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THE COPOLYMERIZATION OF 1-ALKYLVINAZENES WITH STYRENE

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ABSTRACT

Copolymers are formed between styrene and 1-alkyl-4,5-dicyano-2-vinylimidazoles (1-alkylvinazenes). The reactivity ratios for the 1-ethylvinazenes are determined to be high, but also appear to vary with feed composition, with low feed ratios of 1-ethylvinazene giving $r_{\text{EtVz}}=35 \pm 6$ and $r_{\text{Sty}}=0.077 \pm 0.029$, whereas at higher 1-ethylvinazene feed fractions, $r_{\text{EtVz}}=2.5 \pm 2$ and $r_{\text{Sty}}=0.089 \pm 0.021$. Mediation of the 1-methylvinazene/styrene copolymerization with 2,2,6,6-tetramethylpiperidine-N-oxide (TEMPO) leads to a more controlled polymerization which moves closer to ideal copolymerization behavior. The copolymers form with polydispersities approaching 1.5, suggesting bimolecular termination kinetics. The copolymers comply with the Fox relation for T_g .

Key Words: Dicyanoimidazole; Diaminomaleonitrile; Vinazene; Copolymers.

INTRODUCTION

Dicyanoimidazole compounds, synthesized from the well-known HCN tetramer, diaminomaleonitrile (DAMN) were first reported by D. W. Woodward in a patent assigned to Dupont [1]. An early paper by Bredereck and Schmötzner [2] described a number of Schiff base reactions of DAMN. Later, the chemistry of

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DAMN, including oxidation to both imidazoles and diazepines, was explored in depth at Dupont in the 1970's and was reviewed by Donald and Webster [3]. An improved oxidative method for preparing dicyanoimidazoles from Schiff bases of DAMN was reported by Patel [4]. This method was used by Hosogai [5] to prepare 2-vinyl-4,5-dicyanoimidazole (1); however, no polymerizations or other reactions were reported. Our previous work described improvements to Hosogai's synthesis and to the purification of 1, which we refer to by our trivial name, vinazene. This improvement allowed preparation of the first polymers from the vinazene monomer [6]. We have also investigated the kinetics of the polymerizations and characterized the resulting polymers [7].

Copolymerization is an important methodology for the polymer industry. The modification of large volume monomers with small amounts of a comonomer in order to obtain copolymers with desirable physical or chemical properties is commonplace. For example, styrene has a high volume of use, many different applications [8] and thus, is an important target monomer for our copolymerization studies. Our previous work described both a free radical vinylic addition polymerization and a Michael-addition step-growth polymerization for vinazene. When vinazene is alkylated, the Michael-addition pathway is prevented, and only the radical-addition polymerization can occur. In this paper we report on our investigation of the radical copolymerization of 1-alkylvinazene with styrene.

EXPERIMENTAL

Methods

^1H NMR spectra were collected with Varian 300, 400 or 500 MHz field instruments. ^{13}C NMR spectra were collected at 75 or 100 MHz. Elemental analyses were obtained from a Perkin-Elmer CHN 2400. TGA data was collected with a Perkin-Elmer TGA 7. DSC data was collected with a Perkin-Elmer DSC-7 or TA Instruments, Thermal Analyst 2100 DSC 2920 Modulated [16].

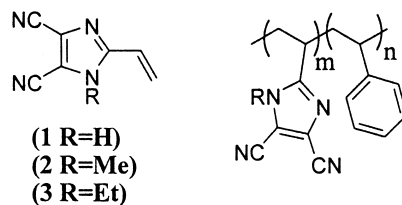


Figure 1. Vinazene and 1-alkylvinazenes, and their styrene copolymers.

Materials

The syntheses of vinazene, 1-methylvinazene, and 1-ethylvinazene have been described in detail [7]. Acetonitrile was distilled from calcium hydride before use. DMSO- d_6 and DMSO were normally used with residual water present; if dryness was required, the DMSO was frozen, and the unfrozen residual water was decanted. AIBN was recrystallized from methanol by cooling a saturated room-temperature solution. Styrene was distilled from basic activated alumina to remove inhibitor prior to copolymerization. All other reagents and solvents were purchased from Aldrich or Fisher Scientific and used as received.

