Poly(vinyliminomethylenes)

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ABSTRACT: Nickel(II)-catalyzed polymerizations of vinyl isocyanides of the type RR′C=CHNC lead to the corresponding poly(vinyliminomethylenes), $[RR'C{=}CHNC{<}]_n$. The polymers obtained from $(CH_3)_2C{=}CHNC$, $(CH_3)_3CCH{=}CHNC$, $C_6H_5CH{=}CHNC$, and $C_6H_5C(CH_3){=}CHCN$ are soluble in chloroform, whereas the polymers obtained from $CH_3CH{=}CHNC$, 2,4,6-$(CH_3)_3C_6H_2CH{=}CHNC$, and $CH_3CH{=}C(CH_3)CH{=}CHNC$ are insoluble in chloroform and other nonreactive organic solvents. NMR spectra of the soluble poly(vinyliminomethylenes) confirm the presence of pendant vinyl groups. Polystyrene equivalent molecular weights in the range 11 000–400 000 and polydispersities in the range 1.7–3.9 have been achieved for the soluble poly(vinyliminomethylenes).

Introduction

Vinyl isocyanides represent a novel type of monomer whose polymerization has not yet been reported despite the presence of two potentially reactive sites for polymerization, namely the isocyanide group and the vinyl double bond. This paper describes the polymerization of several vinyl isocyanides by the use of transition-metal catalysts, particularly nickel(II) derivatives, designed to favor polymerization through the isocyanide group rather than polymerization through the carbon–carbon double bond. The resulting new polymers, poly(vinyliminomethylenes), are of interest in combining the chiral helical rigid-rod structures of known poly(iminomethylenes)[1-4] with pendant vinyl groups. Such pendant vinyl groups provide potential opportunities for controlled cross-linking of soluble poly(vinyliminomethylenes) to give insoluble polymers of higher molecular weight as well as sites for anchoring transition metals to give novel polymer-supported catalysts.

Experimental Section

Microanalyses were performed by Atlantic Microanalytical Laboratory, Atlanta, GA. Proton NMR spectra were recorded on a JEOL FX-90Q spectrometer operating at a nominal frequency of 89.6 MHz. Carbon-13 NMR spectra were recorded on the JEOL FX-90Q spectrometer operating in the pulsed Fourier transform mode at a nominal frequency of 22.5 MHz with proton noise decoupling. Proton and ^{13}C NMR chemical shifts are reported in ppm downfield from internal tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer Model 599B spectrometer. Ultraviolet and visible spectra were recorded on a Varian Cary 219 spectrophotometer using dichloromethane solutions. Viscosity measurements were made by the standard method[5] by using a kinematic viscometer purchased from Fisher Scientific.

The vinyl isocyanides $CH_3CH{=}CHNC$,[6] $(CH_3)_2C{=}CHNC$,[7] $CH_3CH{=}C(CH_3)NC$,[7] $(CH_3)_3CCH{=}CHNC$,[7] $C_6H_5CH{=}CHNC$,[8] $C_6H_5C(CH_3){=}CHNC$,[8] 2,4,6-$(CH_3)_3C_6H_2CH{=}CHNC$,[7] and $CH_3CH{=}C(CH_3)CH{=}CHNC$[7] were prepared by the cited literature methods. Carbon-13 NMR spectra on samples of the vinyl isocyanides of the type $RCH{=}CHNC$ used in this research indicated $CH_3CH{=}CHNC$ and 2,4,6-$(CH_3)_3C_6H_2CH{=}CHNC$ to be single pure stereoisomers, $(CH_3)_3CCH{=}CHNC$ and $CH_3CH{=}C(CH_3)CH{=}CHNC$ to consist of 85–90% of a major stereoisomer and 10–15% of a minor stereoisomer, and $C_6H_5CH{=}CHNC$ to consist of ~60% of a major stereoisomer and ~40% of a minor stereoisomer.[7] Commercial $NiCl_2{\cdot}6H_2O$ was dehydrated with thionyl chloride[9] to give the anhydrous $NiCl_2$ used as a catalyst. The other catalysts $Ni(acac)_2$,[10] $Co(acac)_2$[10] (acac = acetylacetonate), and $Ni(dpm)_2$[11] (dpm = dipivaloylmethide) were prepared by the cited literature procedures.

