700, PDI = 1.49. IR (neat): 1737 ($\nu_{C=O}$), 1654 vs (ν_{C-O}), 1497 bs, 1198 (ν_{C-O}), 700 (C=C_{cis}). ^{1}H NMR ($CDCl_3$) δ: 7.3−6.9 (m, 5 H, Ar), 6.45 (b, 1 H,N*H*), 5.5−5.1 (2 H, *H*C=C*H*), 4.75 (C*H*), 4.1 (O−CH_2), 3.1 (3 H, C*H*-CO, CH_2), 2.8−2.55 (2H, CH_2), 2.5−2.0 (b, 2 H), 1.9−1.7 (2 H, $H_{7a,b}$), 1.15 (3 H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 173.5 (*C*O), 171.7 (*C*O), 136.3 (C=C_{cis}), 136.0 (C=C), 129.3, 128.3, 126.9, 65.8 (CH_2), 61.3 (*C*H), 53.1, 53.0, 49.7 (broad, C*H*CO$_{cis}$), 41.0 (broad, C=CH−CH_{cis}), 38.0, 36.0, 15.2 (CH_3), 14.0 (CH_3).

Poly-*cis*-VI (using **1**): M_w = 5500, PDI = 1.35. IR (neat): 2966 s, 2933 s, 2875 m, 1644 vs, 1549 bs, 1393, 1366, 1223 m, 1153 m, 969 m, 735 m. ^{1}H NMR ($CDCl_3$) δ: 8.6 (bs, 1 H, N*H*), 5.3 (b, 2 H, *H*C=C*H*), 4.0 (bs, 1 H, C*H*), 3.2−2.6 (m, 4 H), 2.2−1.6 (b, 3 H), 1.30 (bs, 9 H, *t*-Bu), 0.88 (bs, 6 H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 174.2 (CO), 166.0 (CO), 136.0 (C=C_{cis}), 128.3, 58.9, 49.1 ($C(CH_3)_3$), 51.3 (broad, *C*H), 49.1, 42.6, 33.9, 28.7 (C($CH_3)_3$), 25.6, 24.9, 19.2 (CH_3), 18.3(CH_3).

Poly-*cis*-VII (using **1**): M_w = 22 500, PDI = 1.46. IR (neat): 1700 vs ($\nu_{C=O}$), 1600 s ($\nu_{C=C}$), 1540 m, 1500 w, 1443 m, 1190 s (ν_{C-O}), 754 s, 693 s (C=C_{cis}). ^{1}H NMR ($CDCl_3$) δ: 9.0 (bs, 1 H, N*H*), 7.55 (m, 2 H, H_o), 7.25 (m, 2 H, H_m), 7.05 (m, 1 H, H_p), 5.8−5.4 (b, 2 H, *H*C=C*H*), 4.2 (bs, 1 H, C*H*), 3.4−3.1 (m, 3 H), 3.0−2.6 (m, 2 H), 1.5 (bs, 2 H), 1.08 (3 H, CH_3), 0.85 (3 H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 176.8 (*C*O), 166.3 (*C*O), 137.5 (C_{ipso}), 129.4 (C=C_{trans}), 129.2 (C=C_{trans}), 129.0 (C_m), 124.2 (C_p), 119.9 (C_o), 66.0 (*C*H), 53.5, 48.6, 45.5, 44.8, 26.2 (*C*H), 19.6 (broad, *C*H_3).

Poly-*trans*-III (using **2**): M_w = 22 500, PDI = 1.66. IR (KBr): 1740 vs ($\nu_{C=O}$), 1654 vs ($\nu_{C=O}$), 1505 m, 1374 m, 1196s (ν_{C-O}), 1028 s, 969 s, 743 s, 700 s. ^{1}H NMR ($CDCl_3$) δ: 7.4−7.0 (m, 5 H, Ar), 6.4 (b, 1 H,N*H*), 5.85 (s, 1 H), 5.5−5.1 (2 H, *H*C=C*H*), 5.0 (1 H), 4.8 (1H), 4.1 (2 H, O−CH_2), 3.1 (1 H, C*H*-CO), 2.8−2.2 (4 H, $C_{1,4}$, CH_2), 1.9 (2 H, $H_{7a,b}$), 1.23 (3 H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 173.7 (*C*O), 171.6 (*C*O), 136.5 (C=C_{trans}), 136.3 (C=C_{trans}), 129.5, 128.5, 126.9, 66.0 (CH_2), 61.5 (*C*H), 53.3, 52.7, 49.8, 48.4, 43.0, 41.1, 39.1, 38.4, 35.6, 14.2 (CH_3). $\alpha(30/\lambda) = +20.5°$ (c = 0.007 in $CHCl_3$).

