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ω-Norbornenyl Polystyrene: An Olefin Metathesis Polymerizable Macromonomer[1]

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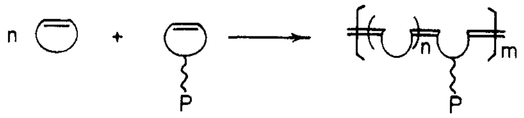
ABSTRACT: Poly(norbornenamer-*graft*-styrene) graft copolymers were prepared by olefin metathesis copolymerization of norbornene and norbornene-end-derivatized polystyrene (a macromonomer) using tungsten hexachloride/tetramethyltin catalysis. The main-chain (poly(norbornenamer)) molecular weight, the graft-chain (polystyrene) molecular weight, and the graft density could be independently controlled: the main-chain molecular weight by use of 1-octene as a chain transfer agent; the graft chain molecular weight in the macromonomer synthesis; the graft density by adjusting the norbornene:macromonomer ratio. Graft copolymers were characterized by ^{1}H NMR and IR spectroscopies and gel permeation chromatography.

Introduction

Copolymerization of a macromonomer (a linear macromolecule with polymerizable functionality at one end) and a standard low molecular weight monomer is the method of choice for preparing graft copolymers.[2,3] This approach offers access to a range of graft copolymers that cannot be prepared by grafting "onto or from" homopolymer backbones. Additionally and importantly, the macromonomer method allows rational design and synthesis of graft copolymers with control over the main-chain and graft-chain molecular weights and the graft density. There are many examples of this synthetic strategy employing free radical, cationic, anionic, coordination, and step-growth copolymerization.[3] We report in this manuscript the application of ring-opening olefin metathesis polymerization to graft copolymer synthesis using the macromonomer strategy. Equation 1 summarizes our synthetic approach in a generic fashion.



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Olefin metathesis has evolved to a mechanistically well-understood and synthetically versatile discipline.[4–6] Many examples of copolymers[7] and several examples of block copolymers[7–10] have been prepared by this chemistry. The recent syntheses of discrete, isolable initiatiors, which can render living polymerizations, offer new versatility to polymer synthesis using olefin metathesis.[9,11–13]

Experimental Section

Materials. Ethylene oxide (Eastman Kodak), norbornene (Aldrich), and chlorobenzene (Aldrich) were distilled from calcium hydride under nitrogen. Styrene (Aldrich) was distilled from calcium hydride at reduced pressure. Benzene (Aldrich) was distilled from sodium benzophenone dianion under nitrogen. Tetramethyltin and 1-octene (Aldrich) were distilled trap-to-trap from calcium hydride on a vacuum manifold. Tungsten hexachloride (Aldrich, Gold Label), *sec*-butyllithium (1.1 M in cyclohexane) (Aldrich), and 5-norbornene-2-carbonyl chloride (Pfaltz and Bauer) were used as received.

Methods. Solutions were prepared and reactions were carried out under nitrogen by using standard Schlenk procedures. Transfers were performed by cannula and syringe techniques. Solvents and solutions were stored under nitrogen in Teflon stopcock sealed storage flasks. Infrared spectra of films cast from chloroform solution were recorded on a Perkin-Elmer 283 spectrophotometer. ^{1}H and ^{13}C NMR spectra of deuteriochloroform solutions were obtained with a Varian XL-200 spectrometer. Gel permeation chromatography (GPC) was carried out by using Polymer Laboratories PL gel columns (10^4, 10^3, 10^2 Å), a Rainin Rabbit pump, a Knauer 98 refractive index detector, and toluene as the mobile phase. GPC data accumulation and analyses were performed by using Interactive Microware GPC software and an Apple IIe computer. Molecular weight data are reported relative to a polystyrene calibration. Gas chromatography was carried out by using a Hewlett Packard 5790A and an Analabs 15% AN 600 column.

Table I
Macromonomer GPC Data

sample	M_n	M_w	M_w/M_n
ω-NBPS-DP6	610	690	1.13
ω-NBPS-DP29	2900	3100	1.07
ω-NBPS-DP55	5500	5900	1.07
ω-NBPS-DP100	10000	11000	1.10

ω-Norbornenyl Polystyrene. Benzene (40 mL) was added to a nitrogen-purged, crown-capped pressure bottle containing a Teflon-coated stirring bar. The appropriate amount (for the desired molecular weight) of *sec*-butyllithium was introduced. Styrene (3 mL) was then added dropwise at room temperature and the polymerization mixture was stirred for 30 min. The living polymer (red solution) was then reacted with ethylene oxide, which was introduced to the reaction bottle as a gas in a stream of nitrogen until the red color was discharged. A slight molar excess (based on *sec*-butyllithium) of 5-norbornene-2-carbonyl chloride was then added. All samples (Table I) except the lowest molecular weight one were isolated by precipitation in methanol and purified by dissolution in tetrahydrofuran, reprecipitation from methanol, and drying at reduced pressure. The reaction solution of the lowest molecular weight sample was transferred to a separatory funnel and washed with water (twice), saturated sodium bicarbonate solution (twice), and then brine. The solution was dried with magnesium sulfate, the benzene was removed by rotary evaporation, and the polymer was dried by using a vacuum pump.