Typical Copolymerization of a 1-Alkylvinazene with Styrene [17]

To a flask containing a stirbar, 0.5 g of 1-ethylvinazene, 2.3 mL of freshly distilled styrene, 6 mg of AIBN and 5 mL of CH_3CN was added. The solution was degassed by nitrogen purge and placed in an oil bath at 65°C. The reaction was quenched after a predetermined period of time by addition to methanol. The solvent was removed by low-vacuum evaporation to yield the product polymer. The polymer typically retained solvent despite vigorous efforts to remove it. NMR analysis of the methanol filtrate confirms incomplete consumption of monomer, as intended. The polymer precipitate was vigorously extracted with ethyl ether to remove unreacted monomer.

The Kinetics of the Non-mediated and TEMPO Mediated Copolymerization of Methyl Vinazene and Styrene by NMR

A solution in DMF was prepared that was ~1M in total monomer, ~0.06M in AIBN and ~0.06M in TEMPO. The sample was heated to 130°C. NMR samples were taken from this solution and quenched by cooling. Aliquots were removed, under nitrogen, from the solution hourly for 9 hours. 1H NMR spectra were taken for each sample. The $\underline{H}CON(Me)_2$ integration of the solvent was compared to the β -*trans* proton of methyl vinazene and the β -*cis* proton of styrene to determine monomer concentrations at specific time intervals.

To study the non-mediated copolymerization, a similar reaction setup was employed. However, the removed aliquot was quenched by addition to solid tetrachlorobenzoquinone and the reaction was heated to 70°C. This procedure was difficult to perform consistently, and the non-mediated copolymerization data have more scatter than the mediated copolymerization experiments.

Data Analysis for Copolymerization Experiments. From the concentrations of the monomers, $[Vz]/[Sty]$ was readily available. For NMR data, we determine the change between pairs data points, $\Delta[Vz]/\Delta[Sty]$, and took this as an approximation for $d[Vz]/d[Sty]$. Elemental analysis data was processed to determine $d[Vz]/d[Sty]$ directly. For the Fineman-Ross treatment, we defined $X = [Vz]/[Sty]$

and $Y = d[Vz]/d[Sty]$, $F = X^2/Y$ and $G = X(Y-1)/Y$, and the linear relation $G = r_{Vz}F - r_{Sty}$ [18]. For the Kelen-Tudos treatment, we introduced an arbitrary positive constant, $\alpha = \sqrt{(F_{\min} * F_{\max})}$. We then assigned $\eta = G/(\alpha + F)$, and $\xi = F/(\alpha + F)$. Plotting $\eta = (r_{Vz} - r_{Sty}/\alpha) * x - r_{Sty}/\alpha$ then gives r_{Vz} by extrapolation to $\xi = 0$, and $-r_{Sty}/\alpha$ by extrapolation to $\xi = 1$ [18].

RESULTS AND DISCUSSION

Determination of Reactivity Ratios. Characterization of the 1-alkylvinazene/styrene copolymerization was initially difficult. The copolymers were highly enriched in 1-alkylvinazene content relative to the feed compositions. The effect was so dramatic that to a first approximation, the degree of copolymerization was dependent upon the 1-alkylvinazene concentration in the reaction. These qualitative observations suggested that the vinazyl radical is much more reactive than the styryl radical. Thus, our primary approach was to achieve a quenched reaction by pouring the products into methanol after a predetermined period, in order to stop the reaction before the monomer composition had drifted significantly.

A variation in sampling procedure was used for studying 1-methylvinazene and styrene, in which aliquots of a polymerization were removed under nitrogen and immediately quenched by addition to a radical scavenger, tetrachlorobenzoquinone. The copolymerization was characterized by either copolymer composition, determined by elemental analysis of precipitated polymer, or by monomer consumption determined from NMR analysis. From this data, we were able to extract feed versus composition values and obtain plots suitable for determination of reactivity ratios.