Polymerization of Vinyl Isocyanides (Tables I and II). The indicated amounts of transition-metal catalyst, vinyl isocyanide, and solvent were stirred overnight at ambient temperature, except for $(CH_3)_2C{=}CHNC$ which was polymerized at 0 °C. In the case of the successful polymerizations conducted in ethanol, the polymer precipitated spontaneously as a yellow solid, which was isolated by filtration. Any transition-metal catalyst present in the crude polymer was removed by repeated washing with ethanol. The crude polymers were treated with chloroform. The polymers listed as "insoluble" in Table I failed to dissolve in chloroform and were washed and dried. The soluble polymers were dissolved in chloroform and were reprecipitated from the chloroform solutions by concentration in vacuum and addition of excess ethanol. Polymerizations conducted in hexane by using the $Ni(dpm)_2$ catalyst led only to partial precipitation of the polymer. Ethanol was added to complete the precipitation. The crude products were purified by dissolving in chloroform and reprecipitating with ethanol as discussed above. The polymer $[(CH_3)_2C{=}CHNC{<}]_n$ was soluble in chloroform when freshly prepared, but became insoluble upon standing, even at −15 °C.

Properties of the Soluble Poly(vinyliminomethylenes). The polystyrene equivalent molecular weights (M_w), polydispersities (M_w/M_n), and intrinsic viscosities $[\eta]$ of the soluble poly(vinyliminomethylenes) are listed in Tables I and II. The maxima and their extinction coefficients in their ultraviolet and visible spectra are listed in Table III. Other properties of the polymers are listed below.

$[(CH_3)_2C{=}CHNC{<}]_n$. Proton NMR spectrum in $CDCl_3$: δ 6.7 (=CH) and 1.7 (CH_3). Proton-decoupled ^{13}C NMR spectrum in $CDCl_3$: δ 160.2 (C=N), 138.7 (C=C), 134.9 (C=C), 22.8 (CH_3), and 18.0 (CH_3); infrared ν(C=N) at 1630 (s,br) cm^{-1}.

$[(CH_3)_3CCH{=}CHNC{<}]_n$. Proton NMR spectrum in $CDCl_3$: δ 7.0 (=CH), 6.1 (=CH), and 1.0 (CH_3). Proton-decoupled ^{13}C NMR spectrum in $CDCl_3$: δ 161.1 (C=N), 147.3 (C=C), 136.8 (C=C), 32.7 (C), 31.8 (C), and 30.3 (CH_3); infrared spectrum ν(C=N) at 1650 (s,br) cm^{-1}, other bands at 1465 (s), 1360 (s), 1260 (s), 1195 (m), 1022 (m), 943 (s), 797 (m), and 753 (m) cm^{-1}. Anal. Calcd for $(C_7H_{11}N)_n$: C, 77.0; H, 10.2; N, 12.8. Found (average of 10 independent preparations): C, 76.3; H, 10.2; N, 12.7.

$[C_6H_5CH{=}CHNC{<}]_n$. Proton NMR spectrum in $CDCl_3$: broad resonance at δ 7.0 ($W_{1/2}$ = 100 Hz). Proton-decoupled ^{13}C NMR spectrum in $CDCl_3$: δ 163.7 (C=N), 134.4 (C=C), 131.6 (C=C), and 129 (C_6H_5). Anal. Calcd for $(C_9H_7N)_n$: C, 83.7; H, 5.5; N, 10.8. Found: C, 80.8; H, 5.7; N, 10.4.

