Scope and limitations of ruthenium-catalyzed metathesis of simple polymer-bound alkenes

Peter G. Breed, James A. Ramsden, and John M. Brown

Abstract: Synthetic procedures for the preparation of two types of functional resin are described, both based on 2% cross-linked polystyrene with a high density (>60%) of side-chains and terminated by a primary alcohol. In the first case the C_{11} side-chain is linked to the polymer through a sulfide, and in the second an ether linkage is employed to incorporate a $(CH_2CH_2O)_4$ unit. In both cases the resins have ^{13}C NMR spectra that are informative in the chain terminus region without special operating conditions. Model intermolecular metathesis reactions were carried out on allylcarbamic acid *tert*-butyl ester and various alkenes with Grubbs' catalyst. On the basis of these experiments, gel-phase metathesis was successfully demonstrated between a polymer-bound allyl ether and simple symmetrical disubstituted alkenes, monitoring the extent of reaction by ^{13}C NMR. These reactions did not go to completion even with recycling and some evidence for competing interchain metathesis is presented, based on the increased broadening and reduced mobility of the ensuing polymer.

Key words: alkene metathesis, ruthenium, gel-phase, ^{13}C NMR.

Résumé : On décrit des méthodes de synthèse de deux types de résines fonctionnelles qui comportent toutes les deux du polystyrène réticulé à 2%, une densité élevée (>60%) de chaînes latérales et qui se terminent par un alcool primaire. Dans le premier cas, la chaîne latérale en C_{11} est liée au polymère par un sulfure et, dans le deuxième cas, on utilise une liaison éther pour incorporer une unité $(CH_2CH_2O)_4$. Dans les deux cas, les spectres RMN du ^{13}C des résines fournissent de l'information sur la région terminale de la chaîne sans nécessiter de conditions spéciales. Utilisant le catalyseur de Grubb, on a effectué des réactions modèles de métathèse intermoléculaire avec l'ester *tert*-butylique de l'acide allylcarbamique et divers alcènes. Sur la base des résultats de ces expériences et faisant appel à la RMN du ^{13}C pour suivre le déroulement de la réaction, on a pu mettre en évidence la métathèse en phase gel entre un oxyde d'allyle lié au polymère et des alcènes simples disubstitués de façon symétrique. Ces réactions ne sont pas complètes, même si on fait du recyclage; de plus, en se basant sur une augmentation de l'élargissement des signaux et sur la mobilité réduite du polymère qui en résulte, on présente des données qui mettent en évidence l'existence de réactions compétitives de métathèse interchaînes.

Mots clés : métathèse d'alcène, ruthénium, phase gel, RMN du ^{13}C.

[Traduit par la Rédaction]

Introduction

With the rapid development of solid-phase organic synthesis in response to the demands of combinatorial chemistry and high-throughput screening (1), suitable reaction types have been appraised. Desirable qualities include the ability to separate the polymer-bound product from reagents, solvents, and other reaction components, appropriate reactivity for the required functional transformation, and above all quantitative conversion so that the product is a coherent species. On this basis homogeneous catalysis seems ideal where applicable, since the solution phase catalyst may be separated from the medium by a simple filtration, and the reaction rate controlled by catalyst concentration. In addition, all the efforts that have been channeled into catalyst specificity applied to chemo-, regio-, and stereo-control may be brought to bear in solid-phase reactions. In some cases, the application of catalysis to solid-phase reactions has been routinely successful (e.g., in Suzuki coupling) (2) but in others it has proved more difficult to reproduce the stereoselectivity of solution-phase results across the board (e.g., in Sharpless dihydroxylation) (3).

As in any other area of synthesis, progress in solid-phase synthesis depends on methods for the analysis of product purity. Although considerable strides have been made in direct on-bead assay by IR (4), NMR (5), and other techniques (6), it remains a challenge for the discipline. This is especially the case when reactions are conducted on resin phases where the loading of reacting sites is low, as in the case of the popular Wang resin (typically 0.5 mmol g^{-1}) (7), Argogel (typically 0.43 mmol g^{-1}) (8), and Tentagel (typically 0.2 mmol g^{-1}) (9). This provided a basis for the synthesis of polystyrene resins with a high level of functionality, based on a readily accessible precursor. The use of 2% cross-linked 63% chloromethylated polystyrene (Fluka) provided

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Dedicated to Professor Brian James, a pioneer of ruthenium organometallic chemistry.

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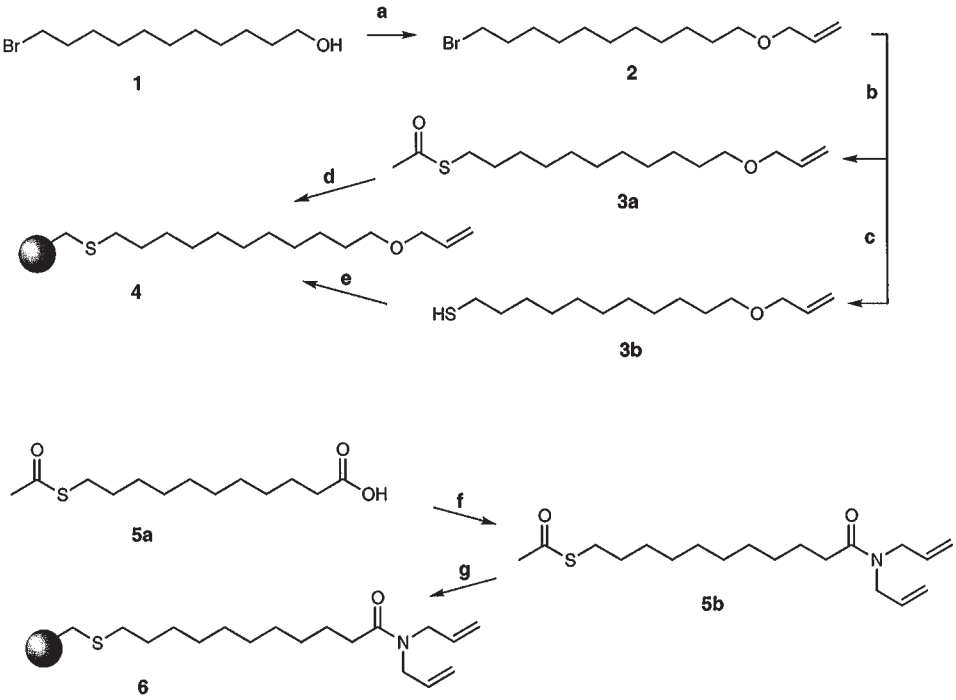
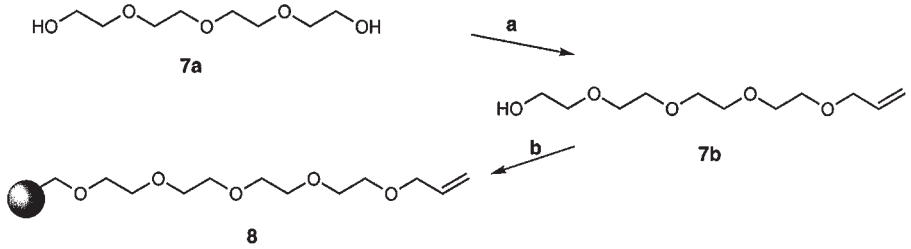
Scheme 1. (*a*) NaH, allyl bromide, THF, reflux 18 h, 76%; (*b*) $KSC(O)CH_3$, DMF, 18 h, RT, 74%; (*c*) NaOH, MeOH, H_2O, reflux 25 min, 49%; (*d*) PS, NaOMe, THF–DMF (1:3), 50°C, 60 h, 98%; (*e*) NaH, PS, THF, 60°C, 14 h, quant.; (*f*) $SOCl_2$ then $(C_3H_5)_2NH$, C_7H_8, 69%; (*g*) NaOMe, THF, 1 h, then PS, THF, 55°C, 18 h, quant.