Poly(norbornenamer-*graft*-styrene). The appropriate amount (for the desired graft density) of ω-norbornenyl polystyrene and a Teflon-coated stirring bar were placed in a Schlenk tube which was then purged with nitrogen. Chlorobenzene (5 mL), 2.0 mL of 2.5 M norbornene in chlorobenzene (5 mmol), 0.4 mL of 0.2 M tetramethyltin in chlorobenzene (0.08 mmol), and the appropriate amount (for the desired poly(norbornenamer) molecular weight) of 0.1 M 1-octene in chlorobenzene were added. The reaction tube was placed in a 80 °C oil bath and allowed to equilibrate to temperature (10 min). Tungsten hexachloride (0.4 mL of 0.1 M in chlorobenzene; 0.04 mmol) was then added; the reaction mixture turned blue-black. After 10 min, the copolymer product was precipitated in a 1:1 mixture of methanol/acetone, redissolved in toluene and reprecipitated in 1:1 methanol/acetone, and dried at reduced pressure. Poly(norbornenamer) (homopolymer) was prepared by using an identical procedure without macromonomer.

Casting of Polymer Films. Films were cast on microscope slides by allowing 5% toluene solutions of graft copolymers or homopolymer mixtures to evaporate in air.

Results and Discussion

Equation 2 summarizes the synthesis of the prototypical olefin metathesis graft copolymers discussed in this paper. We chose to study this system for several reasons: Nor-

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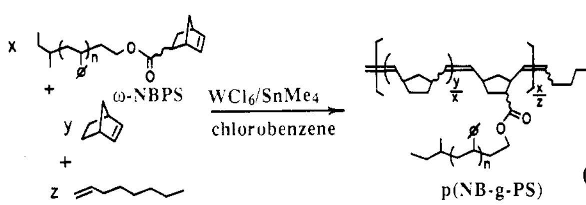

(2)

bornene and a norbornene-terminated macromonomer were chosen because, due to the strain energy of the bicyclic rings, complete reaction of monomer was expected.[14] The polystyrene macromonomer was chosen because it could be prepared with variable molecular weight by using anionic polymerization and the ethylene oxide end-capping and subsequent esterification reaction have precedence.[2] The chain-transfer agent, 1-octene, was selected in the course of this work because it reacted completely under the conditions of copolymerization.[15] The catalyst system, tungsten hexachloride/tetramethyltin, was used because of its compatibility with ester functionality.[16] This catalyst system is also expected to render a random graft copolymer, as the rates of monomer addition are independent of monomer structure and are determined only by the structure of the propagating carbene.[17]

Synthesis of ω-Norbornenyl Polystyrene. Styrene was anionically polymerized in benzene with *sec*-butyllithium as the initiator. The living polymer was then end-capped with ethylene oxide and subsequently allowed to react with 5-norbornene-2-carbonyl chloride to form ω-norbornenyl polystyrene (ω-NBPS). Several different molecular weight samples were prepared and are listed along with their GPC data in Table I. The end-capping chemistry was confirmed by infrared and NMR spectroscopy of ω-NBPS-DP6. Figure 1 shows infrared spectra of ω-NBPS-DP6 and polystyrene (for reference). The macromonomer (which is a mixture of endo and exo isomers) exhibits ester C=O stretching at 1735 cm^{-1} and ester C—O stretching at 1216 and 1177 cm^{-1}. ^1H and ^{13}C NMR spectra of ω-NBPS-DP6 are displayed in Figure 2. Integration of the aromatic (δ 6.35–7.35) and olefinic (δ 5.65–6.20) (due to norbornene) proton resonances yields a ratio of 15.75:1 (aromatic:olefinic) which corresponds to an average DP of 6.3; this is consistent with the GPC data. The ^{13}C spectrum is consistent as well; we make the following assignments: δ 62.7 (methylene carbon bound to ester oxygen); δ 126.1 (para aromatic carbon); δ 128.2 (ortho and meta aromatic carbons); δ 132.6, 136.0 (norbornene 2-carbon, endo and exo ester); δ 137.9, 138.1 (norbornene 3-carbon, endo and exo ester); δ 145 (ipso aromatic carbons); δ 174.6, 176.0 (carbonyl carbon, endo and exo ester).