$[C_6H_5C(CH_3){=}CHNC{<}]_n$. Proton NMR spectrum in $CDCl_3$: broad resonances at δ 6.9 (C_6H_5 + =CH: $W_{1/2}$ = 80 Hz) and 1.9 (CH_3: $W_{1/2}$ = 40 Hz). Proton-decoupled ^{13}C NMR spectrum in $CDCl_3$: δ 161.5 (C=N), 141.2 (C=C), 127.9 (C_6H_5), and 126.3 (C_6H_5). Anal. Calcd for $(C_{10}H_9N)_n$: C, 83.9; H, 6.3; N, 9.8. Found (average of 3 independent preparations): C, 83.1; H, 6.4; N, 9.7.

Molecular Weight Determinations. The polymer samples were dissolved in tetrahydrofuran with approximate concentrations of 5 mg/mL. The resulting solutions were then filtered through a 0.2-μm FG-type filter (Millipore) to remove impurities and gels. The flow rate of the gel permeation chromatography system was maintained at 1 mL/min by using an Atex Model 110A pump. The injector was a Rheodyne Model 7125 equipped with a 500-μL loop. A 100-μL solution was injected for each run. One Jordi Associates (Mills, MA) packed mixed-bed column (10^5 Å, 10^3 Å) was utilized, equipped with a UV detector (Varian UV-50), set at a wavelength of 254 nm, and a differential refractive index detector (Knauer 98). The column was calibrated by using 10 narrow polystyrene fractions supplied by Pressure Chemical Co. (Pittsburgh, PA). The molecular weights calculated are poly-

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Table I
Polymerization of Vinyl Isocyanides to Poly(vinyliminomethylenes) Using Nickel(II) Catalysts

vinyl isocyanide monomer (g, mmol)[a]	catalyst (g, mmol)[b]	solvent[c] (mL)	yield, %	M_w[d]	M_w/M_n	$[\eta]$, dL/g
MeCH=CHNC (1.69, 25.2)	Ni(acac)$_2$ (0.032, 0.12)	EtOH (24)	92	insoluble		
MeCH=CHNC (1.66, 24.8)	Ni(dpm)$_2$ (0.052, 0.12)	EtOH (24)	100	insoluble		
MeCH=CHNC (1.65, 24.5)	Ni(dpm)$_2$ (0.052, 0.12)	hex (24)	35	insoluble		
Me$_2$C=CHNC (1.65, 20.4)[e]	Ni(acac)$_2$ (0.026, 0.10)	EtOH (20)	62			
Me$_2$C=CHNC (1.76, 21.7)[e]	Ni(dpm)$_2$ (0.042, 0.10)	EtOH (20)	70	[f]		0.65[e]
Me$_2$C=CHNC (1.72, 21.2)[e]	Ni(dpm)$_2$ (0.043, 0.10)	hex (20)	85			
Me$_3$CCH=CHNC (2.79, 25.6)	NiCl$_2$ (0.034, 0.26)	EtOH (20)	43	71 300	1.82	0.31
Me$_3$CCH=CHNC (0.72, 6.6)	Ni(acac)$_2$ (0.016, 0.062)	EtOH (10)	48	51 200	1.91	0.26
PhCH=CHNC (3.42, 26.5)	NiCl$_2$ (0.035, 0.27)	EtOH (27)	66	14 000	1.79	0.098
PhCH=CHNC (3.25, 25.2)	Ni(acac)$_2$ (0.066, 0.26)	EtOH (25)	55	11 000	1.72	0.095
PhMeC=CHNC (3.53, 24.7)	NiCl$_2$ (0.033, 0.26)	EtOH (24)	37	42 800	2.30	0.28
PhMeC=CHNC (2.26, 15.8)	NiCl$_2$ (0.020, 0.15)	EtOH (16)	25	74 500	2.39	0.46
PhMeC=CHNC (3.47, 24.2)	NiCl$_2$·6H$_2$O (0.058, 0.24)	EtOH (24)	21	46 300	2.15	0.27
PhMeC=CHNC (2.31, 16.1)	NiCl$_2$·6H$_2$O (0.038, 0.16)	EtOH (16)	29	58 700	2.32	0.35
PhMeC=CHNC (3.57, 24.9)	Ni(acac)$_2$ (0.066, 0.26)	EtOH (24)	28	40 200	2.22	0.22
PhMeC=CHNC (2.35, 16.4)	Ni(acac)$_2$ (0.043, 0.17)	EtOH (16)	30	63 300	1.98	0.36
MesCH=CHNC (2.06, 12.0)	NiCl$_2$ (0.015, 0.12)	EtOH (115)	79	insoluble		
MesCH=CHNC (2.09, 12.2)	Ni(acac)$_2$ (0.03, 0.12)	EtOH (115)	95	insoluble		
MeCH=CMeCH=CHNC (2.57, 24.0)	NiCl$_2$ (0.03, 0.23)	EtOH (23)	91	insoluble		
MeCH=CMeCH=CHNC (2.48, 23.1)	NiCl$_2$·H$_2$O (0.057, 0.24)	EtOH (23)	89	insoluble		
MeCH=CMeCH=CHNC (2.52, 23.5)	Ni(acac)$_2$ (0.06, 0.23)	EtOH (23)	96	insoluble		