Scheme 2. Polymer synthesis in the polyoxyethylene series: (*a*) Na, allyl bromide, 18 h at RT, then 100°C, 50%; (*b*) PS, NaH, THF, 60°C, 18 h, 90% conversion.



Scheme 3. Examples of successful polymer-phase metatheses: (*a*) of polymer **4** with but-2-ene (50% in CH_2Cl_2, 3 mol% catalyst, sealed tube, ambient, 84 h), quantitative; (*b*) of polymer **6** (CH_2Cl_2, 10 mol% catalyst, 48 h), quantitative; (*c*) of polymer **8** with *Z*-but-2-en-1,4-diol (40% in diglyme, 3 mol% catalyst), 83–87% with reexposure to the catalyst.

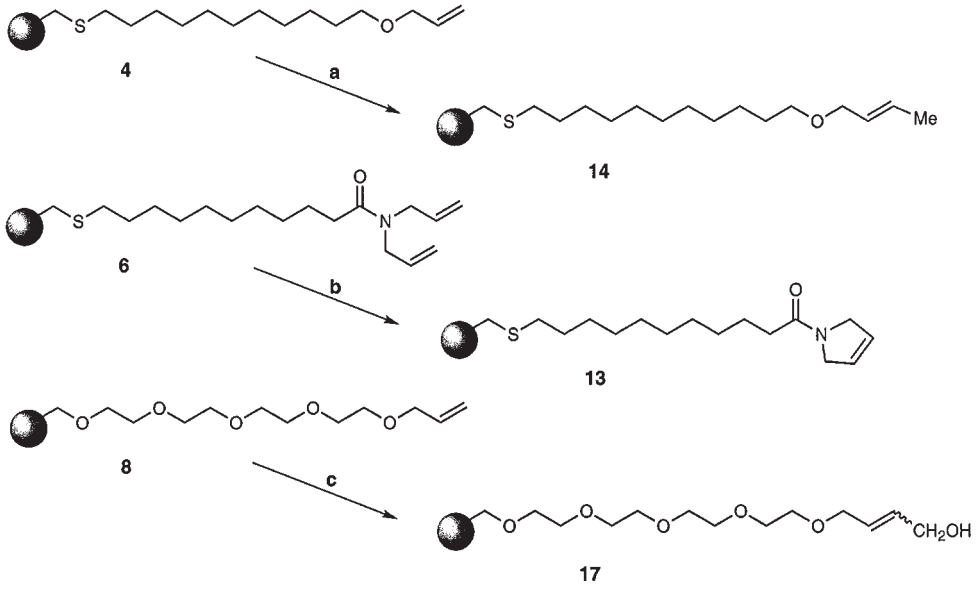
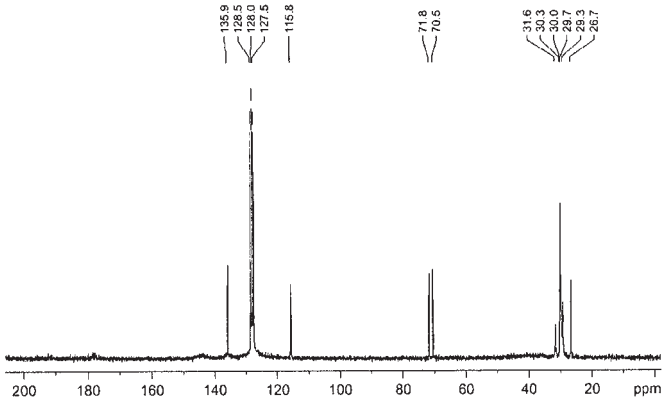


Fig. 1. MAS ^{13}C NMR spectrum of polymer **4** suspended in benzene-d_6.



polymers that were suitable for our purpose based on the criteria of mechanical stability and solvent-swelling properties, where the loading is in the 2 to 3 mmol g^{-1} region (for an alternative dendrimer-based approach to high–loading polystyrene, see ref. 10). Methods for the incorporation of side-chains, and the ease of obtention of good quality ^{13}C NMR spectra that reveal signals from the terminal region of the side-chain have already been reported (11).

In the present paper the application of alkene metathesis to solid-phase chemistry is described, using high-loading resins. In prior work, Bletcher and co-workers (12) demonstrated that Tentagel or polystyrene bound dialkenes could be subjected to efficient Ru-complex catalyzed intramolecular metathesis leading from 70 to >90% of the ring-closed product based on isolation by cleavage from the resin. In addition intermolecular metathesis between polymer-bound terminal alkenes and disubstituted alkenes was similarly shown to occur in 46 to >95% yield. A contemporary study employed solid-phase metathesis for the simultaneous cyclization and release of the product from the polymer (13). The high reactivity of norbornene in ring-opening metathesis has been exploited with styrene as the solution coreactant (14); the reverse strategy with vinylpolystyrene and norbornene leads to ring opening methathesis polymerization (ROMP) in the solid state and results in a support with a far higher density of functional sites than the original (15). The significance of solid-phase reactions has been recognized in recent reviews on alkene metathesis by Grubbs and others (16).

Results and discussion

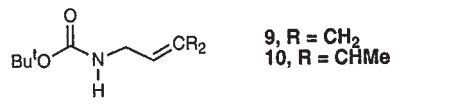
Polymer synthesis

For the preparation of sulfide-linked polymers, the synthetic route of Scheme 1 was adopted. Commercially available 11-bromoundecanol (**1**) was converted into its allyl ether **2**, which was in turn converted into the *S*-thioester **3a** by S_N2 displacement. Hydrolysis then produced the thiol **3b**. Two strategies were adapted for the polymer linkage step; either the thiolate anion was generated in situ from **3a**, or directly from the thiol. In both cases the reaction with 63% chloromethylated polystyrene (2% crosslinked) gave polymer **4** quantitatively within experimental error. Although most use was made of standard ^{13}C NMR spectra in the characterization of polymers, magic angle spinning (MAS) was occasionally also used, and Fig. 1 records the spectrum of **4** swollen in C_6D_6. For initial studies of metathesis, a related synthesis was conducted. 11-Acetylthioundecanoic acid (**5a**) (17) was converted into the corresponding diallylamide **5b** via the corresponding acid chloride, and then attached to polymer in the manner described for **3a**, again the reaction to form polymer **6** was quantitative as judged by weight gain and ^{13}C NMR results.

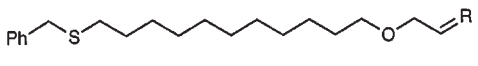
The related synthesis of O-linked polymers is shown in Scheme 2. The allyl ether **7b** of tetraethylene glycol **7a** was prepared, and its Na salt was reacted with PS for 18 h at 60°C in THF. These conditions, the result of some optimization efforts, produced polymer **8** in 90% yield, with characteristic ^{13}C NMR fingerprint.

Metathesis experiments

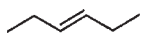
Conditions suitable for cross-metathesis of a terminal alkene **9** with *Z*-but-2-ene were established first. In these and subsequent reactions the "standard" Grubb's catalyst (bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride) was utilized. It was found that employing a 100-fold excess of *Z*-but-2-ene in CH_2Cl_2 at ambient temperature with 2 mol% catalyst gave complete reaction to form a *Z*:*E* mixture (1:3) of the disubstituted alkene **10**. Applying these exact conditions to the metathesis of polymer **4** did not result in observable metathesis or significant change in weight. At first the thiolate residue was suspected, and hence, monomer **11** was synthesized. This was shown to be reactive under the conditions of metathesis, giving **12** as an *E*/*Z* mixture in 85% yield. Furthermore, the intramolecular metathesis of polymer **6** to give the corresponding pyrroline **13** occurred smoothly, although 10% Ru catalyst and a reaction time of 48 h were required. It was noted that although the product polymer gave a good ^{13}C NMR spectrum corresponding to complete loss of starting material and the formation of cyclopentene, it appeared dark green-black under a microscope, despite intensive washings with a variety of solvents.