Poly-*trans*-VI (using **2**): M_w = 12 100, PDI = 1.46. IR (KBr): 1694 vs ($\nu_{C=O}$), 1541 vs, 1505 m, 1457 vs, 1384 s, 1366 s, 1192 vs (ν_{C-O}), 1028 s, 967 s, 625 m, 581 m. ^{1}H NMR ($CDCl_3$) δ: 6.7 (bs, 1 H, N*H*), 5.7 (b, 2 H, *H*C=C*H*), 4.1 (bs, 1 H, C*H*), 3.4−3.1 (m, 4 H), 2.9 (b, 2 H, $H_{7a,b}$), 2.7 (b, 1 H, C*H*($CH_3)_2$), 1.32 (s, 9 H, *t*-Bu), 1.03 (3 H, CH_3), 0.80 (3 H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 175.3 (CO), 166.0 (CO), 135.9 (C=C_{trans}), 128.7, 63.6, 49.7, 47.0, 43.8, 27.1 (C($CH_3)_3$), 18.7 (CH_3), 18.2(CH_3). $\alpha(30/\lambda) = -1.4°$ (c = 0.025 in $CHCl_3$).

Poly-*trans*-VII (using **2**): M_w = 58 500, PDI = 1.96. IR (KBr): 1702 vs ($\nu_{C=O}$), 1602 s ($\nu_{C=C}$), 1542 s, 1381 m, 1365 s, 1179 s (ν_{C-N}), 1028 s, 969 m, 754 s, 693 s. ^{1}H NMR ($CDCl_3$) δ: 9.0 (bs, 1 H, N*H*), 7.55 (m, 2 H, H_o), 7.25 (m, 2 H, H_m), 7.05 (m, 1 H, H_p), 5.8−5.5 (b, 2 H, *H*C=C*H*), 4.4 (bs, 1 H, C*H*), 3.5−2.8 (m, 5 H), 1.5 (bs, 2 H), 1.08 (3 H, CH_3), 0.85 (3 H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 178.7 (CO), 166.7 (CO), 137.9 (C_{ipso}), 135.0 (C_{trans}), 129.2 (C_m), 124.6 (C_p), 119.9 (C_o), 65.4 (*C*H), 52.6 (C_2, C_3), 45.9 ($C_{1-trans}$), 45.8 ($C_{4-trans}$), 45.5, 45.4, 26.8 (*C*H), 19.9 (CH_3), 19.8 (CH_3).

Poly-*trans*-IX (using **2**): M_w = 9200, PDI = 1.58. IR (KBr): 1700 vs ($\nu_{C=O}$), 1619 s ($\nu_{C=C}$), 1601 s, 1542 s, 1382 s, 1338 s, 1179 s (ν_{C-N}), 969 m (C=C_{trans}), 754 s, 692 s. ^{1}H NMR ($CDCl_3$) δ: 9.0 (bs, 1 H, N*H*), 7.45 (m, 2 H, H_o), 7.15 (m, 2 H, H_m), 5.8−5.3 (b, 2 H, *H*C=C*H*), 4.30 (bs, 1 H, C*H*), 3.5−2.8 (m, 5 H), 1,5 (bs, 2H), 1.00 (3 H, CH_3), 0.80 (3 H, CH_3). ^{13}C NMR ($CDCl_3$) δ: 179.0 (CO), 137.9, 137.6, 135.0 (C=C_{trans}), 130.4, 128.7, 124.5, 119.9, 65.3 (*C*H), 52.6 (C_2,C_3), 45.9 ($C_{1-trans}$), 45.7 ($C_{4-trans}$), 45.5 (C_5), 45.4 (C_6), 26.7 (*C*H), 19.9 (*C*H_3), 19.7 (CH_3). $\alpha(30/\lambda) = -6.21°$ (c = 0.025 in $CHCl_3$).