[a] Me = methyl, Ph = phenyl, Mes = mesityl. [b] Ni(acac)$_2$ = nickel(II) acetylacetonate; Ni(dpm)$_2$ = nickel dipivaloylmethide. [c] EtOH = ethanol, hex = hexanes. [d] Polystyrene equivalent molecular weight determined by gel permeation chromatography (see Experimental Section). [e] These polymerizations were conducted at 0 °C. These polymers were soluble in CHCl$_3$ only when freshly prepared. The viscosity measurement was done on a freshly prepared sample. [f] The molecular weight M_w of this polymer was estimated to be 103 000–279 000 from its intrinsic viscosity $[\eta]$ of 0.65, depending upon which constants K and a were used in the Mark–Houwink equation (see text).

Table II
Effect of Polymerization Conditions on the Properties of the Poly(*tert*-butylvinyliminomethylene) Obtained from $(CH_3)_3C{-}CH{=}CH{-}NC$

catalyst	solvent	temp, °C	yield, %	M_w[a]	M_w/M_n
Ni(acac)$_2$, 0.088%	EtOH	25	52	165 000	1.8
Ni(acac)$_2$, 0.20%	EtOH	25	58	144 000	1.8
Ni(acac)$_2$, 0.47%	EtOH	25	58	144 000	1.9
Ni(acac)$_2$, 0.95%	EtOH	25	48	51,000	1.9
Co(acac)$_2$, 0.94%	EtOH	25	20	145 000	1.8
Ni(acac)$_2$, 0.51%	EtOH	40	57	150 000	1.9
Ni(acac)$_2$, 0.48%	EtOH	0	62	270 000	1.9
Ni(acac)$_2$, 0.48%	EtOH	−78 to 25[b]	63	400 000	3.9
Ni(dpm)$_2$, 0.50%	EtOH	25	69	97 000	2.0
Ni(dpm)$_2$, 0.48%	hexane	25	73	192 000	2.3

[a] Polystyrene equivalent. [b] Polymerization appeared to begin when the temperature of the reaction reached −16 °C.

Table III
Ultraviolet/Visible Maxima in Poly(iminomethylenes)

polymer	UV/visible maxima in CH$_2$Cl$_2$, $\lambda_{max}(\epsilon_{max})$
$[\mathrm{Me_3CN{=}C\langle}]_n$	338 (431)[a]
$[\mathrm{PhMeCHN{=}C\langle}]_n$	264 (1300)[a]
$[\mathrm{Me_2C{=}CHN{=}C\langle}]_n$	297 (5440)
$[\mathrm{Me_3CCH{=}CHN{=}C\langle}]_n$	288 (9010)
$[\mathrm{PhCH{=}CHN{=}C\langle}]_n$	239 (6710), 370 (5270)
$[\mathrm{PhMeCH{=}CHN{=}C\langle}]_n$	241 (4690), 353 (10500)

[a] These polymers were prepared as described in ref 14.

styrene equivalent molecular weights. Data were acquired and processed with a Minc 11/23 computer (DEC) which used A/D interfaces and software from LDC/Milton Roy.