9, R = CH_2
10, R = CHMe



11, R = CH_2
12, R = CHMe



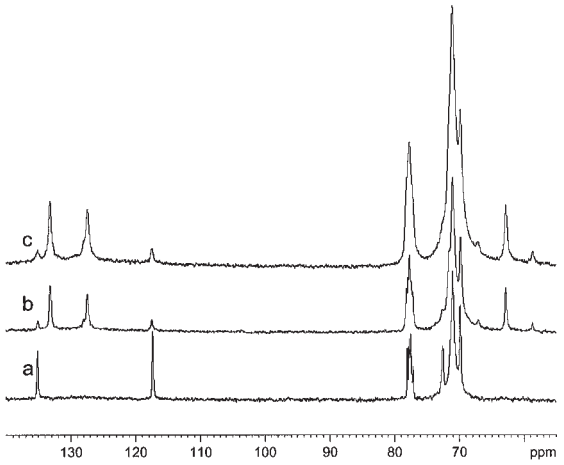
15

16a R = TBDMSi
16b R = H
16c R = Me
16d R = $CH_2OCH_2CH_2OMe$

This appeared to indicate some catalyst decomposition and irreversible reaction with the polymer.

On the basis of this set of experiments there appeared to be two further explanations for the failure of polymer cross-metathesis; firstly that the concentration of reagent and (or) catalyst in the polymer interstices was intrinsically low, and

Fig. 2. (*a*) Polymer **8** swollen in $CDCl_3$, 125 MHz; (*b*) after one cycle of metathesis with *Z*-but-2-en-1,4-diol to give predominantly **17**; (*c*) after two cycles of metathesis. Note the broadening of both resin and solvent (78 ppm) resonances.



secondly that the polymer environment led to a lowered reactivity. The first of these possibilities was tested in part by changing the reaction conditions, conducting metathesis of polymer **4** in CH_2Cl_2:*Z*-but-2-ene (1:1) in a sealed tube with 3 mol% catalyst. After 3.5 days at ambient temperature, workup gave a polymer whose ^{13}C NMR spectrum indicated complete reaction to form an *E*:*Z* isomeric mixture of the butenyl ether **14** (Scheme 3). This success could not, however, be duplicated with other alkenes and cross-metathesis of polymer **4** with either *E*-hex-2-ene (**15**) or the bis-TBDMS ether of *Z*-but-2-en-1,4-diol **16a** failed.

Appraisal of the results at this stage suggested that the reactivity of polymer **4** in metathesis was substantially lower than expected from the model experiments. One possibility was that the polarity of the polymer medium was lower than that of the solution because of the high density of hydrocarbon chains. This could lead to both unfavourable partition and lower reactivity of the catalyst in the polymer phase. For these reasons further metathesis experiments were carried out with the polymeric allyl ether **8**. Since the initial experiments failed completely for alkenes other than *Z*-but-2-ene, the polyether polymer **8** was reacted first with *Z*-but-2-en-1,4-diol **16b**. Under a variety of conditions slow metathesis was observed, but the ^{13}C NMR of the product **17** always showed some unreacted starting material. A single run with the corresponding ether **16c** went to completion, however. For the diol, best results were obtained when the solvent was diglyme (83%, 3 mol% catalyst, 168 h) Less successful experiments were conducted in CH_2Cl_2 (63%, 18 h) and THF (30%, 18 h). The presence of 10% of MeOH appeared to slow the turnover rate in CH_2Cl_2 even though it makes the partly immiscible diol fully soluble. In DMSO, DMF, or MeCN turnover was not observed, although there is some swelling of the polymer in these solvents. No discernable reaction took place in water (18).

Since only 83% yield was observed under the most favourable conditions, the polymer **17**, thus formed, was resubjected to the same reaction conditions. This, however, led to a rather small enhancement of the overall yield (83–87%). At the same time it was noted that the ^{13}C NMR resonances of the polymer became broader after each cycle (Fig. 2). This indicates that a change in the morphology of the polymer takes place during metathesis. The simplest interpretation is that crosslinking takes place within the bead by interchain metathetical reactions. Indeed an additional 1 to 2% of linkages would be expected to make a profound difference to the mobility of polymer-bound chains and thus affect the ^{13}C NMR line-widths. At this level there should be detectable additional signals in the NMR spectrum and there was an unassigned shoulder at 127.5 ppm in the spectra of samples of polymer **17**. This was close to, but not coincident with, the alkene carbon resonance of model compound **16d** at 129 ppm, taken in the presence of polymer **8** to best simulate the signal environment of the trace impurity in **17**.

In summary these experiments demonstrate the feasibility of metathesis reactions on the pendant side-chains of high-loading polystyrene resins, and the feasibility of monitoring the product directly by ^{13}C NMR. Under the conditions described, the utility is limited because of the low on-polymer reactivity and the lack of quantitative reaction (a prerequisite for successful solid-state combinatorial chemistry) with any but the most simple alkene reactants.

Experimental

General

Reactions involving air-sensitive reagents were performed under a dry argon atmosphere, using standard vacuum line techniques in Schlenk glassware. Solvents were deoxygenated where necessary by repeated freeze-thaw-freeze cycles, in which the solvent was frozen using liquid nitrogen, and allowed to warm until fully molten in vacuo or by pump-fill degassing, in which case the solvent was cooled to near freezing, usually using a dry ice – acetone bath, evacuated, and refilled with argon while swirling using a Whirlimixer™ to facilitate complete gas exchange. Transfers were carried out using stainless steel cannula wire or by syringe. For reactions using resin bound substates, "Swirler" refers to a Büchi Rotavapor M and "Bubbler" refers to a designed piece of glassware where the resin was supported on a glass sinter in solvent and agitated by argon passage.

Solvents were purchased from Rathburns, Fisons, Ultrafine, Aldrich, or Prolabo and dried immediately before use by distillation from standard drying agents (19). Merrifield resin was purchased from Fluka, and was 2% crosslinked with divinylbenzene (~4.3 mmol Cl per g resin) 200–400 mesh. Flash chromatography was performed using Fluorochem Silca gel 60, 40–63 μm, 550 $m^2\ g^{-1}$, or with commercial Biotage apparatus; KP-Sil™ 90 g cartridges (32–63 μm, 60 Å, 500–550 $m^2\ g^{-1}$ silica). Melting points were recorded by the author on a Reichert–Koffler block apparatus and are uncorrected. Infrared spectra were recorded on PerkinElmer 1750 or PerkinElmer Paragon 1000 FT spectrometers. ^1H and ^{13}C NMR spectra were recorded on Varian Gemini 200 (200 MHz), Bruker AM 200 (200 MHz), Bruker WH 300 (300 MHz), Bruker DPX 400 (400 MHz), Bruker AMX 500 (500 MHz), or Bruker AM 500 (500 MHz) spectrometers. MAS spectra were recorded on a Bruker MSL 200 (50.3 MHz) spectrometer. Polymer samples to be analyzed were prepared by placing an appropriate amount of polymer (usually ~120–130 mg) in a 5 mm

NMR tube and small amounts of solvent until the polymer was fully swollen and 2–4 mm of excess solvent remained. The tube was then vibrated either using a sonicator, whirlimixer, or by gently tapping the tube on a wooden surface until no air bubbles were visible and the suspension appeared homogeneous. The samples were then allowed to settle for a minimum of 10 min before being place in the spectrometer. For MAS samples by swelling the polymer in the solvent and transferring to a sinter. The excess solvent was removed by brief suction (~30 s) the sample was then transferred to the rotor. Unless otherwise stated operations were performed at room temperature.

