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Effects of Side-Chain Structure on Polymer Conformation: Synthesis and Dilute Solution Properties

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ABSTRACT: Two imidazole-containing polymers, poly(*N*-vinylimidazole) (PVI) and poly[*N*-(1,1-dimethyl-3-imidazolylpropyl)acrylamide] (PDIA), were used to study the effects of side-chain length and flexibility on backbone-chain conformation. Both polymers were synthesized by free-radical polymerization in organic media and characterized by light scattering and intrinsic viscosity in methanol and in aqueous salt solutions. For neutral PVI and PDIA, the characteristic ratios are identical, indicating that backbone-chain flexibilities of these vinyl polymers are not affected by the length and flexibility of the side chain that joins the imidazole ring to the backbone. For protonated PVI, the characteristic ratio is similar to that for uncharged PVI when the counterion of the protonated imidazolium ring is chloride but increases when the counterion is changed to acetate or propionate. This effect is diminished, however, for protonated PDIA, where the imidazole group is far removed from the backbone by a long and flexible amide linkage.

Introduction

The functions of imidazole or imidazolium groups in polymers, such as metal-ion complexation, counterion binding, and dye binding, are dictated by their distribution along or distance from the backbone chain. In an earlier paper[1] we described conformations of poly(*N*-vinylimidazole) (PVI) polymers in terms of the nature of solvent, quaternizing group, ionic strength, and counterion type. The solution behavior of these polymers was correlated with their binding characteristics to an azo dye, methyl orange.[2]

In the present study, we investigated chain dimensions of a similar polymer, poly[*N*-(1,1-dimethyl-3-imidazolylpropyl)acrylamide] (PDIA), where the imidazole moiety is linked to the vinyl backbone by a long and flexible amide side chain. The unperturbed dimensions were determined by light scattering and intrinsic viscosity for several fractionated samples. These results were compared with those for PVI to examine the effects of side-chain structure on overall chain conformation. Further correlation between conformation, counterion binding, and dye binding of these two polymers will be reported in a separate paper.[3]

Experimental Section

Materials. *N*-(1,1-Dimethyl-3-imidazolylpropyl)acrylamide (DIA). The vinyl monomer was synthesized by the two methods shown in Schemes I and II.

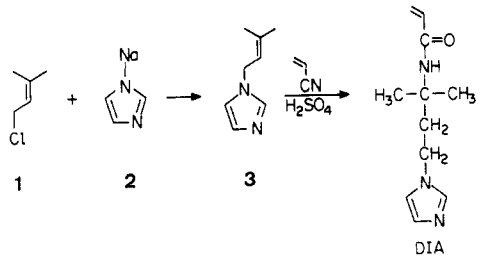
Scheme I. To sodium imidazole (300 g, 3.3 mol) in DMF (1.5 L) at 0–5 °C was added 1-chloro-3-methyl-2-butene (**1**) (346.5 g, 3.3 mol; Kodak Laboratory Chemicals). The mixture was kept overnight and then heated to 80 °C for 2 h and filtered, and the solvent was removed. The residue was distilled to give 2-methyl-4-imidazolyl-2-butene (**3**): bp 75–78 °C (0.1 mmHg); yield 75%. Anal. Calcd for $C_8H_{12}N_2$: C, 70.6; H, 8.9; N, 20.6. Found: C, 66.3; H, 8.3; N, 19.8.

The structure of compound **3** was verified by mass and NMR spectra.

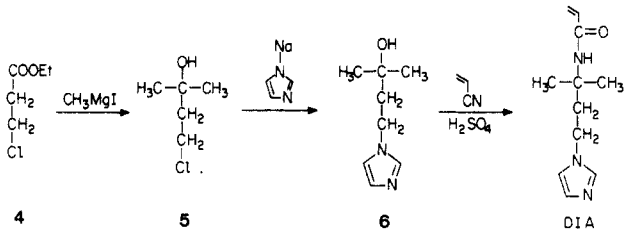
A mixture of acrylonitrile (201 g, 3.8 mol; Kodak Laboratory Chemicals), water (27.5 mL), 2,6-di-*tert*-butyl-*p*-cresol (4.5 g), and compound **3** (250 g, 1.8 mol) was cooled to 0 °C, and concentrated H_2SO_4 (468 g, 4.5 mol) was added slowly while the temperature was kept at 0–5 °C. The mixture was allowed to reach ambient temperature overnight and then heated to 80 °C for 2 h. The mixture was cooled to 0 °C and diluted with methanol (3 L). The excess acid was neutralized with anhydrous ammonia while the temperature was kept below 20 °C. The salts were filtered, and the solvent was removed. The residue was dissolved in ethyl acetate, dried over anhydrous magnesium sulfate, and filtered. On cooling to −16 °C, the product crystallized from ethyl acetate to give the vinyl monomer (DIA): mp 104–107 °C; yield 70%. Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.7; H, 8.3; N, 20.3. Found: 63.5; H, 8.3; N, 20.2.