Results and Discussion

All vinyl isocyanides of the type RR′C=CHNC studied in this work were found to precipitate as polymers in fair to excellent yields upon treatment with catalytic quantities of nickel(II) compounds in ethanol solution (Table I). In some cases the polymers were soluble in chloroform and could be purified by dissolving in chloroform and reprecipitating with ethanol. In other cases the polymers were insoluble in chloroform and any other nonreactive organic solvents tried. The polymers obtained from $(CH_3)_2C{=}CHNC$ were soluble in chloroform when freshly prepared, but become insoluble upon standing for several days, even at −10 °C.

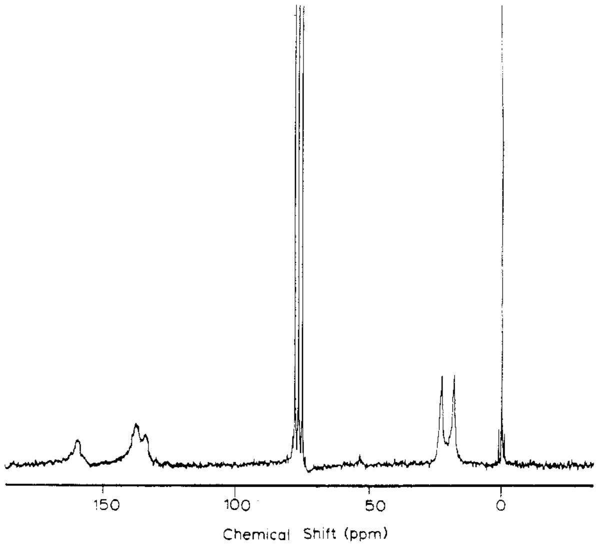

Figure 1. Carbon-13 NMR spectrum in CDCl$_3$ solution of the polymer $[(CH_3)_2C{=}CHNC\langle]_n$. The triplet centered at δ 77.0 is the CDCl$_3$ resonance, and the singlet at δ 0.0 is the resonance of the $(CH_3)_4Si$ internal standard.

The NMR spectra of the soluble polymers obtained from the aliphatic vinyl isocyanides $(CH_3)_2C{=}CHNC$ and $(CH_3)_3CCH{=}CHNC$ were most useful in elucidating their structures, although all NMR spectra obtained from the polymers exhibit relatively broad and poorly resolved resonances. Figure 1 shows a representative ^{13}C NMR spectrum of the polymer obtained from $(CH_3)_2C{=}CHNC$. The ^{13}C NMR spectrum of the polymer obtained from $(CH_3)_3CCH{=}CHNC$ exhibits vinyl resonances at δ 147.3 and 136.8, indicating that the polymerization process involves the isocyanide group rather than the carbon–carbon double bond. This polymer is therefore formulated as the poly(vinyliminomethylene) $[(CH_3)_3CCH{=}CHN{=}C\langle]_n$. Similar vinyl resonances (δ 138.7 and 134.9) were observed in the ^{13}C NMR spectrum of the polymer obtained from $(CH_3)_2C{=}CHNC$ (Figure 1) and in the proton NMR spectra of the soluble polymers obtained from both of the aliphatic vinyl isocyanides. Unambiguous observation of the vinyl ^{13}C and proton resonances in the soluble polymers derived from the aromatic vinyl isocyanides $C_6H_5CH{=}CHNC$ and $C_6H_5C(CH_3){=}CHNC$ was hindered by the presence of phenyl resonances in approximately the same region. Nevertheless, the ^{13}C and proton NMR data on the polymers obtained from the vinyl isocyanides provide clear evidence for their formulations as poly(vinyliminomethylenes) having pendant vinyl groups attached to the rigid-rod poly(iminomethylene) structure.[1-4] Other important spectroscopic features of all of the poly(vinyliminomethylenes) obtained in this work include a ^{13}C resonance at δ 160–164 assigned to the C=N imine carbon atom and a relatively strong broad infrared band at $\sim$1630 cm^{-1} assigned to the $\nu(C{=}N)$ stretching frequency overlapping the much weaker $\nu(C{=}C)$ stretching frequency.