The data presented in Figure 2 was typical for all 1-alkylvinazene copolymerizations with styrene. The data indicate a strong preference for vinazene incorporation over styrene into the polymer at low mole fractions of 1-ethylvinazene. In practice, reactions at higher concentrations of 1-ethylvinazene proved too difficult to quench reliably in methanol and attempts to quench with tetrachlorobenzoquinone gave similar problems.

Analysis of the copolymerization reactions required care. The simplest method, the Finemann-Ross treatment [9] defines relationships 1-3:

$$r_{Vz} = k_{Vv}/k_{Vs} \quad (1)$$

$$r_{Sty} = k_{Ss}/k_{Sv} \quad (2)$$

$$\frac{[Vz]d[Sty](d[Vz]/d[Sty] - 1)}{d[Vz]} = \frac{r_{Vz}[Vz]^2d[Sty]}{[Sty]^2d[Vz]} - r_{Sty} \quad (3)$$

This analysis did not give good linear regressions, and the values obtained were not in good agreement with the empirical trend evident in Figure 2.

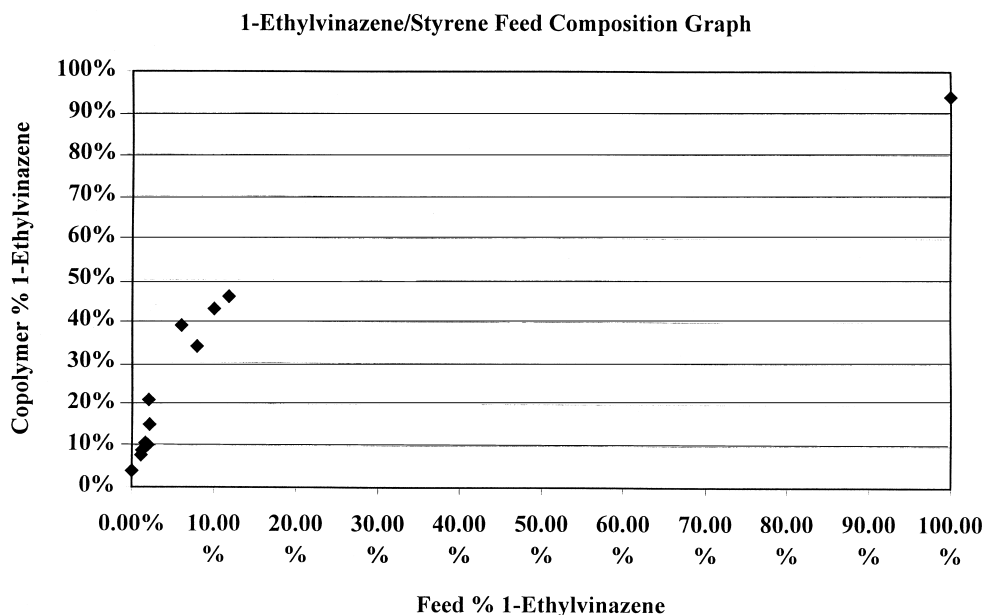


Figure 2. 1-Ethylvinazene/styrene feed vs. composition graph.

To derive better reactivity ratios, we applied the Kelen-Tudos treatment, in which the introduction of an arbitrary parameter spreads the data out more linearly [10]. This treatment yielded $r_{\text{EtVz}} = 1.3 \pm 1$, and $r_{\text{Sty}} = 0.10 \pm 0.09$, in general agreement with the compositional graph. However, the behavior of the 1-ethylvinazene in the low feed composition regions prompted further analysis.