The structure of DIA was confirmed by mass and NMR spectra.

Scheme I



Scheme II



Scheme II. 2-Methyl-4-chloro-2-butanol (**5**) (174 g, 1.4 mol), prepared[4] from **4**, was added dropwise at room temperature with constant stirring to a sodium imidazole (117 g, 1.3 mol) suspension prepared from 50% sodium hydride (75.0 g, 1.56 mol) and imidazole (88.0 g, 1.33 mol) in DMF (1.0 L). The mixture was stirred continuously at room temperature overnight and heated to 80 °C the next day for 2 h. Methanol (60 mL) was added to react with

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Table I
Light-Scattering and Intrinsic Viscosity Data for PDIA in MeOH/0.01 M TBABr

fraction	$10^{-5}\bar{M}_w$	10^4A_2, mL·mol/g^2	$\langle s_z^2\rangle^{1/2}$, Å	$[\eta]$, dL/g	$\bar{M}_w/\bar{M}_n$[a]
F_1	36.5	1.5	730	4.30	1.4
F_2	20.2	1.7	550	2.81	1.6
F_3	9.2_8	2.2	430	1.53	1.6
F_4	7.0_3	2.7	340	1.23	1.8
F_5	5.0_4	2.6	285	0.96	2.1
F_6	2.6_0	3.2	195	0.57	3.4
F_7	1.0_7	4.0	165	0.30_8	3.4

[a] The molecular weight distribution was determined by size-exclusion chromatography, and details were reported in ref 5.

excess sodium hydride. The mixture was filtered, and the solvent was removed. The residue was distilled, giving **6**: bp 130–140 °C (0.5 mmHg); yield 42%. Anal. Calcd for $C_8H_{14}N_2O$: C, 62.3; H, 9.2; N, 18.2. Found: C, 61.0; H, 8.9; N, 18.2. The structure of **6** was verified by mass and NMR spectra. Reaction of acrylonitrile with **6** by the procedure described in Scheme I gave only 55% yield.

Poly[*N*-(1,1-dimethyl-3-imidazolylpropyl)acrylamide] (PDIA). A mixture of *N*-(1,1-dimethyl-3-imidazolylpropyl)-acrylamide (DIA) (20 g, 0.1 mol) and 2,2′-azobis(2-methylpropionitrile) (0.2 g) in 100 mL of dimethyl sulfoxide (Me_2SO) was purged with nitrogen and heated at 60 °C overnight. The polymer (95% yield) was isolated by precipitation in acetone, filtered, and dried under vacuum at 40 °C. The inherent viscosity of the whole (unfractionated) polymer was 0.95 dL/g in 0.25% methanol in aqueous solution. Anal. Calcd for $C_{11}H_{17}N_3O$: C, 63.7; H, 8.3; N, 20.3. Found: C, 61.2; H, 8.1; N, 19.8.

Fractionation. A 3% solution of the whole polymer was dissolved in methanol, and stepwise precipitation was carried out at 10 °C with mesitylene as the nonsolvent. The coacervate liquids were separated and freeze-dried, and the solids were heated to 40 °C under vacuum in the presence of P_2O_5 for several weeks. The polydispersity indices of seven of the fractions chosen for this study were determined by size-exclusion chromatography as reported elsewhere.[5]

Methods. Light Scattering and Intrinsic Viscosity. Light-scattering measurements for seven fractions of PDIA in MeOH/0.01 M TBABr (tetrabutylammonium bromide) were made at 25 °C with a Sofica photometer with unpolarized light at 436 nm. A Cornell Styron polystyrene in toluene was used as a working standard for scattering intensity. Intrinsic viscosity data were determined with Ubbelohde microviscometers. Detailed procedures were reported earlier for other polymers.[6] The refractive index increment dn/dc was 0.209 and was identical for dialyzed and undialyzed samples. Experimental uncertainties were estimated to be the following: dn/dc, ±2%; $\bar{M}_w$, ±5%; second virial coefficient A_2, ±10%; radius of gyration $\langle s_z^2\rangle^{1/2}$, ±10%; intrinsic viscosity $[\eta]$, ±2%.