Standard gel permeation chromatography methods indicate that the soluble polymers obtained by polymerization of vinyl isocyanides with 0.5–1.0% of a nickel(II) catalyst in ethanol solution at ambient temperature have polystyrene equivalent molecular weights (M_w) in the range 10 000–80 000 and polydispersities in the range 1.7–2.4. Attempts to determine absolute M_w values by light-scattering methods failed because the polymer solutions were too deeply colored. The polystyrene equivalent molecular weight data (Table I) combined with viscosity measurements in the Mark–Houwink equation,[12] $[\eta] = KM_w{}^a$, give the parameters $K = 7.45 \times 10^{-4}$ and $a = 0.54$ for $[(CH_3)_3CCH{=}CHNC{<}]_n$ and $K = 1.58 \times 10^{-6}$ and $a = 1.12$ for $[C_6H_5C(CH_3){=}CHNC{<}]_n$. These parameters compare with the reported[3] parameters for $[C_6H_5CH(CH_3)NC{<}]_n$ of $K = 1.1 \times 10^{-4}$ and $a = 0.8$ for unfractionated samples and $K = 3.8 \times 10^{-7}$ and $a = 1.3$ for fractionated samples. The parameters for $[C_6H_5C(CH_3){=}CHNC{<}]_n$ are suggestive of a rigid-rod structure found for other poly(iminomethylenes),[1-4] but physical measurements on *fractionated* samples of the poly(vinyliminomethylenes) are necessary before more reliable conclusions can be made.

Our samples of the polymer $[(CH_3)_2C{=}CHNC{<}]_n$ became insoluble too quickly to survive shipment intact to the 3M Co. for molecular weight measurements. The intrinsic viscosity of a freshly prepared sample of this polymer was 0.65 dL/g, corresponding to a molecular weight (M_w) of 279 000 or 103 000 from the Mark–Houwink equation depending upon whether the parameters K and a for $[(CH_3)_3CCH{=}CHNC{<}]_n$ or $[C_6H_5C(CH_3){=}CHNC{<}]_n$, respectively, are used.

The polymerization of the vinyl isocyanide $(CH_3)_3CCH{=}CHNC$ was investigated under a variety of different conditions (Table II). The following observations were made: (1) Changes in the catalyst concentration have relatively little effect on the resulting polymer molecular weight until catalyst concentrations of $\sim$1% are reached. (2) An increase in the polymerization temperature leads to a lower polymer molecular weight, consistent with other types of polymerization reactions.[13] (3) Use of $Co(acac)_2$ rather than $Ni(acac)_2$ under otherwise identical conditions gives a polymer of higher molecular weight but in a much lower yield. (4) Use of the hydrocarbon-soluble catalyst $Ni(dpm)_2$ gives a polymer of higher molecular weight in hexane solution than in ethanol solution.

Polymerization of isocyanides to poly(iminomethylenes) in *hydrocarbon* solvents using transition metal catalysts has not been reported previously. We therefore investigated the polymerization of various simple isocyanides in hexane solution using the soluble catalyst $Ni(dpm)_2$. However, both methyl isocyanide and cyclohexyl isocyanide were found to give insoluble polymers under these conditions, similar in general appearance to those previously[14] reported. It thus appears that a change in the polymerization solvent for isocyanides from ethanol to a hydrocarbon using an appropriately soluble nickel(II) catalyst does not lead to a major change in the structure and properties of the resulting polymer but only to relatively minor differences in the molecular weight.