When we separated the data into two sets with less than 2 mol% 1-ethylvinazene feed, and greater than 2 mol% 1-ethylvinazene feed, the data analysis described the high reactivity of 1-ethylvinazene much better. At very low 1-ethylvinazene comonomer feed, the calculated reactivity ratios were $r_{\text{EtVz}} = 35 \pm 6$ and $r_{\text{Sty}} = 0.077 \pm 0.03$, while above this region, we calculated $r_{\text{EtVz}} = 2.5 \pm 2$ and $r_{\text{Sty}} = 0.089 \pm 0.02$. While the separation of the data into two sets gave a better description of the copolymerization behavior at low vinazene feed, the higher 1-ethylvinazene feed regions still have significant variability in their confidence intervals.

We also studied the rates of copolymerization for 1-methylvinazene and styrene. In this case, we measured the competitive rates of copolymerization using the quenched aliquot approach.

Again, the data clearly show that 1-methylvinazene is depleted from the reaction mixture much faster than styrene. However, in this case neither the application of the Fineman-Ross treatment nor the Kelen-Tudos treatment gave results that accurately described the kinetic data. Additionally, the resulting reactivity ratios, $r_{\text{MeVz}} = 1.37 \pm 0.2$ and $r_{\text{Sty}} = 1.05 \pm 0.1$, do not accurately reflect the ratio of monomer propagation, $k_{\text{Vz}}/k_{\text{Sty}} = 2.78$.

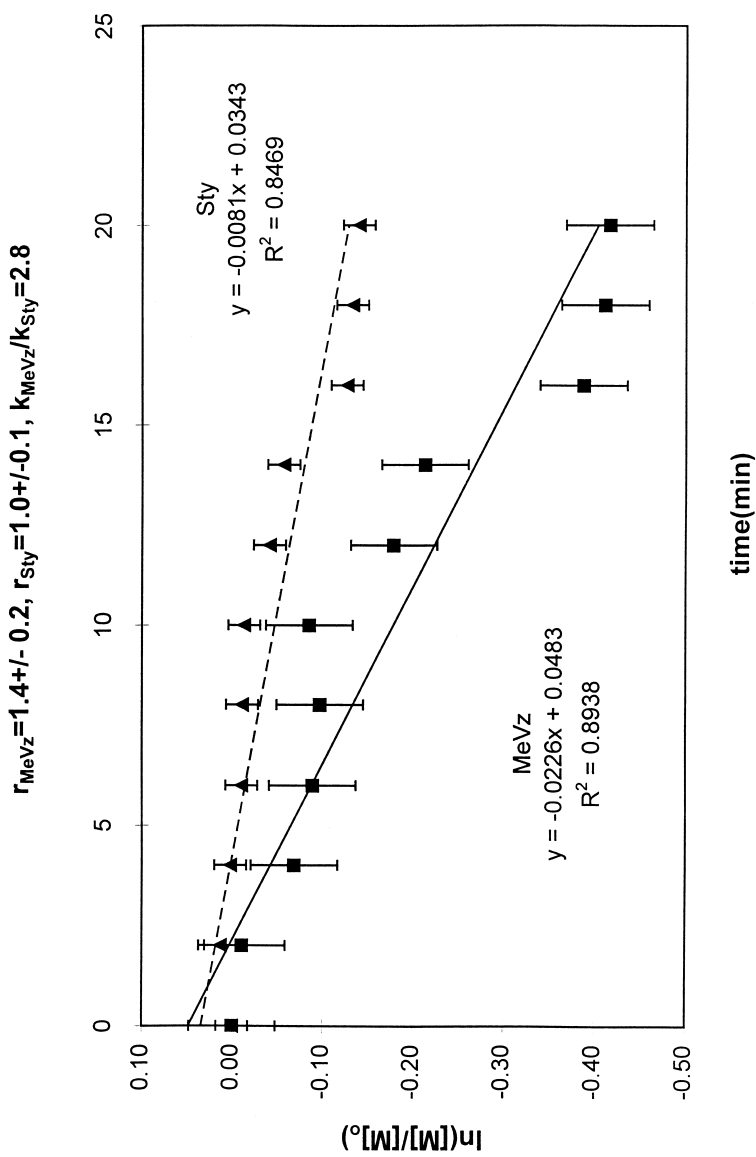


Figure 3. Copolymerization kinetics for 1-methylvinazene/styrene.