Results and Discussion

Solubility. Light-scattering and intrinsic viscosity data were determined for seven neutral PDIA fractions in MeOH/0.01 M TBABr (Table I). The Mark–Houwink linear relationship

$$[\eta] = K\bar{M}_w^{\nu} \tag{1}$$

where K and ν are empirical parameters, was observed for these data as shown in Figure 1. Similar relationships were also found for the protonated PDIA in a variety of solutions containing aqueous acid and salt. Table II summarizes these results and gives the corresponding K and ν values reported earlier[1] for neutral and protonated PVI.

The ν values of 0.63 and 0.75 for neutral PVI and PDIA, respectively, suggest that MeOH is a good solvent for these imidazole-containing polymers, particularly for PDIA with a long, flexible, H-bond-forming amide side chain. The

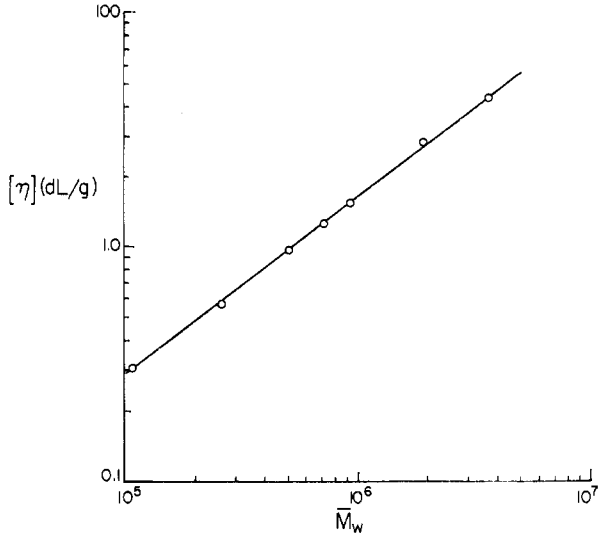

Figure 1. Mark–Houwink plot, $[\eta] = K\bar{M}_w^{\nu}$, for neutral PDIA in MeOH/0.01 M TBABr.

Table II
Mark–Houwink Relationships $[\eta] = K\bar{M}_w^{\nu}$ for PVI and PDIA

PVI ν	PVI K	PDIA ν	PDIA K	solvent
		Neutral		
0.63	4.85×10^{-4}	0.75	5.26×10^{-5}	MeOH/0.01 M TBABr
		Protonated		
		0.71	4.49×10^{-5}	0.1 M HCl/0.25 M NaSCN
0.50	1.69×10^{-3}	0.78	3.35×10^{-5}	0.1 M HCl/1 M NaCl
0.51	4.14×10^{-3}	0.79	3.48×10^{-5}	0.1 M HAc/1 M NaAc
0.51	3.92×10^{-3}	0.80	3.50×10^{-5}	0.1 M HPr/1 M NaPr

ν values are almost 0.5 for protonated PVI in aqueous salt media, indicating Θ-condition, but those for protonated PDIA remain relatively high (0.71–0.8). These results are attributed to a great extent of hydration. Furthermore, protonated PDIA could not be precipitated in excess added monovalent salt, demonstrating the favorable solubility of this polymer in aqueous media.