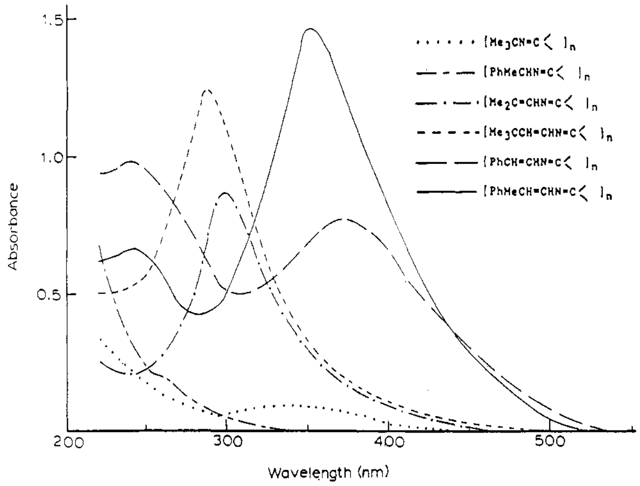

Figure 2. Ultraviolet and visible spectra of six poly(iminomethylenes) in dichloromethane; pathlength 1.0 cm; concentration 1.6×10^{-4} mol repeating units/mL.

In general, the poly(vinyliminomethylenes) appear to have deeper colors (yellow to yellow-brown) than poly(iminomethylenes) having saturated (sp^3) carbon atoms bonded to the poly(iminomethylene) unit. The ultraviolet and visible spectra (Table III and Figure 2) indicate that conjugation of a vinyl group with the poly(iminomethylene) chain increases the extinction coefficients of the maxima and shifts them toward the visible region. Thus, the polymers $[(CH_3)_2C{=}CHNC{<}]_n$ and $[(CH_3)_3CCH{=}CHNC{<}]_n$ exhibit maxima at 297 and 288 nm, respectively. This effect is more pronounced when the vinyl group is conjugated with a phenyl group. Thus, the polymers $[C_6H_5CH{=}CHNC{<}]_n$ and $[C_6H_5C(CH_3){=}CHNC{<}]_n$ exhibit maxima at 370 and 353 nm, respectively.

The factors affecting the solubility of poly(vinyliminomethylenes) appear to be rather complicated but seem to include the size of the substituents on the vinyl group and the stereoisomeric purity of the vinyl isocyanide used. Thus $CH_3CH{=}CHNC$ gives an insoluble polymer, but both $(CH_3)_2C{=}CHNC$ and $(CH_3)_3CCH{=}CHNC$ give soluble polymers at least initially, providing some evidence for an increase in polymer solubility caused by an increase in the substituent bulk. However, 2,4,6-$(CH_3)_3C_6H_2CH{=}CHNC$ gives an insoluble polymer, whereas the less bulky substituted $C_6H_5CH{=}CHNC$ gives a soluble polymer. Here the difference appears to be the stereoisomeric purity of the vinyl isocyanides used in this polymerization study: the $(CH_3)_3C_6H_2CH{=}CHNC$ was shown by ^{13}C NMR to be a single stereoisomer, whereas the $C_6H_5CH{=}CHNC$ was shown to be a 60:40 mixture of the two stereoisomers.[7]

Not all unsaturated isocyanides appear to form polymers when treated with catalytic amounts of nickel(II) compounds. Thus treatment of $CH_3CH{=}C(CH_3)NC$ with 0.5% $NiCl_2$, $Ni(acac)_2$ or $Ni(dpm)_2$ in ethanol solution at room temperature failed to precipitate any polymer, nor could significant quantities of a soluble polymer be obtained after removal of the ethanol solvent in vacuum. This single example suggests that a methyl group on the vinyl carbon bearing the isocyanide group is sufficient to block polymerization. Allyl isocyanide also failed to precipitate a polymer upon treatment with catalytic nickel(II) acetylacetonate in ethanol solution under conditions similar to those used for the polymerizations of vinyl isocyanides reported in this paper. Thus conjugation of the carbon–carbon double bond with the isocyanide group appears to facilitate polymerization.