Transhalogenation of Chloromethylated PS-DVB with Sodium Bromide. The following procedure is typical: A suspension of chloromethylated PS-DVB (0.50 g, 4.3 mmol of Cl/g of resin, 37−74 μm, 2% DVB) and sodium bromide (0.221 g, 2.15 mmol) in 12 mL of 2:1 (v/v) DMF:dibromomethane was stirred at 100 °C for 18 h. The reaction product was filtered off and washed thoroughly with methanolic water and stirred in concentrated hydrobromic acid for 5 h. The product was once again filtered off, washed thoroughly with methanolic water, THF, and diethyl ether, and finally dried in high vacuum. The same results were achieved when a mixture of DMF and dibromomethane (5:1) was used as the solvent. Elemental analysis calcd for Br: 34.35%. Found: 27.86% (corresponding to 80% conversion).

Direct Bromomethylation of PS-DVB. Trioxane (4.5 g, 50 mmol) and bromotrimethylsilane (19.4 mL, 150 mmol) were dissolved in 10 mL of dry methylene chloride. PS-DVB (5.0 g) and tin(IV) bromide (6.5 mL, ρ = 3.34 g/mL, 10 mmol) were added at 0 °C. The reaction mixture was stirred at 0 °C for 30 min and 40 h at room temperature. Finally, the PS-DVB was

filtered off, washed with THF, water, methanol, and diethyl ether, and dried in vacuo. Elemental analysis found: Br, 15.98% (2 mmol of Br/g).

Synthesis of Norborn-2-ene-5-methoxy Derivatives of PS-DVB (NOR-O-PS-DVB). Norborn-2-ene-5-methyl alcohol (1.068 g, 8.6 mmol) was added to a suspension of NaH (0.37 g, 16 mmol) in dry THF at 0 °C over 5 min. The suspension was stirred for 30 min at room temperature and 1 h at 40 °C. Excess NaH was filtered off, and the filtrate was added to bromomethylated PS-DVB (2.0 g). The reaction mixture was stirred overnight at 60 °C. The norborn-2-ene-5-methoxy derivative of PS-DVB was filtered off and washed thoroughly with methanolic water, THF, and diethyl ether. IR (KBr): 1090 cm^{-1} (ν_{C-O}).

Synthesis of Norborn-2-ene-5-yl-methylsilyl Derivatives of Silica (NOR-SI-silica). Nucleosil 300-5 (5.1 g) was dried in refluxing toluene for 12 h using a Dean Stark water separator. 5-Bicyclohept-2-enyltrichlorosilane (5 mL) and triethylamine (6 mL) were added, and the mixture was stirred at 40 °C for 6 h. The norborn-2-ene content was determined from an aliquot by titration with $KMnO_4$/sulfuric acid. Finally, a mixture of dichlorodimethylsilane and chlorotrimethylsilane (3 mL, 1:2 v/v) was added, and stirring was continued overnight. The silylated silica was filtrated, washed with methylene chloride, and dried in vacuo. In the case of silica 60 (150 g), norborn-2-ene-5-yl-trichlorosilane (23 mL), triethylamine (100 mL), dichlorodimethylsilane (10 mL), and chlorotrimethylsilane (20 mL) were used.

Surface Grafting (Method A). The initiator **1** (1−2% with respect to the support) was added to a well-stirred solution of the monomer (10% with respect to the support) in methylene chloride, and the mixture was stirred for 30 min at room temperature. The support (NOR-O-PS-DVB or NOR-Si-silica) was added, and stirring was continued for a further 4 h. Polymerizations were terminated with ferrocene aldehyde. Finally, the resin was extensively washed with THF and methylene chloride and dried in vacuo.