Unperturbed Dimensions. The unperturbed dimensions, or the end-to-end distances of a chain molecule in the absence of solvent–polymer interaction, can be used to compare backbone flexibility among polymers. In general, these dimensions can be measured at Θ-condition or estimated by linear extrapolation based on the intrinsic viscosity/molecular weight data, measured in good solvent, according to the Stockmayer–Fixman[7] equation:

$$[\eta]/\bar{M}_w^{1/2} = K_0 + 0.51\phi_0 B\bar{M}_w^{1/2} \tag{2}$$

Here K_0 is the intercept for the plot of $[\eta]/\bar{M}_w^{1/2}$ vs. $\bar{M}_w^{1/2}$, B is related to the second virial coefficient and is assumed to be constant for all molecular weights, and ϕ_0 is the Flory viscosity constant (2.6×10^{21} in units of deciliters per gram for $[\eta]$). The unperturbed end-to-end distance $\langle r_0^2\rangle$ is related to K_0 by[8]

$$\langle r_0^2\rangle = (K_0/\phi_0)^{2/3}\bar{M}_w \tag{3}$$

For a comparison of overall chain flexibility, it is more convenient to use the characteristic ratio, defined as

$$C_\infty = \langle r_0^2\rangle/nl^2 = (K_0/\phi_0)^{2/3}M_0/2l^2 \tag{4}$$

where M_0 is the monomer molecular weight, n is the number of backbone bonds, and l is the corresponding bond length.

Figure 2 is the Stockmayer–Fixman plot for PDIA in MeOH/0.01 M TBABr. Except for the very high molec-

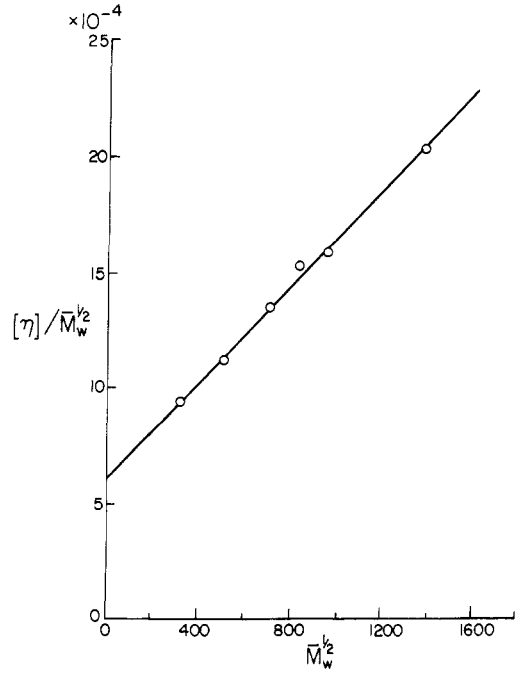

Figure 2. Stockmayer–Fixman plot, $[\eta]/\bar{M}^{1/2}$ vs. $\bar{M}^{1/2}$ for PDIA in MeOH/0.01 M TBABr.

Table III
Unperturbed Dimensions $C_\infty = \langle r_0^2 \rangle / nl^2$

PVI	PDIA	solvent
	Neutral	
15 (±2)	16 (±2)	MeOH/0.01 M TBABr
	Protonated	
	12.3	0.1 M HCl/0.25 M NaSCN
15	16	0.1 M HCl/1 M NaCl
28	16	0.1 M HAc/0.1 M NaAc
28	16	0.1 M HPr/0.1 M NaPr

ular weight fraction ($M = 3.4 \times 10^6$), all points fall on a straight line. Since the theory is applicable only to polymers with moderate molecular weights, only the lower six fractions were used for the extrapolation. Similar deviations from the straight line were observed for other polymers with high molecular weight fractions.[9] From the intercept, C_∞ can be calculated. These values are summarized in Table III for neutral and protonated PDIA along with those reported earlier for neutral and protonated PVI. The uncertainty in C_∞ is ±10–15%.

For neutral polymers in MeOH, the C_∞ values are similar for the two polymers regardless of the position of the imidazole group. For protonated PVI, however, our previous data[1] (shown in Table III) suggest that the flexibility of the chain is dependent on the counterion associated with the protonated imidazole ring. A larger C_∞ value was obtained for the polymer with a weaker binding counterion such as acetate or propionate. Nevertheless, this finding was not substantiated with the present polymer, protonated PDIA. With the exception of the value in NaSCN, C_∞ remains approximately constant at 16. This result suggests that the backbone-chain flexibility is insensitive to the counterion type associated with the imidazolium site when the latter is linked by a long and flexible side chain.