Synthesis of polymers and their precursors

*Preparation of 3-(11-bromo-undecyloxy)propene (**2**)*

Sodium hydride (2.24 g, 60% in paraffin, 56 mmol) was washed with pentane (3 × 10 mL) and then suspended in THF (80 mL) and allyl bromide (10.4 mL, 120 mmol). 11-Bromoundecanol (10 g, 40 mmol) in THF (50 mL) was added dropwise. The solution was heated under reflux for 18 h. The solvent was removed in vacuo, the residue was dissolved in water (100 mL) and extracted with dichloromethane (1 × 125 mL, 1 × 100 mL). The combined organic extracts were washed with water (100 mL), dried over magnesium sulfate, and the solvent was removed in vacuo. The product was further purified by column chromatography (SiO_2, pentane–toluene, 2:1) and Kugelrohr distilled (150°C, 4 mbar) to give a colourless oil (8.86 g, 76%). IR (thin film) (cm^{-1}): 3080 (m, C=C-H_2, str), 2928 (s, C-H_2, str), 2856 (s, C-H_2, str), 1728 (m), 1647 (w, C=C, str), 1464 (s, C-H, def), 1346 (s, CH_3, def), 1254 (m), 1106 (s, C-O, str), 996 (m, -CH=CH_2, def), 922 (s, -CH=CH_2, def), 722 (w, CH_2, rocking), 645 (m, C-Br). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.92 (ddt, J = 17.2, 10.6, 5.2 Hz, 1H, $H_{2'}$), 5.27 (dq, J = 17.2, 1.6 Hz, 1H, $H_{3'a}$), 5.17 (dq, J = 10.4, 1.3 Hz, 1H, $H_{3'b}$), 3.96 (dt, J = 6.8, 1.3 Hz, 2H, $H_{1'}$), 3.42 (t, J = 7.0 Hz, 2H, H_1 or H_{11}), 3.41 (t, J = 7.1 Hz, 2H, H_{11} or H_1), 1.85 (tt, J = 7.5, 7.0 Hz, 2H, H_{10}), 1.58 (tt, J = 7.0, 7.0 Hz, 2H, H_2), 1.43–1.26 (m, 14H, H_{3-9}). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 135.1 ($C_{2'}$), 116.6 ($C_{3'}$), 71.7 ($C_{1'}$), 70.5 (C_1), 34.0 (C_{11}), 32.8 (C_{10}), 29.7, 29.5, 29.4, 29.4, 28.7, 28.1 ($C_{2,4-9}$), 26.1 (C_3).

Preparation of thioacetic acid S*-(11-allyloxy-undecyl) ester (**3a**)*

To a solution of potassium thioacetate (5.71 g, 50 mmol) in dimethylformamide (50 mL) was added 3-(11-bromo-undecyloxy)propene (27.28 g, 25 mmol). The solution was stirred for 18 h, then added to water (350 mL). This solution was then extracted with ether (3 × 100 mL, 2 × 50 mL). The combined ether extracts were washed with potassium carbonate solution (100 mL, 10%) and saturated potassium carbonate (2 × 100 mL), dried over sodium carbonate, and the solvent was removed in vacuo. The product was further purified by column chromatography (SiO_2, pentane–dichloromethane, 1:1) to give the product as a colourless oil (5.29 g, 74%). CI-MS (NH_4) *m/z* (%): 287 ($[M + H]^+$, 38), 245 ($[M + H - CH3CO]^+$, 39), 227 ($[M + H - CH_2CHCH_2OH]^+$, 27), 187 ($[M - CH_3CO - OCH_2CH{=}CH_2]^+$, 100). HRMS calcd.: 287.2045; found: 287.2047. IR (thin film) (cm^{-1}): 3369 (w, COC-H_3, str), 3079 (m, C=C-H_2, str), 2924 (s, C-H_2, str), 2853 (s, C-H_2, str), 1694 (s, C=O, str), 1647 (w, C=C, str), 1464 (s, C-H, def), 1429 (m, C-H, def), 1353 (s, CH_3, def), 1262 (m), 1107 (s, C-O, str), 998 (m, -CH=CH_2, def) 954, 923 (s, -CH=CH_2, def), 801 (w), 722 (w, CH_2, rocking), 672 (w), 627. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.92 (ddt, J = 17.2, 10.8, 5.5 Hz, 1H, $H_{2'}$), 5.27 (dq, J = 17.2, 1.4 Hz, 1H, $H_{3'a}$), 5.16 (dq, J = 10.8, 1.4 Hz, 1H, $H_{3'b}$), 3.96 (dt, J = 5.6, 1.4 Hz, 2H, $H_{1'}$), 3.42 (t, J = 6.7 Hz, 2H, H_1), 2.86 (t, J = 7.4 Hz, 2H, H_{11}), 2.32 (s, 3H, H_{13}), 1.67–1.52 (m, 4H, H_2, H_{10}), 1.34–1.26 (m, 14H, H_{3-9}). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 196.0 (C_{12}), 135.1 ($C_{2'}$), 116.6 ($C_{3'}$), 71.7 ($C_{1'}$), 70.5 (C_1), 30.58 (C_{11}), 29.7, 29.5, 29.4, 29.1, 29.1, 28.9 ($C_{2,4-10,13}$), 26.1(C_3).

*Preparation of poly[1-(11-allyloxy-undecylsulfanylmethyl)-4-vinyl benzene-co-vinyl-benzene-co-divinyl-benzene] (**4**)*

From thioacetic acid S*-(11-allyloxy-undecyl)ester:* To a suspension of sodium methoxide (730 mg, 13.5 mmol) in THF (5 mL) was added dropwise, via cannula, a solution of thioacetic acid *S*-(11-allyloxy-undecyl)ester (3.22 g, 11.25 mmol) in THF (5 mL). After 1 h, THF (10 mL) was added, followed by dimethylformamide (30 mL). This solution was added via cannula to a flask containing Merrifield resin (1.74 g, 4.3 mmol g^{-1}) and this suspension was swirled at 50°C for 60 h The suspension was then transferred to a sinter and washed with dichloromethane (3 × 50 mL), dimethylformamide (3 × 50 mL), dichloromethane (3 × 50 mL), water (50 mL), methanol (50 mL), dichloromethane (3 × 50 mL), dimethylformamide (3 × 50 mL), dichloromethane (3 × 50 mL), and pentane (3 × 50 mL). Drying in vacuo gave the product as a colourless opaque tacky polymer (3.28 g, 98%). IR (KBr disk) (cm^{-1}): 3082 (vw, C=C-H_2, str) 3058 (vw, C=C-H_2, str), 3024 (w, Ar-H, str), 2924 (s, C-H_2, str), 2852 (m, C-H_2, str), 1723 (w) 1702 (w), 1647 (w, C=C, str), 1604 (w, ar), 1510 (m, ar), 1494 (w), 1452 (m, C-H, def), 1421 (w, C-H, def), 1347 (m), 1271 (w), 1239 (w), 1137 (vw), 1104 (s, C-O, str), 1018 (vw), 997 (w, -CH=CH_2, def), 920 (s, -CH=CH_2, def), 827 (m, para Ar, C-H bnd), 760 (m, Ph), 700 (s, Ph). ^{13}C MAS NMR (50.3 MHz, C_6D_6) δ: 135.9 ($C_{2'}$), 115.8 ($C_{3'}$), 71.8 ($C_{1'}$), 70.5 (C_1), 30.3, 30.0, 29.7, 29.3, 26.7 (C_{2-11}).

