

Copolymers of 2-Vinyl-4,4-Dimethylazlactone with Styrene and Ethyl α -Hydroxymethylacrylate

JENO MUTHIAH and LON J. MATHIAS*

University of Southern Mississippi, Department of Polymer Science, Hattiesburg, Mississippi 39406-0076

SYNOPSIS

The monomer reactivity ratios for copolymerization of 2-vinyl-4,4-dimethylazlactone (VA) and ethyl α -hydroxymethylacrylate (EHMA) were 0.20–0.24 and 0.53–0.74, respectively, which show that EHMA is slightly more reactive with VA than with itself and should lead to random copolymers favoring alternation. The VA–styrene (VA–St) system also has a tendency to form random copolymers but with increased tendency for alternation with both r_1 and r_2 between 0.18–0.22. T_g 's of VA–EHMA and VA–St copolymers varied between 100 and 136°C, and 96 and 117°C, respectively. Thermolysis of VA–EHMA copolymers resulted in crosslinking via the ring-opening reaction of VA groups by EHMA alcohols, followed by transesterification involving EHMA units at higher temperatures leading to highly crosslinked structures. The preformed dimer of EHMA and VA was also synthesized and found to be an effective crosslinking agent in free radical vinyl polymerizations.

INTRODUCTION

2-Vinyl-4,4-dimethylazlactone (VA) is a vinyl monomer with reactive functionality that can be used to generate a variety of derivatives before and after polymer formation.¹ Ethyl α -hydroxymethylacrylate (EHMA) is one member of another family of multifunctional vinyl monomers whose synthesis and applications we have been exploring recently.^{2–5} For example, EHMA has been used to make a variety of new acrylate crosslinking agents.³ Its methyl ester analog (MHMA) was copolymerized with styrene to determine reactivity ratios which were found to be very close to those of methyl methacrylate with styrene.⁴ EHMA was converted to its chloro derivative, copolymerized with styrene and subsequently substituted via nucleophilic reaction at the $-\text{CH}_2\text{Cl}$ group.⁵ EHMA was chosen for copolymerization with VA because the OH functionality of EHMA can react with the VA heterocycle through ring-opening addition to give crosslinked materials before, during, or after polymerization.

For eventual application, it is important to have an estimate of the radical reactivity of VA in copolymerization with EHMA and styrene (the other monomer envisioned for a terpolymer system to reinforce wood³). Two series of copolymers were synthesized and analyzed for composition using several techniques. Monomer reactivity ratios (MRR's) were then determined using the extended Kelen–Tüdös method based on previous evaluations of the copolymerization of MHMA with styrene.⁴ The thermal properties were studied to evaluate stability and crosslinking activity of the various function groups in the polymers.

EXPERIMENTAL

EHMA was synthesized by reacting ethyl acrylate with paraformaldehyde using catalytic amounts of 1,4-diazabicyclo[2.2.2]octane (DABCO) at 65°C.² Vinylazlactone (VA) was used as obtained from 3M. Styrene (St) was purified by distillation just before use. 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU), methyl methacrylate, 2,2-dimethoxy-2-phenylacetophenone (Irgacure) were used as obtained. 2,2'-Azobisisobutyronitrile (AIBN) was purified by recrystallization from methanol. ¹H- and ¹³C-NMR

* To whom correspondence should be addressed.

spectra were obtained on a Bruker AC-300 spectrometer using an acquisition delay for the latter of 5 s to facilitate quantitation. IR analysis was performed on a Perkin-Elmer 1600 FT-IR and all spectral data are given in wave-numbers (cm^{-1}). Standardization involved known quantities of homopolymers of EHMA and VA which were mixed and mechanically ground to a fine powder along with KBr before IR quantitation. UV data for VA-St copolymers were obtained with a Perkin-Elmer Lambda 6 UV spectrometer. A DuPont 9900 data station equipped with DSC and TGA modules was used to obtain the thermograms.