Poly(norbornenamer-*graft*-styrene) [p(NB-*g*-S)] Synthesis. Several graft copolymers were prepared by the chemistry detailed in eq 2 and a summary of these materials is given in Table II. The workup conditions were optimized to give high-purity samples of entries 2a–d in Table II; the average yield of purified graft copolymer for entries 2a–d was 53%. Identical workup conditions were used for all copolymerizations and comparable yields were obtained for entries 1, 3–5, and 7. Entries 6 and 8 gave low isolated yields, likely because of the solubility of the graft copolymers with short main chains (entry 6) or long graft chains (entry 8) in the precipitation solvent. The data listed for entries 6 and 8 are probably not indicative of the majority of the reaction products, which were not isolated. Some unreacted macromonomer was present in the isolated reaction product of entry 8 (observed by GPC); this may be due to incompatibility of the large macromonomer and the growing polymer chain,[18] which also may explain the small number of average grafts per chain observed.

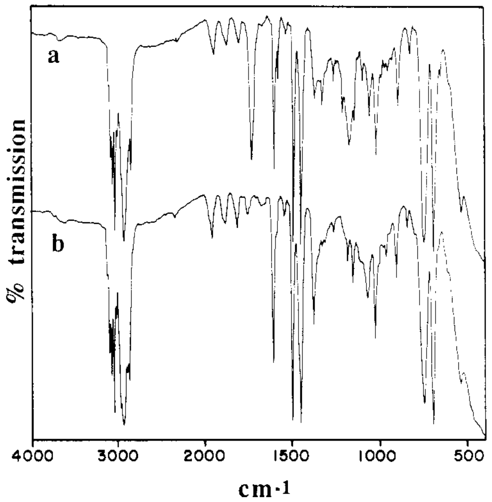

Figure 1. Infrared spectra of (a) ω-NBPS-DP6 and (b) polystyrene.

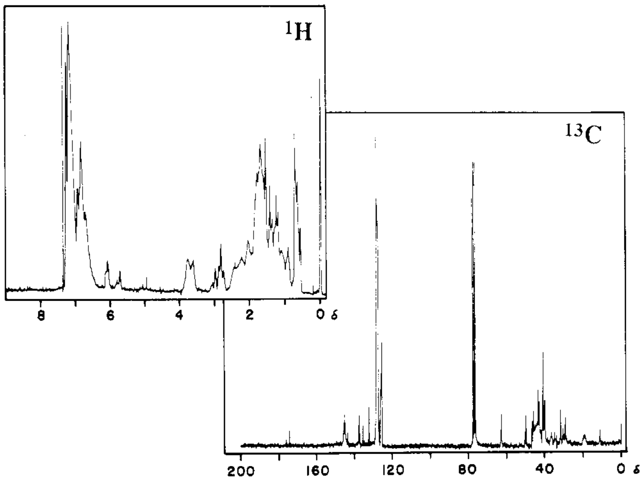

Figure 2. ^1H and ^{13}C NMR spectra of ω-NBPS-DP6.

Norbornene and 1-octene are not present in the crude reaction products (they are completely reacted), allowing the estimates of the backbone molecular weights listed in Table II. These estimates are based solely on the ratio of chain-transfer agent to monomer and macromonomer and assume that no molecular weight fractionation occurs in the purification.

Figure 3 shows representative (entry 2a in Table II) GPC data for a copolymerization. The crude product, isolated by precipitation in methanol, clearly contains a small amount of unreacted macromonomer. The purified graft copolymer (precipitated twice in methanol/acetone) is free of unreacted macromonomer but may contain some ungrafted poly(norbornenamer). The GPC data listed in Table II yield no useful quantitative information since the molecular weight values obtained (based on a polystyrene calibration) do not follow any pattern; this is likely due to a complex dependence of hydrodynamic volume on graft density, graft location, and backbone length. The data are of no use to our analyses here and are included only for their potential use to others.