In an attempt to control the highly reactive 1-methylvinazene, we added the stable free-radical, 2,2,5,5-tetramethylpiperidine-N-oxide(TEMPO), to the polymerizations. Nitroxide-mediated polymerizations of styrenes have often been established as having 'living' or 'pseudoliving' characteristics [11]; the addition of TEMPO to copolymerizations has recently become a common procedure [12].

The data from the mediated copolymerization of 1-methylvinazene with styrene showed a more closely ideal polymerization than the unmediated case [13]. Using the Finemann-Ross method, we extracted reactivity ratios of $r_{\text{MeVz}} = 1.19 \pm 0.07$ and $r_{\text{Sty}} = 0.91 \pm 0.06$, which gave a closer indication of the behavior of reaction in which $k_{\text{Vz}}/k_{\text{Sty}} = 1.42$. Thus, under TEMPO mediation, the polymerization behaved much more like an 'ideal' random copolymerization than in the non-mediated case.

The experimental conditions for this polymerization were set up so there was a slight excess of TEMPO, relative to the amount of AIBN initiator. The nitroxide coupling/decoupling equilibria with the propagating radicals appeared to inhibit the vinazyl radical more strongly than the styryl radical. This argued for a lower concentration of vinazyl radical in the presence of TEMPO mediation, and hence, a higher instability relative to the styryl radical. This data supports our earlier conclusion that the vinazyl radical is more reactive [14].

Copolymer Properties

The homopolymers of vinazene and 1-alkylvinazene tend to be insoluble in solvents such as methylene chloride and THF. However, the styrene copolymers of 1-ethylvinazene were soluble in tetrahydrofuran at the lower vinazene content end of the compositional range. This allowed us to characterize their molecular weights using GPC. Our results clustered around a polydispersity index (pdi) of 1.5, as is typical for a reaction in which termination is predominantly via bimolecular coupling.

We also measured the T_g values of several poly(1-ethylvinazene) co-styrene copolymers. We find that the ethylvinazene/styrene copolymers obey the Fox relation [15]:

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}} \quad (4)$$

For the homopolymer of 1-ethylvinazene, the glass transition does not occur below the decomposition temperature. Variations in the T_g of poly(1-ethylvinazene-co-styrene), from samples with 8%-47% ethylvinazene composition, allowed us to extrapolate to a crude estimate for 'virtual' T_g for the homopolymer using Equation 4, as $257 \pm 17^\circ\text{C}$.