TYPICAL COPOLYMERIZATIONS

Carefully weighed amounts of EHMA and VA were mixed with known quantities (ca 0.5–1 mol %) of AIBN. The mixture was degassed by purging with N_2 before polymerization in an oil bath at 65°C . Photopolymerization was done with a UV lamp using 0.5 wt % Irgacure as initiator. Polymers were dissolved in CHCl_3 , precipitated into diethyl ether and vacuum dried. The VA-St copolymerizations were all done at 65°C with AIBN. The VA-St copolymers were dissolved in CHCl_3 , precipitated into petroleum ether, and dried under vacuum. In all cases, low conversions were used to improve the accuracy of monomer reactivity ratio (MRR) evaluations. Despite this, some polymerization mixtures turned cloudy due to crosslinking. The VA-EHMA copolymers were analyzed for composition using ^{13}C gated decoupling NMR, ^1H -NMR, and quantitative IR. The compositions of VA-St copolymers were determined through ^{13}C gated decoupling NMR, ^1H -NMR and UV spectroscopy. ^{13}C gated decoupling typically involved dissolving the VA-EHMA copolymers in hexafluoroisopropanol and the VA-St copolymers in CDCl_3 .

DIMER FROM REACTION OF EHMA AND VA

VA undergoes facile ring-opening through addition of amines and alcohols.⁶ A 1 : 1 mole ratio of EHMA and VA was reacted at 65°C in the presence of catalytic amounts of DBU. After 30 h, 85% of the reactants were converted to the dimer as monitored by GC. ^{13}C -NMR (in CDCl_3 , δ in ppm): 13.48, CH_3 (EHMA); 24.30, CH_3 (VA); 55.39 — CH_2OH ; 60.42, — $\text{CO}_2\text{CH}_2\text{CH}_3$; 62.25, — $\text{C}(\text{CH}_3)_2$ —; 125.68, 126, 134.74, 139.80, $\text{C}=\text{C}$ carbons; 164.41, 164.71,

173.10, $\text{C}=\text{O}$ carbons. Excess reactants were not removed and the dimer was not purified before evaluation of its crosslinking ability. It was not felt necessary to further characterize this dimer since the chemistry of VA in ring-opening is well known, and for use as a crosslinker, unreacted monomers will simply be incorporated into the polymer backbone during cure. This dimer reaction mixture was then used as a crosslinking agent at approximately 5 mol % to St and methyl methacrylate (MMA) for polymerization at 65°C with ca 0.5 mol % AIBN.

RESULTS AND DISCUSSIONS

Figure 1 gives overall copolymerization schemes investigated here. During the course of copolymerizations of VA and EHMA, mixtures containing low amounts of VA turned cloudy whereas mixtures containing higher amounts of VA remained clear. The copolymers obtained were white in color varying from hard solids to powders. The VA-St copolymers remained clear during the course of polymerization for all the different compositions and were isolated as white powders. Molecular weights and polydispersities of copolymers are difficult to obtain accurately, and no attempt was made to determine these parameters for any of the copolymers synthesized here.

A typical ^{13}C -NMR spectrum for the VA-EHMA copolymer in $\text{DMSO}-d_6$ is given in Figure 2. Compositions of the copolymers were determined using the spectra obtained with ^{13}C gated decoupling by integrating the methyl peaks of monomer units at 23 ppm for VA and 13 ppm for EHMA. The mol % values were calculated using eq. (1)

$$\text{Mol \% of VA} = 100[0.5A_1]/[0.5A_1 + A_2] \quad (1)$$

where A_1 = area for the two identical methyl carbons of VA, and A_2 = area for the single methyl carbon of EHMA.

Typical ^{13}C -NMR spectra (120–200 ppm regions) of different compositions of VA-St copolymers in CDCl_3 are given in Figure 3. The peaks used for integration for these material are those of the ring $\text{C}=\text{N}$ of VA at 164 ppm and the ipso ring carbon (attached to the backbone) of St at 141 ppm. The amounts of VA in the copolymers were calculated using eq. (2)