*Through isolation of the intermediate 11-allyloxy-undecane-1-thiol (**3b**):* Thioacetic acid *S*-(11-allyloxy-undecyl) ester (4.29 g, 15 mmol) in methanol (50 mL) was placed in round-bottom flask, and a solution of sodium hydroxide (2.40 g, 60 mmol) in water (3.8 mL) – methanol (10 mL) was added via cannula. The solution was heated at reflux for 25 min, then poured into phosphate buffer (pH 5.5, 100 mL). The solution was extracted with dichloromethane (2 × 100 mL, 1 × 25 mL). The combined extracts were washed with water (1 × 100 mL), and solvent was removed in vacuo. The product was further purified by column chromatography (SiO_2, pentane–toluene, 1:1) to give 11-allyloxy-undecane-1-thiol as a colourless oil (1.784 g, 49%). CI-MS (NH_4) *m/z* (%): 262 ($[M + NH_4]^+$, 22). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.91 (ddt, J = 17.3, 10.6, 5.5 Hz, 1H, $H_{2'}$), 5.26 (dq, J = 17.3, 1.6 Hz, 1H, $H_{3'a}$), 5.16 (dq, J = 10.3, 1.5 Hz, 1H, $H_{3'b}$), 3.95 (dt, J = 5.5, 1.5 Hz, 2H, $H_{1'}$), 3.41 (t, J = 6.6 Hz, 2H, H_1), 2.51 (q, J = 7.3 Hz, 2H, H_{11}), 1.75 (br s, 1H, SH), 1.63–1.54 (m, 4H, H_2, H_{10}), 1.40–1.22 (m, 14H, H_{3-9}). ^{13}C NMR

(125 MHz, $CDCl_3$) δ: 135.0 ($C_{2'}$), 116.6 ($C_{3'}$), 71.7 ($C_{1'}$), 70.5 (C_1), 34.0 (C_{10}), 29.7, 29.5, 29.4, 29.0, 28.3 ($C_{2,4-9}$), 26.1 (C_3), 24.6 (C_{11}). Sodium hydride (288 mg, 60% in paraffin, 7.2 mmol) was washed with pentane (3 × 10 mL) and suspended in THF (10 mL). Merrifield resin (1.047 g, 4.5 mmol) was added washing into flask with THF (20 mL), followed by 11-allyloxy-undecane-1-thiol (1.650 g, 6.75 mmol), rinsing the syringe with THF (15 mL). Upon addition of the thiol, effervescence was observed. The suspension was swirled at 60°C overnight. Water (10 mL) was added, and the suspension was swirled for 10 min. The suspension was transferred to a sinter and washed with dichloromethane (25 mL), water (25 mL), dichloromethane (3 × 25 mL), and ethanol (25 mL), and then dried in vacuo to give the product as a colourless tacky polymer (1.993 g, quant.).

*Preparation of (11-allyloxy-undecylsulfanylmethyl)benzene (**11**)*

Sodium hydride (180 mg, 60% in paraffin, 4.5 mmol) was washed with pentane (3 × 5 mL) and suspended in THF (6 mL). *S*-Benzylisothiouronium chloride (405 mg, 2 mmol) was added and the mixture was heated at reflux for 150 min. THF (10 mL) was added and the mixture was heated at reflux for 4 h. 3-(11-Bromo-undecyloxy)propene (583 mg, 2 mmol) was added and the mixture was heated at reflux for 18 h. After cooling, toluene (20 mL) and water (10 mL) were added and the THF was removed in vacuo. Toluene (40 mL) was added and the mixture was washed with water (3 × 30 mL). The combined water washings were extracted with toluene (20 mL), and the combined toluene extracts were dried over sodium sulfate. The product was isolated by column chromatography (SiO_2, dichloromethane–pentane, 1:1) giving the product as a pale yellow oil (466 mg, 69%). CI-MS (NH_4) *m*/*z* (%): 335 ($[M + H]^+$, 100). HRMS calcd.: 335.2409; found: 335.2410. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31 (s, 2H, H_{15} or H_{14}), 7.30 (s, 2H, H_{14} or H_{15}), 7.27–7.20 (m, 1H, H_{16}), 5.92 (ddt, *J* = 17.2, 10.4, 5.6 Hz, 1H, $H_{2'}$), 5.27 (dq, *J* = 17.2, 1.7 Hz, 1H, $H_{3'a}$), 5.17 (ddt, *J* = 10.4, 1.9, 1.3 Hz, 1H, $H_{3'b}$), 3.96 (dt, *J* = 5.64, 1.4 Hz, 2H, $H_{1'}$), 3.70, (s, 2H, H_{12}), 3.42 (t, *J* = 6.7 Hz, 2H, H_1), 2.40, (t, *J* = 7.4 Hz, 2H, H_{11}), 1.62–1.51 (m, 4H, H_2, H_{10}), 1.38–1.20 (m, 14H, H_{3-9}). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.6 (C_{13}), 135.1 ($C_{2'}$), 128.8 (C_{15}), 128.4 (C_{14}), 126.8 (C_{16}), 116.7 ($C_{3'}$), 71.8 ($C_{1'}$), 70.5 (C_1), 36.2 (C_{12}), 31.3 (C_{11}), 29.7, 29.5, 29.5, 29.2, 28.8 ($C_{2,4-10}$), 26.1 (C_3).

Preparation of thioacetic acid S*-(10-diallylcarbamoyl decyl) ester (**5b**)*

To a solution of 11-acetylsulfamyl-undecanoic acid (1.820 g, 7 mmol) in toluene (10 mL) was added thionyl chloride (2 mL, 27 mmol), and the mixture was heated at reflux for 2 h. The solvent was removed in vacuo. The acid chloride was dissolved in toluene (10 mL), and diallylamine (5 mL, 40 mmol) was added. The mixture was stirred for 1 h before the addition of saturated sodium hydrogen carbonate (20 mL). Dichloromethane (100 mL) was then added; the solution was washed with saturated sodium hydrogen carbonate (50 mL) and phosphate buffer (pH 5.5, 50 mL), then dried over magnesium sulfate. The product was further purified by column chromatography (SiO_2, pentane – ethyl acetate, 5:1) to give the product as a pale yellow oil (1.569 g, 69%). CI-MS (NH_4) *m*/*z* (%): 340 ($[M + H]^+$, 100), 298 ($[M - C_3H_5]^+$, 14). HRMS calcd.: 340.2310; found: 340.2309. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.84–5.70 (m, 2H, $H_{2'}$), 5.25–5.05 (m, 2H, $H_{3'}$), 3.98 (br d, *J* = 5.8 Hz, 2H, $H_{1'a}$), 3.86 (br d, *J* = 4.5 Hz, 2H, $H_{1'b}$), 2.85 (t, *J* = 2.4 Hz, 2H, H_{11}), 2.32 (s, 3H, H_{13}), 2.30 (t, *J* = 7.6 Hz, 2H, H_2), 1.63 (q, *J* = 7.3 Hz, 2H, H_3 or H_{10}), 1.55 (q, 7.4 Hz, 2H, H_{10} or H_3), 1.37–1.22 (m, 16H, H_{4-9}). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 196.0 (C_{12}), 173.2 (C_1), 133.4 ($C_{2'a}$), 133.0 ($C_{2'b}$), 117.0 ($C_{3'a}$), 116.5 ($C_{3'b}$), 49.1 ($C_{1'a}$), 47.8 ($C_{1'b}$), 32.9 (C_2), 30.6 (C_{11}), 29.4, 29.4, 29.4, 29.1, 29.0, 28.8 ($C_{4-10,\ 13}$), 25.3 (C_3).

*Preparation of poly-[*N,N*-diallyl-11-(4-vinyl-benzyl sulfanylundecanoic acid amide)-co-vinyl-benzene-co-divinyl-benzene] (**6**)*

To sodium methoxide (194 mg, 3.6 mmol) was added a solution of thioacetic acid *S*-(10-diallylcarbamoyl decyl) ester (1.018 g, 3 mmol) in THF (2 mL). The solution was stirred for 1 h, then a small aliquot removed and analyzed by ^{1}H NMR, which showed complete deacetylation. The solvent was then removed in vacuo, the solid was redissolved in THF (10 mL), and the solution was added via cannula to a flask containing Merrifield resin (465 mg, 4.3 mmol g^{-1}) swollen in THF (5 mL). The suspension was swirled at 55°C for 18 h, then transferred to a sinter and washed with dichloromethane (2 × 40 mL), water (40 mL), dimethylformamide (4 × 40 mL), and dichloromethane (5 × 40 mL), then dried in vacuo yielding the product as a colourless polymer (1.019 g, quant.). IR (KBr disk) (cm^{-1}): 3081 (w, C=C-H_2, str), 3024 (w, C=C-H or Ar-H, str), 2921 (s, C-H, str), 2852 (m, C-H, str), 1701 (m, C=O, str), 1654 (s, C=C, str), 1636 (s, C=C, str), 1458 (m, C-H, def), 1420 (m, C-H, str), 1213 (br, m), 1113 (w), 1016, 989 (m, -CH=CH_2, def), 912 (m, -CH=CH_2, def), 824 (m), 761 (m, Ph), 698 (m, Ph). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 173.2 (C_1), 133.5, 133.0 ($C_{2'}$), 117.1, 116.5 ($C_{3'}$), 49.2, 47.8 ($C_{1'}$), 33.0 (C_2), 31.7, 29.4 (C_{4-11}), 25.3 (C_3).