Dependence of A_2 and $\langle s_z^2 \rangle$ on M. The linear relationships

$$A_2 = m\bar{M}_w^{-a} \tag{5}$$

and

$$\langle s_z^2 \rangle^{1/2} = k\bar{M}_w^{b} \tag{6}$$

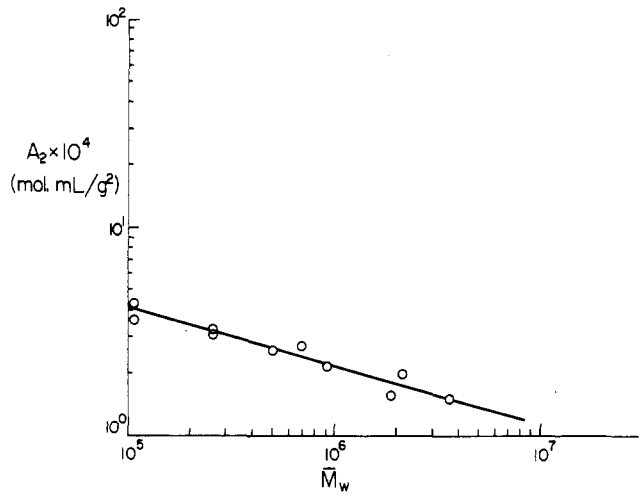

Figure 3. A_2 vs. $\bar{M}_w$ for PDIA in MeOH/0.01 M TBABr.

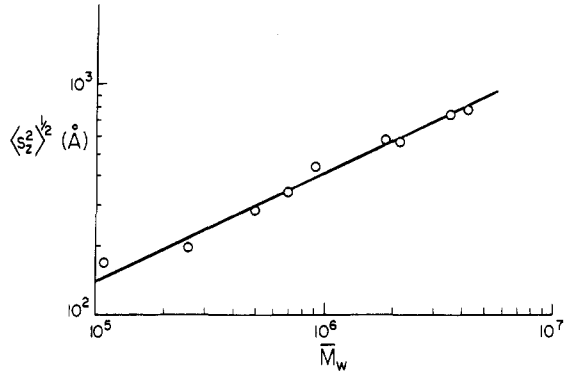

Figure 4. $\langle s_z^2 \rangle^{1/2}$ vs. $\bar{M}_w$ for PDIA in MeOH/0.01 M TBABr.

Table IV
Molecular Weight Dependence of A_2 and $\langle s_z^2 \rangle$ for PVI and PDIA in MeOH/0.01 M TBABr[a]

	PVI	PDIA	coillike limit	rodlike limit
a	0.62	0.28	≤1.0	>0
b	0.51	0.46	≥0.5	<1.0

[a] $A_2 = m\bar{M}_w^{-a}$. $\langle s_z^2 \rangle^{1/2} = k\bar{M}_w^{b}$.

for neutral PDIA in MeOH/0.01 M TBABr are shown in Figures 3 and 4, respectively. On the basis of the excluded-volume consideration,[10] we obtain $A_2 \propto M^{-1.0}$ for solid spheres and $A_2 \propto M^0$ for rigid rods. According to the wormlike-coil model,[11] $\langle s_z^2 \rangle^{1/2} \propto \bar{M}_w^{0.5}$ for the coil limit and $\langle s_z^2 \rangle^{1/2} \propto \bar{M}_w^{1.0}$ for the rod limit. Table IV summarizes the values of these exponents for the two neutral polymers PVI[1] and PDIA. For PVI, a and b are within the limits corresponding to the behavior of a coillike chain. For PDIA, the exponent a in eq 5 is relatively low (0.28). This may be a result of solvation of the side-chain amide linkages through H-bonding with the solvent molecules so that A_2 is dominated by the segment–solvent interaction on the side chain and is insensitive to chain length or M_w. Small values of a are well-known, however, for nonionic polymers in good organic solvents such as polystyrene in toluene[12] ($a = 0.22$) and polyisobutylene in cyclohexane[13] ($a = 0.14$).

The exponent b in eq 6 for PDIA (0.46) is also lower than that for the coillike limit (0.5), suggesting that although the polymer may be solvated, the backbone-chain is not extended but rather coiled. The lack of a long-range electrostatic repulsive force may be a possible cause of this coillike behavior.