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Registry No. MeCH═CHNC (homopolymer), 96806-12-1; Me$_2$C═CHNC (homopolymer), 96806-10-9; Me$_3$CCH═CHNC (homopolymer), 96806-07-4; PhCH═CHNC (homopolymer), 96806-08-5; PhMeC═CHNC (homopolymer), 96806-11-0; MesCH═CHNC (homopolymer), 96806-14-3; MeCH═CMeCH═CHNC (homopolymer), 96806-16-5; MeCH═CHNC (SRU), 98705-04-5; Me$_2$C═CHNC (SRU), 98705-05-6; Me$_3$CCH═CHNC (SRU), 98705-06-7; PhCH═CHNC (SRU), 98705-07-8; PhMeC═CNC (SRU), 98705-08-9; MesCH═CHNC (SRU), 98705-09-0; MeCH═CMeCH═CHNC (SRU), 98705-10-3; Ni(acac)$_2$, 3264-82-2; Ni(dpm)$_2$, 41749-92-2; NiCl$_2$, 7718-54-9; Co(acac)$_2$, 14024-48-7.

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Effect of Alkyl Groups on the Asymmetric Induction Copolymerization of Alkyl Vinyl Ethers with Indene Using (−)-Menthoxyaluminum Dichloride Initiator

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ABSTRACT: Copolymerizations of *tert*-butyl, isobutyl, *n*-butyl, isopropyl, and ethyl vinyl ethers with indene were undertaken with (−)-menthoxyaluminum dichloride as the initiator. The optically active copolymers were obtained and ether-cleaved with HBr gas. The optical rotation of the ether-cleaved copolymers was proportional to their values of $P_2(\mathrm{m_1m_2})$, the probability of an $\mathrm{m_1m_2}$ diad sequence. The largest optical rotation per $P_2(\mathrm{m_1m_2})$ was obtained in the case of the ether-cleaved *tert*-butyl vinyl ether/indene copolymer. These results suggested that real asymmetric carbon atoms were introduced in the vinyl ether units and that the bulkiness of the alkyl group of the vinyl ethers played an important role in the asymmetric induction of this system. Furthermore, the mechanism of the asymmetric induction was discussed.

Introduction

We have been studying the asymmetric copolymerization of vinyl and α,β-disubstituted monomers.[1-7] In the cationic copolymerization of (−)-menthyl vinyl ether and indene,[3-5] the copolymers were still optically active after the removal of the chiral menthyl groups. The authors concluded that the addition of α,β-disubstituted monomer to a growing chain end during the propagation was sterically controlled by the chiral menthyl groups and one of the configurations was preferentially produced in the main chain.

In our previous paper,[8] we reported the copolymerization of isobutyl vinyl ether and indene initiated by (−)-menthoxyaluminum dichloride (**1**) and (−)-menthoxytitanium trichloride (**2**). From the linear relationship between the optical rotation and $P_2(\mathrm{m_1m_2})$ values of the copolymers, it was found that real asymmetric carbon atoms of the vinyl ether units were introduced under the influence of the chiral counteranion. The relative extent of the asymmetric copolymerization depended on solvents and initiators.

In this paper, the copolymerizations of several alkyl vinyl ethers and indene were carried out in cyclohexane using **1**. To investigate the effect of alkyl groups of the vinyl ethers on asymmetric induction copolymerization, the copolymers were ether-cleaved.

Experimental Section

Materials. Toluene, benzene, cyclohexane, methanol, and tetrahydrofuran (THF) were purified by the usual methods. Commericially available *l*-menthol (mp 43 °C, $[\alpha]_\mathrm{D}$ −49.3° in ethanol, c = 0.1 g/L, l = 1.0 cm), ethylaluminum dichloride, tetralin, and bromine were used without further purification. Isopropyl vinyl ether (*i*-PrVE) and *tert*-butyl vinyl ether (*t*-BVE) were synthesized form *n*-butyl vinyl ether (*n*-BVE) and the corresponding alcohols with mercuric acetate as a catalyst according to Watanabe's method.[9] Ethyl vinyl ether (EVE), *n*-butyl vinyl ether (*n*-BVE), isobutyl vinyl ether (*i*-BVE), and indene (In) were commercial materials, distilled over sodium metal under vacuum before use. **1** ($[\alpha]_\mathrm{D}$ −39.7° in toluene, c = 0.1 g/L, l = 1.0 cm) was prepared from *l*-menthol and ethylaluminum dichloride according to Furukawa's method.[10]

Copolymerization. Copolymerizations were carried out in polymerization tubes equipped with three-way ground-glass

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