*Preparation of 2-(2-(1-(2-allyloxy-ethoxy)-ethoxy)-ethoxy)-ethanol (**7**) (20)*

A 500 mL round-bottom flask was charged with sodium (5.93 g, 0.257 mol) and tetraethylene glycol (200 g). The solution was stirred at 80°C for 18 h. The solution was allowed to cool to room temperature, then 3-bromopropene (23 mL, 0.266 mol) was added dropwise over 15 min. The solution was warmed to 70°C for 90 min and 100°C for 60 min. The solution was allowed to cool to room temperature and added to a mixture of saturated sodium chloride (400 mL) and water (200 mL). The aqueous solution was extracted with dichloromethane (2 × 200 mL, 4 × 50 mL). The combined extracts were extracted with water (2 × 200 mL, 11 × 100 mL), however TLC showed that some product remained in the dichloromethane layer. The solvent was reduced in vacuo to 150 mL and the solution was further extracted with water (2 × 150 mL). The solvent was then totally removed in vacuo, and the oil was redissolved in ether (500 mL) and extracted with water (5 × 100 mL). Sodium chloride was added to the combined water extracts until the solution was saturated. The solution was extracted with dichloromethane (3 × 150 mL, 6 × 100 mL), and the combined extracts were

reduced in vacuo to 500 mL. The solution was dried over sodium sulfate and solvent was removed in vacuo. The oil was then fractional distilled using a 5 inch Vigreux column, and the fraction at 102–112°C at 0.03–0.04 mm Hg (1 mm Hg = 133.32 kPa) was collected. TLC showed this to be a mixture consisting mainly of the desired product, but contained small amounts of tetraethyleneglycol diallyl ether and tetraethylene glycol. The oil was redissolved in saturated sodium chloride (300 mL), and extracted with ether (2 × 200 mL, 5 × 100 mL). The combined extracts were dried over magnesium sulfate, and solvent was removed in vacuo. The oil was triturated with pentane (2 × 50 mL). Solvent was removed in vacuo giving a colourless oil (30.76 g, 50%), which contained a slight trace of the diallyl ether of tetraethyleneglycol, bp 102–112°C, 0.03–0.04 mm Hg ((lit. (21) 99–101°C, 0.2 mm Hg). CI-MS (NH_4) *m/z* (%): 235 ($[M + H]^+$, 100). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.87 (ddt, *J* = 17.2, 10.3, 5.7 Hz, 1H, $H_{2'}$), 5.22 (dq, *J* = 17.2, 1.6 Hz, 1H, $H_{3'a}$), 5.13 (dm, *J* = 10.3 Hz, 1H, $H_{3'b}$) 3.98 (dm, *J* = 5.6 Hz, 2H, $H_{1'}$), 3.68–3.54 (m, 8H, $H_{1–8}$), 2.81 (br s, 1H, OH). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 134.7 ($C_{2'}$), 116.8 ($C_{1'}$), 72.5 (C_7), 72.0 ($C_{1'}$), 70.5, 70.5, 70.5, 70.2 ($C_{2–7}$), 69.3 (C_1), 61.6 (C_8).

*Preparation of poly[1-(2-(2-(1-(2-allyloxy-ethoxy)-ethoxy)-ethoxy)-ethoxy methyl)-4-vinyl benzene-co-vinyl-benzene-co-divinyl-benzene] (**8**)*

Merrifield resin (1.164 g, 4.3 mmol g^{-1}), sodium hydride (800 mg, 60% in paraffin, 20 mmol), THF (20 mL), and 2-(2-(1-(2-allyloxy-ethoxy)-ethoxy)-ethoxy)-ethanol (**7**) (4.686 g, 20 mmol) were placed in 50 mL round-bottom flask, and swirled at 60°C for 18 h. The suspension was transferred to a sinter with THF, and washed with DMF (3 × 30 mL), water (3 × 30 mL), methanol (3 × 30 mL), tetraethyleneglycol dimethyl ether (3 × 30 mL), methanol (3 × 30 mL), and dichloromethane (3 × 30 mL) and dried in vacuo giving the product as colourless opaque tacky polymer (2.056 g, 90%). ^{13}C MAS NMR (50.3 MHz, $(CD_3)_2SO$) δ: 134.1 ($C_{2'}$), 115.1 ($C_{3'}$), 71.1 ($C_{1'}$), 70.0 ($C_{2–8}$), 69.1 (C_1).

Experimental for metathesis reactions

Diallylcarbamic acid *tert*-butyl ester (21, 22), 2,5-dihydropyrrole-1-carboxylic acid *tert*-butyl ester (23), and allyl-carbamic acid *tert*-butyl ester (23) were prepared by literature procedures.

Preparation of but-2-enylcarbamic acid-tert-*butyl ester (**10**) (24)*

Bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (27.4 mg, 1 mol%) and allylcarbamic acid-*tert*-butyl ester (**9**) (524 mg, 3.33 mmol) were placed in a Schlenk tube fitted with a dry ice condenser. Dichloromethane (65 mL) was added via cannula. *Z*-2-Butene was condensed into a Schlenk tube cooled in a dry ice – acetone bath, and 3.5 mL was transferred into the tube using a dry ice cooled syringe. The solution was stirred for 6 h, the condenser was then removed, a needle was inserted into the septum, and the solution was left overnight. The solvent was then removed in vacuo and the product was isolated by column chromatography (SiO_2, pentane – ethyl acetate, 2:1) to give the product as brown oil (510 mg, 89%). A small quantity of the two isomers was partially separated by preparative GLC (Peg 20M, 15%, 175°C). ^{1}H NMR (500 MHz, $CDCl_3$) δ (*Z*)-isomer: 5.60 (dqd, *J* = 10.4, 6.7, 1.0 Hz, 1H, H_2), 5.42 (dtd, *J* = 10.4, 7.0, 1.0 Hz, 1H, H_3), 4.48 (br s, 1H, NH), 3.78 (br s, 2H, H_4), 1.67 (dd, *J* = 6.7, 0.9 Hz, 3H, H_1), 1.45 (s, 9H, H_7); (*E*)-isomer: 5.60 (dq, *J* = 14.7, 7.0, 1H, H_2), 5.45 (dt, *J* = 14.7, 6.3 Hz, 1H, H_3), 4.54 (br s, 1H, NH), 3.66 (br s, 2H, H_3), 1.67 (d, *J* = 7.0 Hz, 3H, H_1), 1.45 (s, 9H, H_7). ^{13}C NMR (125 MHz, mixed isomers, $CDCl_3$) δ: 155.8 (C_{5Z}), 155.7 (C_{5E}), 127.6 (C_{3E}), 127.5 (C_{2E}), 127.2 (C_{3Z}), 126.7 (C_{2Z}), 79.1 (C_6), 42.5 (C_{4E}), 37.3 (C_{4Z}), 28.4 (C_7), 17.6 (C_{1E}), 12.9 (C_{1Z}).

General procedure for screening of metathesis of allyl-carbamic acid tert-*butyl ester (**9**)*

Allyl-carbamic acid *tert*-butyl ester (78.6 mg, 0.5 mmol) and bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (8.2 mg, 10 μmol) were placed in a Schlenk tube and degassed. In a separate Schlenk tube dichloromethane (10 mL) and the alkene (5 mmol) were degassed. The liquid was transferred via cannula to the first Schlenk tube. The reactions were followed both by TLC and (or) by removing aliquots (0.5 mL), removing the solvent in vacuo, and analyzing by ^{1}H NMR.