Surface Grafting (Method B). The initiator (**1** or **2**, 1.0−1.5% with respect to the support) was added to a suspension of NOR-O-PS-DVB or NOR-Si-silica in the appropriate solvent. In the case of **2**, the mixture was heated to 60 °C. After 15 min, a monomer solution (10% with respect to the support) was added, and stirring was continued overnight. Methylene chloride was used for polymerizations initiated with **1**, and DMF was used for those initiated with **2**. Polymerizations using **2** were terminated by addition of 1-hexene. Workup was identical as described for method A.

Poly(*endo-endo*-norborn-2-ene-5,6-dicarboxylic anhydride)-Grafted NOR-O-PS-DVB. Mo(N-2,6-Me_2-C_6H_3)($CHMe_2$-Ph)($OMe(CF_3)_2$)$_2$ (50 mg, 0.07 mmol) was added to a suspension of NOR-O-PS-DVB (5 g, 8 μm). The reaction mixture was stirred for 1 h. Norborn-2-ene-5,6-carbanhydride (1.98 g, 12.1 mmol) dissolved in 20 mL of methylene chloride was added, and stirring was continued overnight. The reaction product was filtered off and stirred for 1 h in 10% sodium hydroxide solution and then another hour in 2 M hydrochloric acid. Finally, the resin was washed with methanolic water, THF, and diethyl ether. IR (KBr, cm^{-1}): 1732 ($\nu_{C=O}$), 1090 (ν_{C-O}).

Poly-*trans*-III-Grafted NOR-O-PS-DVB (8.0 μm). Surface grafting and workup were performed as described above. IR (KBr, cm^{-1}): 1725 ($\nu_{C=O}$), 1683 ($\nu_{C=O}$), 1447 (ν_{CH2}), 1385 (ν_{CH3}). Elemental analysis found: N, 0.21%.

Poly-*trans*-VI-Grafted NOR-O-PS-DVB. Surface grafting was performed as described above. The precipitated product was washed with THF, water, methanol, and diethyl ether. IR (KBr, cm^{-1}): 1701 ($\nu_{C=O}$), 1090 (ν_{C-O}). Elemental analysis found: N, 7.71%.

Poly-*trans*-VII-Grafted NOR-SI-silica. Surface grafting and workup were performed as described above. IR (KBr, cm^{-1}): 1703 ($\nu_{C=O}$), 1090 (ν_{C-O}). Elemental analysis found: N, 7.52%.

X-ray Structure Determinations. Compounds **I**, **II**, **III**, **VI**, and **VII** were examined by similar procedures. The corresponding crystal was fixed to a glass fiber and measured on a Bruker P4 diffractometer with graphite-monochromatized Mo Kα radiation (λ = 0.710 73 Å). The unit cell parameters were determined and refined from 26 to 29 randomly selected reflections in the 2Θ range 10.5°−24.0°, obtained by P4 automatic routines. Data were measured via ω-scans and corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections were taken from the International Tables for Crystallography.[40] Structures were solved by direct methods (SHELXS-86)[41] and refined by full matrix least squares against F^2 (SHELXL-93).[42] The function minimized was $\sum[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ with $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms at the carbon atoms were successfully located by difference Fourier methods. They were included in idealized positions with displacement parameters 1.2 (1.5 for methyl group) times higher than U_{eq} of the attached carbon atoms. The hydrogen atoms at the nitrogen and oxygen atoms were normally refined, with restraints of the bond distances for **I** and **III**. A disordering occurs in the crystals of two compounds. In **I,** one terminal carbon atom of the isopropyl group is splitted into two positions with the multiplicity of 0.5 for each. In **III**, the position of the norborn-2-enyl group, which has three chiral carbon atoms, is partially overlapped by the second enantiomeric norborn-2-enyl group with a relative ratio of 2:1. Consequently, the diastereomeric molecules require the same space within the unit cell. The complete set of X-ray data of compounds **I**, **II**, **III**, **VI**, and **VII** has been deposited with the Cambridge Crystallographic Data Centre under CCDC numbers 127381−127385 and may be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, Lensfield Rd., Cambridge, CB2 1EW, UK.

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