Hydrodynamic Interaction and the Excluded-Vol-

Table V
Hydrodynamic Expansion Factor, α_η, and Viscosity Constant ϕ[a] for PDIA in MeOH/0.01M TBABr

fraction	$\bar{M}_w$, 10^5	α_η	ϕ, 10^{21}
F_1	36.5	1.55	2.70
F_2	20.2	1.49	2.30
F_3	9.28	1.38	1.22
F_4	7.03	1.35	1.50
F_5	5.04	1.31	1.42
F_6	2.60	1.23	1.36
F_7	1.07	1.16	0.50

[a] In units of deciliters per gram for $[\eta]$ and meters for $\langle s^2\rangle^{1/2}$.

ume Effect. The viscosity constant relating intrinsic viscosity and light-scattering data is expressed as follows:

$$\phi(h,\epsilon) = [\eta]M/6^{3/2}\langle s^2\rangle^{3/2} \quad (7)$$

Several theories[9,14] taking into account hydrodynamic interaction and excluded-volume effects were developed to describe the relationship between viscous flow and chain dimensions. The h and ϵ in eq 7 are the parameters for hydrodynamic draining and excluded-volume effects, respectively. In the limit of nondraining coil ($h \to \infty$) at Θ-condition ($\epsilon = 0$), the theoretically[9] calculated value for ϕ ranges from 2.30×10^{21} to 2.87×10^{21} (in units of deciliters per gram for $[\eta]$ and meters for $\langle s^2\rangle^{1/2}$). In the presence of partial draining and excluded-volume effects, ϕ was predicted to decrease with decreasing h and increasing ϵ.

Although most nonionic polymers in organic media show fairly good constancy for ϕ, mostly in the low coil expansion region, greater deviation from constancy was observed for many polyelectrolytes.[15,16] In the latter systems, the viscosity constant decreases as the hydrodynamic interaction decreases (i.e., h decreases or the expansion factor α_η increases) or the excluded-volume effect increases (i.e., A_2 increases).

To examine the dependence of ϕ on coil expansion for our polymer, we have calculated the viscosity constant according to eq 7 using the measured $[\eta]$ and $\bar{M}_w$ and $\langle s_z^2\rangle^{1/2}$ from light scattering. These values are listed in Table V. The corresponding hydrodynamic expansion factor, α_η, according to eq 8

$$\alpha_\eta = \left(\frac{[\eta]}{[\eta_0]}\right)^{1/3} = \left(\frac{[\eta]}{K_0M^{1/2}}\right)^{1/3} \quad (8)$$

is also shown in Table V. The Mark-Houwink parameter at Θ-condition, K_0, is estimated from the Stockmayer–Fixman extrapolation in Figure 2.

An increase in ϕ with increasing α_η is obvious in these data. Further correction of the radius of gyration from $\langle s_z^2\rangle$ to $\langle s_w^2\rangle$ by incorporating the polydispersity parameter would not alter the variation of ϕ with respect to α_η. Because of the polydisperse nature of these polymer fractions (see Table I), a comparison of experimental data and theories was not attempted.

Conclusions

Solution properties of two imidazole-containing polymers, PVI and PDIA, were compared to assess the effects of side-chain structure on overall polymer conformation. The backbone-chain flexibilities of these two polymers in their neutral forms are approximately the same, i.e., C_∞ = 15 and 16, respectively. For protonated PVI, the unperturbed chain dimensions are greatly affected by the type of counterion associated with the imidazolium site, i.e., the weaker the counterion-binding strength, the less flexible the backbone. This sensitivity was not observed, however, for protonated PDIA, where the imidazolium group is far removed from the backbone by a long and flexible amide linkage.

On the basis of light-scattering data, the PDIA polymer is believed to behave as a coillike chain with a highly solvated side chain. More accurate data on very narrow molecular weight distribution fractions and reexamination of theories are needed to study the relation between hydrodynamic interaction and size of this polymer.

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Registry No. 1, 503-60-6; 2, 5587-42-8; 3, 106039-49-0; 4, 623-71-2; 5, 1985-88-2; 6, 106017-19-0; DIA, 106017-20-3; PDIA, 106039-50-3; NCCH=CH_2, 107-13-1.

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