The compositions of the purified graft copolymers were determined by ^1H NMR spectroscopy. Figure 4 displays a representative (entry 2a in Table II) ^1H NMR spectrum. Integration of the aromatic and olefinic resonance yields relative styrene and norbornene compositions. Figure 5 indicates that the graft copolymer composition is well controlled by adjusting the monomer/macromonomer feed ratio. The average graft density was calculated from the

Table II
Graft Copolymers

entry	macromonomer	styrene, mol % feed	styrene, mol % prod	aug no. grafts/chain	main-chain DP	p(NB-*g*-S) M_n	p(NB-*g*-S) M_w
1	ω-BNPS-DP29	10	14	2.8 (1.9)[a]	500	30 000	123 000
2a	ω-NBPS-DP29	19	18	3.8 (4.0)	500	85 000	152 000
2b	ω-NBPS-DP29	19	24	5.4 (4.0)	500	31 000	111 000
2c	ω-NBPS-DP29	19	23	5.2 (4.0)	500	35 000	216 000
2d	ω-NBPS-DP29	19	21	4.6 (4.0)	500	87 000	182 000
3	ω-NBPS-DP29	32	31	7.8 (8.1)	500	35 000	120 000
4	ω-NBPS-DP29	48	48	16.0 (15.9)	500	70 000	153 000
5	ω-NBPS-DP29	19	17	1.8 (2.0)	250	30 000	79 000
6	ω-NBPS-DP29	19	14	0.6 (0.8)	100	15 000	37 000
7	ω-NBPS-DP55	19	21	2.4 (2.1)	500	105 000	122 000
8	ω-NBPS-DP100	19	<10[b]	<0.5[b] (1.2)	500	71 000	128 000

[a] Numbers in parentheses are theoretical values based on stoichiometry. [b] These values are upper limits since unreacted macromomonomer is present.

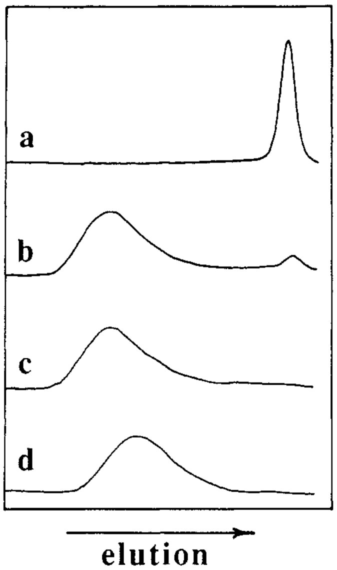

Figure 3. GPC data for (a) ω-NBPS-DP29, (b) crude graft copolymerization products, (c) purified graft copolymer, and (d) poly(norbornenamer) DP = 500. See text for details.

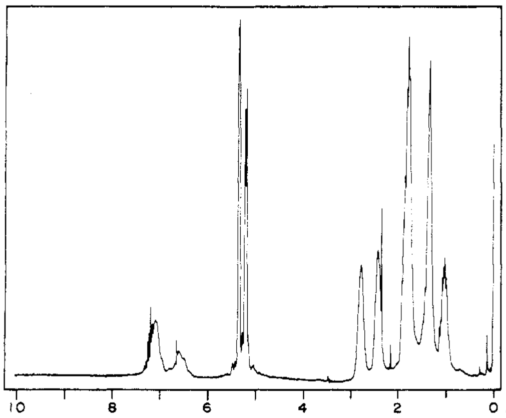

Figure 4. ^{1}H NMR spectrum of p(NB-*g*-PS); entry 2a of Table II.

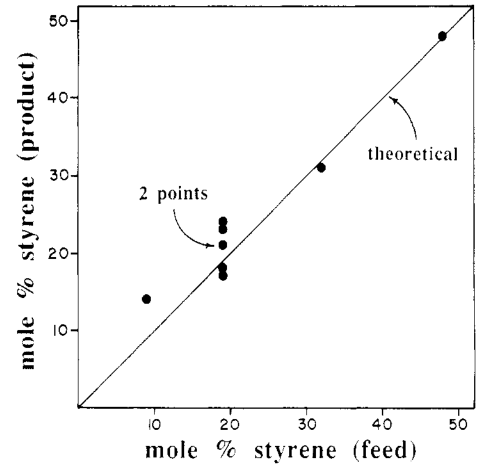

Figure 5. Plot of mole percent styrene in graft copolymer versus mole percent styrene in feed. Entries 6 and 8 are not included for reasons mentioned in the text.

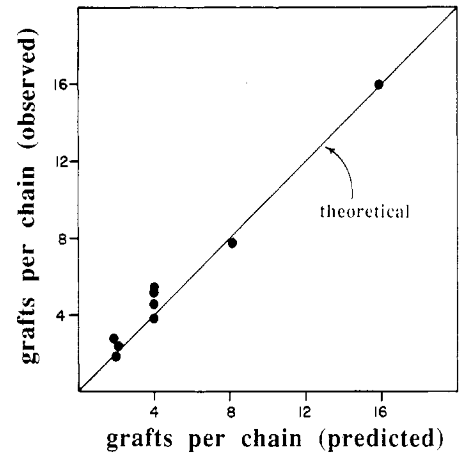

Figure 6. Plot of the average number of grafts per chain versus theoretical amount based on monomer/macromonomer/chain-transfer agent feed. Entries 6 and 8 are not included for reasons mentioned in the text.