Pent-2-enyl-carbamic acid tert-*butyl ester (25):* Using *E*-2-hexene; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 5.63 (dtt, *J* = 15.3, 6.2, 1.3 Hz, 1H, H_3), 5.43 (dt, *J* = 15.3, 5.9 Hz, 1H, H_4), 4.55 (br s, 1H, NH), 3.68 (br t, 2H, H_5), 2.02 (qddd, *J* = 7.3, 6.2, 1.5, 1.2, 2H, H_2), 1.44 (s, 9H, H_8), 0.97 (td, *J* = 7.4, 1.2, 3H, H_1). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 155.7 (C_6), 134.6 (C_4), 125.3 (C_3), 79.1 (C_7), 42.5 (C_5), 28.4 (C_8), 25.2 (C_2), 13.4 (C_1).

*4-*tert-*Butoxycarbonylamino-but-2-enyl)-carbamic acid* tert-*butyl ester:*

Bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (97 mg, 2 mol%) and allyl-carbamic acid *tert*-butyl ester (1.00 g, 5.92 mmol) were placed in a Schlenk tube. Chloroform (50 mL) was added via cannula and the solution was stirred at 50°C for 3 days. More bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (97 mg, 2 mol%) was added and the solution was stirred for a further 3 days at 50°C. The solvent was removed in vacuo and the stereoisomeric products were separated by chromatography on a Biotage apparatus (ethyl acetate – pentane, 1:4). ^{1}H NMR (500 MHz, $CDCl_3$) *E*-isomer δ: 5.55 (br s, 2H, H_1), 4.88 (br s, 2H, NH), 3.77 (br s, 4H, H_2), 1.44 (s, 18H, H_1). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 155.7 (C_3), 128.4 (C_1), 79.4 (C_4), 41.9 (C_2), 28.4 (C_5). ^{1}H NMR (500 MHz, $CDCl_3$) *Z*-isomer δ: 5.61 (br s, 2H, H_1), 4.63 (br s, 2H, NH), 3.72 (br s, 4H, H_2), 1.44 (s, 18H, H_5). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 155.9 (C_3), 128.9 (C_1), 79.4 (C_4), 37.1 (C_2), 28.4 (C_5).

*Preparation of 11-(but-2-enyloxy-undecyl)-sulfanylmethylbenzene (**12**)*

Bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (8.2 mg, 2 mol%) was placed in a Schlenk tube fitted with a dry ice condenser. *Z*-2-butene was condensed into a Schlenk tube cooled in a dry ice – acetone bath, and 0.5 mL was transferred into the tube using a dry ice cooled syringe.

11-(Allyloxy-undecylsulfanylmethyl)benzene (0.5 mmol, 167 mg) in dichloromethane (10 mL) was added via cannula, and the solution was stirred for 5.5 h. The solvent was removed in vacuo and the product was further purified by column chromatography (SiO_2, dichloromethane–pentane, 1:1) yielding the product as a yellow oil (134 mg, 85%). CI-MS (NH_4) *m*/*z* (%): 349 ($[M + H]^+$, 100), 293 ($[M - C_4H_7]^+$, 2). HRMS calcd.: 349.2565; found: 349.2575. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.31 (s, 2H, H_{14} or H_{15}), 7.30 (s, 2H, H_{15} or H_{14}), 7.27–7.20 (m, 1H, H_{16}), 5.75–5.53 (m, 2H, $H_{2'}$ and $H_{3'}$), 4.02 (ddt, *J* = 6.6, 1.5, 1.0 Hz, 2H, $H_{1'Z}$), 3.88 (dt, 6.2, 1.2 Hz, 2H, $H_{1'E}$), 3.70 (s, 2H, H_{12}), 3.41 (t, *J* = 6.9 Hz, 2H, H_{1Z}), 3.39 (t, *J* = 6.9 Hz, 2H, H_{1E}), 2.40 (t, *J* = 7.6 Hz, 2H, H_{11}), 1.71 (ddt, *J* = 6.5, 1.6, 1.2 Hz, 3H, $H_{4'E}$), 1.66 (ddt, *J* = 6.8, 1.7, 0.9 Hz, 3H, $H_{4'Z}$), 1.61–1.51 (m, 4H, H_2 and H_{10}), 1.40–1.14 (m, 14H, H_{3-9}). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 138.7 (C_{13}), 129.2 ($C_{2'E}$), 128.8 (C_{15}), 128.4 (C_{14}), 127.8 ($C_{3'E}$), 127.5 ($C_{2'Z}$), 127.1 ($C_{3'Z}$), 126.8 (C_{16}), 71.5 (C_{1E}), 70.4 (C_{1Z}), 70.3 ($C_{1'E}$), 66.0 (C_{1Z}), 36.3 (C_{12}), 31.4 (C_{11}), 29.8, 29.5, 29.5, 29.2, 28.9 ($C_{2,4-10}$), 26.2 (C_3), 17.7 ($C_{4'E}$), 13.2 ($C_{4'Z}$).

*Preparation of poly[1-(2,5-dihydro-pyrrol-1-yl)-11-(4-vinyl benzyl sulfanyl)-undec-1-one-co-vinyl-benzene-co-divinyl-benzene] (**6**)*

Bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (26 mg, 31 μmol) and resin **75** (150 mg, 312 μmol) were placed in a round-bottom flask and dichloromethane (6 mL) was added. The suspension was swirled under argon for 48 h, before being transferred to a sinter with dichloromethane, and washed with dichloromethane (3 × 25 mL), dimethylformamide (3 × 25 mL), and various combinations of ethanol, methanol, dimethylformamide, pentane, toluene, acetonitrile, and dimethylsulfoxide. However no washing solvent, or combination successfully removed the dark-green colour from the bead. The polymer was finally washed with dichloromethane (3 × 25 mL), and dried in vacuo, giving the product as a dark green polymer (142 mg, 92%). IR (KBr disc) (cm^{-1}): 3081 (w), 3055 (w), 3024 (m), 2926 (s), 2848 (m), 1944 (br, m), 1719 (s), 1702 (s), 1654 (s), 1648 (s), 1420 (m), 1263 (m), 1198 (m), 1107 (m), 1069 (w), 997 (m), 917 (m), 823 (s), 737 (s), 695 (m, Ph), 669 (s). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 171.8 (C_1), 126.0 ($C_{2'}$), 53.5 ($C_{1'a}$), 52.9 ($C_{1'b}$), 34.5, 33.2, 29.44, 26.3, 25.0 (C_{2-11}).

*Preparation of poly-[11-but-2-enyloxy-undecyl sulfanyl methyl-(4-vinyl benzene)-co-vinyl-benzene-co-divinyl-benzene] (**14**)*

*From metathesis of resin **4** with Z-2-butene:* Resin **4** (200 mg, 2.27 mmol g^{-1}) was placed in a thick walled glass tube (12 mm bore) and washed down with THF. The solvent was removed by blowing argon over the suspension until no solvent was visible outside the polymer. The polymer was then dried in vacuo. The tube was then cooled in a dry ice – acetone bath. *Z*-2-Butene was condensed into a Schlenk tube cooled in a dry ice – acetone bath, and 0.6 mL was transferred into the tube using a dry ice cooled syringe. Bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (11.2 mg, 3 mol%) in dichloromethane (0.6 mL) was then added to the tube. The bottom of the tube was cooled in liquid nitrogen before sealing. The tube was left at room temperature for 84 h. The lower half of the tube was then cooled in liquid nitrogen and the upper part was broken. The polymer was transferred to a sinter with dichloromethane and washed with dimethylformamide (3 × 25 mL), dichloromethane (3 × 25 mL), and pentane (3 × 25 mL), and dried in vacuo yielding the pale orange product polymer (206 mg, 94%). IR (thin film) (cm^{-1}): 3052 (w, C-H, str), 3023 (m, Ar-H or C=C-H, str), 2926 (s, C-H, str), 2850 (m, C-H, str), 1720 (m), 1702 (m), 1603 (m, Ar-H, def), 1509 (m, Ar-H, def), 1492 (m, Ar-H, def), 1440 (m, C-H, def), 1420 (m, C-H, def), 1364 (w, C-H_3, def), 1312 (w), 1260 (m), 1212 (w), 1180 (w, C-O, str), 1144 (w), 1108 (m, C-O, str), 1066 (w), 1018 (w), 965 (m, (E)-H-C=C-H, def), 908 (w), 823 (m, para Ar, C-H bnd), 759 (m, Ph, bnd), 747 (m), 698 (m, Ph, bnd), 672 (w), 661 (m). ^{13}C NMR (125 MHz, $CDCl_3$) δ: 128.9 ($C_{2'}$), 127.6 ($C_{3'}$), 71.2 (C_1), 70.0 ($C_{1'}$), 31.2, 29.3, 25.8 (C_{2-11}), 17.6 ($C_{4'E}$), 13.0 ($C_{4'Z}$).