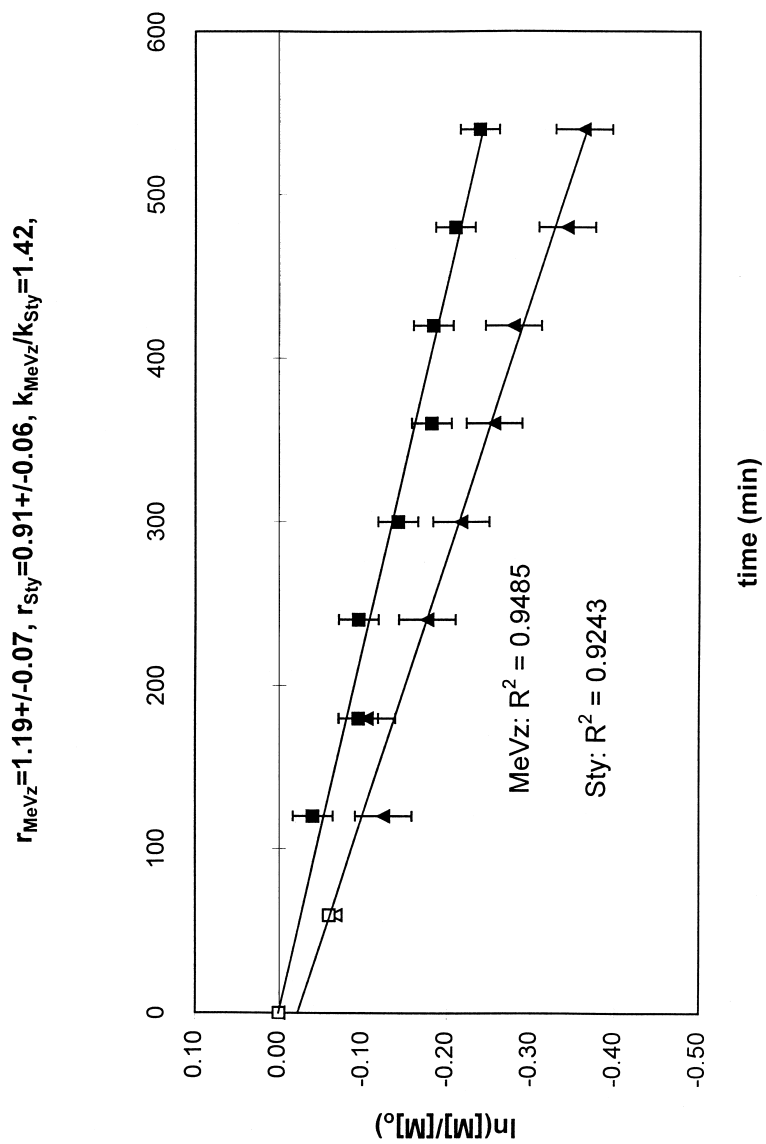


Figure 4. TEMPO Mediated copolymerization kinetics for 1-methylvinazene/styrene.

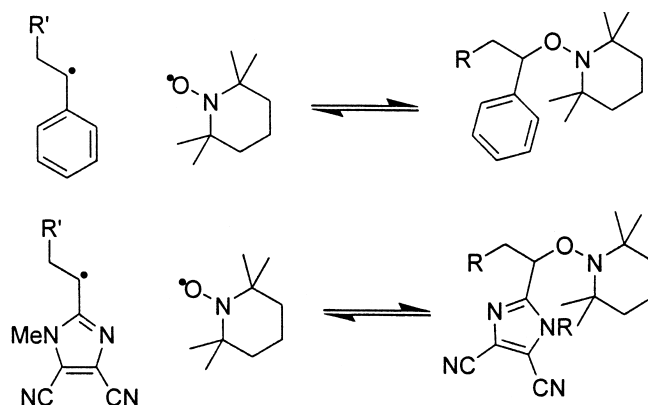


Figure 5. TEMPO equilibrium during copolymerization of styrene and 1-methylvinazene.

Table 1. Copolymer Molecular Weight and Polydispersity Data

Mol % EtVz(feed)	M_n	M_w	pdi
2%	1.45×10^5	2.1×10^5	1.45
4%	1.74×10^5	2.63×10^5	1.54
6%	1.88×10^5	3.03×10^5	1.60
8%	2.05×10^5	3.33×10^5	1.63
20%	1.769×10^5	2.96×10^5	1.64

CONCLUSION

We have established that 1-alkylvinazenes copolymerize readily with styrene. The very high reactivity of 1-alkylvinazene leads to its significant enrichment in copolymer composition, compared to the feed ratio. The linear methods used for determining radical reactivity ratios provides a semi-quantitative description of the reactivity and suggests that the vinazyl radical is considerably more reactive than the styryl radical. Apparently, the vinazyl radical gains less stabilization from the adjacent heteroaromatic ring than styrene gains from the adjacent phenyl ring. In future work, we will examine the penultimate effects and their influence upon the copolymerization of 1-alkylvinazenes and styrene that is implied by our current data.

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13. It should be noted that while other workers in the field typically have studied nitroxide mediation as a method for 'living' radical polymerization, we have not determined if this mediated copolymerization has any of the 'living' characteristics.
14. We are comparing the reactivity of the 1-ethylvinazyl radical, as determined by feed/composition to the reactivity of the 1-methylvinazyl radical, as determined by TEMPO inhibition. We expect the difference in reactivity due to changing the alkyl groups will be small; however, we have not established this quantitatively.
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