^{1}H NMR data and the estimated main-chain molecular weight, which was controlled by adjusting the ratio of monomer to 1-octene. Figure 6 shows the relationship between the actual and theoretical (based on feed ratios) average grafts per chain. We have exercised reasonably precise control of the relative graft density but emphasize that the absolute graft density is based on an estimate of the average main-chain molecular weight. We expect from the polymerization an equilibrium mixture of graft copolymers containing a distribution of graft densities and our purification procedure could fractionate a portion of the product. Although GPC (Figure 3b,c) does not suggest fractionation upon purification, we qualify the absolute values of the data in Figure 6.

Careful physical studies were not performed on these materials, but one experiment is worthy of mention: Films of graft copolymers cast from solution are clear and transparent, whereas films of mixtures of macromonomer and poly(norbornenamer) are hazy. This indicates that phase separation (which is undoubtedly present) occurs in domains smaller than the wavelength of visible light.

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Registry No. (NB)(S) (graft copolymer), 108771-86-4; WCl_6, 13283-01-7; $SnMe_4$, 594-27-4; 1-octene, 111-66-0.

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Ylide-Initiated Polymerization of 4-Vinylpyridine

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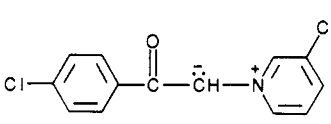
ABSTRACT: Ylide-initiated radical polymerization of 4-vinylpyridine using CCl_4 as diluent has been carried out at 60 °C. The system follows ideal kinetics at low [initiator]; however, it follows nonideal kinetics at high [initiator] which is attributed to active-center deactivation by chain transfer to solvent.

Introduction

In recent years, there has occurred a wide spread upsurge of interest in the application of ylides in polymer chemistry. This activity has undoubtedly stimulated interest in the use of nitrogen ylides partially due to inherent difficulties in synthesis and characterization. A number of papers using ylide as an initiator/accelerator/retarder for the polymerization of methyl methacrylate,[1,2] methyl acrylate,[3] styrene[4], and vinyl acetate[5] have been published by us. Moreover, the effect of ylides on copolymerization systems has also been investigated from this laboratory.[6,7] In this continuation, we report in this paper the first example of a nitrogen ylide (β-picolinium *p*-chlorophenacylide) to be used as an initiator for the polymerization of 4-vinylpyridine (4-VP).



β-PCPY

Experimental Section

Purified reagent grade 4-vinylpyridine (Fluka) and solvents were used. β-Picolinium *p*-chlorophenacylide (β-PCPY) was prepared by the method of Krohnke[8,9] and Lumb.[10]

The solution polymerizations of 4-VP using carbon tetrachloride as diluent were carried out in a borosilicate glass tube under nitrogen atmosphere. The polymer, precipitated with deionized water, was dried to a constant weight. The latter was used to calculate the convension (%). Average rates of polymerization (R_p) for a series of initiator and monomer concentration are then calculated from the slope of linear conversion–time plot (Figure 1). All R_p's were measured at low conversions (<10%).

The intrinsic viscosity $[\eta]$ of the polymer(s), determined in ethanol at 25 °C by using an Ubbelohde viscometer, was used to calculate the average molecular weight ($\bar{M}_v$) with the help of following equation:[11]

$$[\eta] = 2.5 \times 10^{-4} M^{0.68}$$

Results and Discussion

The results of the kinetic investigations of the solution polymerization of 4-VP initiated by β-PCPY at 60 °C for 120 min have been presented in Figures 1–5.

The dependence of R_p of 4-VP in CCl_4 as a function of initiator concentration is investigated by varying [β-PCPY] from 2.04×10^{-3} to 12.22×10^{-3} mol L^{-1} at constant [4-VP] (2.34 mol L^{-1}). The polymerizations were associated with short induction periods (<15 min), depending on [β-PCPY] (Figure 1). The R_p gradually increases with increasing [β-PCPY] and the initiator exponent, calculated from the slope of the log R_p versus log [β-PCPY], is 0.5 at low [initiator], i.e., upto 6.11×10^{-3} mol L^{-1}, above which it is effectively 1.20 order (Figure 2), indicating that some additional termination occurs along with the usual bimolecular termination. The $\bar{M}_v$ decreases with increasing [β-PCPY] as expected for radical polymerization. A plot of $1/\bar{M}_v$ versus R_p shows a straight line passing through origin

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