From Resin-OH and crotyl bromide: Potassium hydride (35% in mineral oil) was placed in a preweighed Schlenk tube and washed with pentane (3 × 10 mL). The residual pentane was removed in vacuo to give (120 mg, 3.0 mmol). The Schlenk tube was cooled in dry ice – acetone bath, and solution of 18-crown-6 (555 mg, 2.1 mmol) in THF (22 mL) was added slowly via cannula. Resin-OH (12) was placed in the swirler, and the potassium hydride solution was added via cannula. As the suspension warmed to room temperature effervescence was observed. The suspension was allowed to warm to room temperature and swirled for 30 min. Crotyl bromide (1.0 mL, 10 mmol) was added and the suspension was swirled overnight, then transferred to a sinter with dichloromethane, and washed with dimethylformamide (3 × 30 mL), dichloromethane (30 mL), and pentane (30 mL), then dried in vacuo to give the product as a colourless tacky polymer (521 mg, 18% (by ^{13}C NMR)).

*General procedure for screening of metathesis of resin **8** and various alkenes*

Resin **8** (150 mg, 0.32 mmol) and bis(tricyclohexylphosphine)benzylidineruthenium(IV) dichloride (7.8 mg, 3 mol%) were loaded into a small Schlenk tube with a small magnetic follower. The contents of the Schlenk tube were degassed. The alkene and solvent were placed in a separate Schlenk tube, degassed, and added via cannula. The suspension was stirred slowly for the stated amount of time, then transferred to a sinter with a solvent (usually dichloromethane) and washed with some of the following solvents: dichloromethane, dimethylformamide, methanol, pentane, tetraglyme, THF, and dried in vacuo For the cross-metathesis product with *Z*-but-2-en-1,4-diol. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 133.2 ($C_{3'}$), 127.4 ($C_{2'}$), 70.9 ($C_{3'}$), 69.8, 67.2 (C_{1-8}), 62.8 ($C_{1'}$), 58.6 ($C_{4'}$).

References

1. (*a*) C.L. Kingsbury, S.J. Mehrman, and J.M. Takacs. Curr. Org. Chem. **3**, 497 (1999); (*b*) B.A. Lorsbach and M.J. Kurth. Chem. Rev. **99**, 1549 (1999); (*c*) R.C.D. Brown. J. Chem. Soc. Perkin Trans. 1, 3293 (1998).
2. (*a*) S. Chamoin, S. Houldsworth, C.G. Kruse, W.I. Bakker, and V. Snieckus. Tetrahedron Lett. **39**, 4179 (1998); (*b*) S.R. Piettre and S. Baltzer. Tetrahedron Lett. **38**, 1197 (1997);

(*c*) R. Frenette and R.W. Friesen. Tetrahedron Lett. **35**, 9177 (1994); (*d*) R. Franzén. Can. J. Chem. **78**, 957 (2000).
3. R. Riedl, R. Tappe, and A. Berkessel. J. Am. Chem. Soc. **120**, 8994 (1998).
4. B. Yan, J.B. Fell, and G. Kumaravel. J. Org. Chem. **61**, 7467 (1996).
5. (*a*) R. Warrass and G. Lippens. J. Org. Chem. **65**, 2946 (2000); (*b*) T. Wehler and J. Westman. Tetrahedron Lett. **37**, 4771 (1996); (*c*) R. Jelinek, A.P. Valente, K.G. Valentine, and S.J. Opella. J. Magn. Reson. **125**, 185 (1997); (*d*) Y.R. de Miguel, N. Bampos, K.M. Nalin de Silva, J.K.M. Sanders, and S.A. Richards. Chem. Commun. 2267 (1998); (*e*) G. Lippens, M. Bourdonneau, C. Dhalluin, R. Warrass, T. Richert, C. Seetharaman, C. Boutillon, and M. Piotto. Curr. Org. Chem. **3**, 147 (1999).
6. S.R. McAlpine and S.L. Schreiber. Chem. Eur. J. **5**, 3528 (1999).
7. S.S. Wang. J. Org. Chem. **40**, 1235 (1975).
8. M. Grotli, C.H. Gotfredsen, J. Rademann, J. Buchardt, A.J. Clark, J.O. Duus, and M. Meldal. J. Comb. Chem. **2**, 108 (2000).
9. R. Quarrell, T.D.W. Claridge, G.W. Weaver, and G. Lowe. Mol. Diversity, **1**, 223 (1996).
10. A. Basso, B. Evans, N. Pegg, and M. Bradley. Tetrahedron Lett. **41**, 3763 (2000).
11. (*a*) J.M. Brown and J.A. Ramsden. Chem. Commun. 2117 (1996); (*b*) I.P. Thomas, J.A. Ramsden, T.Z. Kovacs, and J.M. Brown. Chem. Commun. 1507 (1999).
12. M. Schuster, J. Pernerstorfer, and S. Blechert. Angew. Chem. Int. Ed. Engl. **35**, 1979 (1996)
13. J.H. van Maarseveen, J.A.J. den Hartog, V. Engelen, E. Finner, G. Visser, and C.G. Kruse. Tetrahedron Lett. **37**, 8249 (1996).
14. (*a*) G.D. Cuny, J.R. Cao, A. Sidhu, and J.R. Hauske. Tetrahedron, **55**, 8169 (1999); (*b*) J.U. Peters and S. Blechert. Synlett, 348 (1997).
15. A.G.M. Barrett, S.M. Cramp, and R.S. Roberts. Org. Lett. **1**, 1083 (1999).
16. (*a*) M. Schuster and S. Blechert. Angew. Chem. Int. Ed. Engl. **36**, 2037 (1997); (*b*) R.H. Grubbs and S. Chang. Tetrahedron, **54**, 4413 (1998); (*c*) T. Naota, H. Takaya, and S.I. Murahashi. Chem. Rev. **98**, 2599 (1998).
17. (*a*) F.S. Varveri, J. Nikokavouras, A.E. Mantaka-Marketou, and M. Micha-Screttas. Monatsh. Chem. **120**, 967 (1989); (*b*) R.N. Reddie. Synth. Commun. **17**, 1129 (1987).
18. T.A. Kirkland, D.M. Lynn, and R.H. Grubbs. J. Org. Chem. **63**, 9904 (1998).
19. D.D. Perrin, W.L.F. Armarego, and D.R. Perrin. Purification of laboratory reagents. Pergamon Press, Oxford. 1988.
20. R. Riemschnieder and H.J. Koetzsch. Monatsh. Chem. **90**, 787 (1959).
21. G.C. Fu, S.T. Nguyen, and R.H. Grubbs. J. Am. Chem. Soc. **115**, 9856 (1993).
22. B.A. Johns and C.R. Johnson. Tetrahedron Lett. **39**, 749 (1998).
23. T. Horiuchi, T. Ohta, E. Shirakawa, K. Nozaki, and H. Takaya. J. Org. Chem. **62**, 4285 (1997).
24. (*a*) M.A. Walters and A.B. Hoem. J. Org. Chem. **59**, 2645 (1994); (*b*) H. Nemoto, H.N. Jimenez, and Y. Yamamoto. J. Chem. Soc. Chem. Commun. 1304 (1990).
25. J.C. Anderson, D.C. Siddons, S.C. Smith, and M.E. Swarbrick. J. Chem. Soc. Chem. Commun. 1835 (1995).