$$\text{Mol \% of VA} = 100A_1/(A_1 + A_2) \quad (2)$$

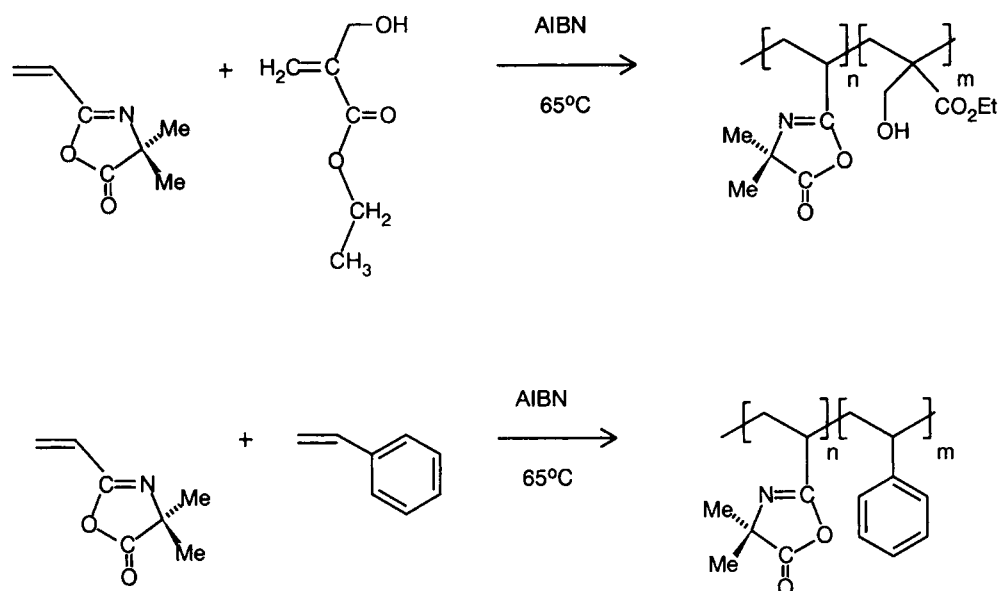


Figure 1. Overall schemes for copolymerization of VA with EHMA (upper reaction) and St (lower).

where A_1 = area under the $C=N$ peak of VA and A_2 = area under the peak for the ipso carbon of St.

The spectra in Figure 3 show the presence of microcomposition differences along the polymer chain, which is more pronounced in polymers containing higher amounts of VA. The multiple peaks for some of the carbon positions is assumed to be due to sequence distribution, and therefore should correlate with calculated values. The average sequence lengths for VA were calculated using eq. (3)⁷

VA ave sequence length

$$= 1 + r_1([M_1]/[M_2]) \quad (3)$$

The values for VA and St (with the latter calculated using the complementary equation⁷) for the 80 : 20, 50 : 50, and 20 : 80 feed compositions were 1.88 and 1.05, 1.22 and 1.19, and 1.06 and 1.76, respectively. The microstructural compositions appear to correlate qualitatively with the changes in intensity for

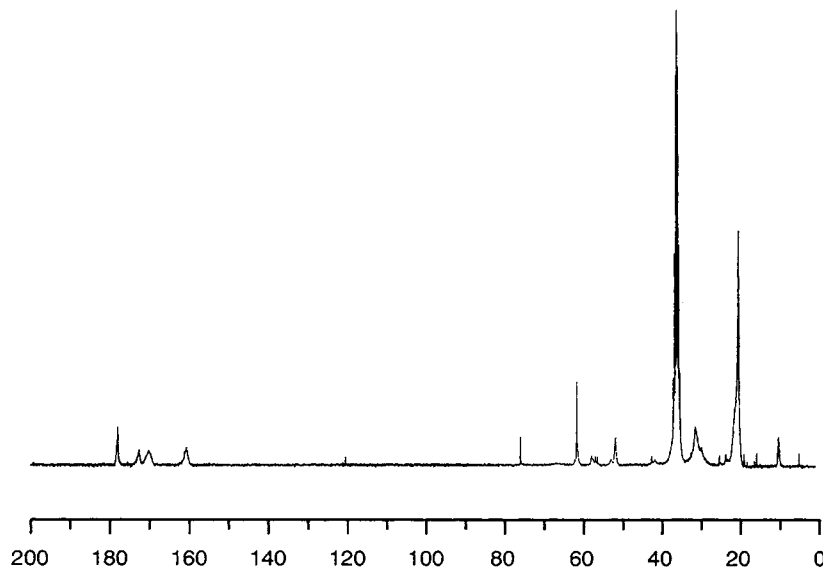


Figure 2. ¹³C-NMR spectrum in DMSO-*d*₆ of VA-EHMA copolymer formed with 90 : 10 mol % of VA and EHMA in the feed.

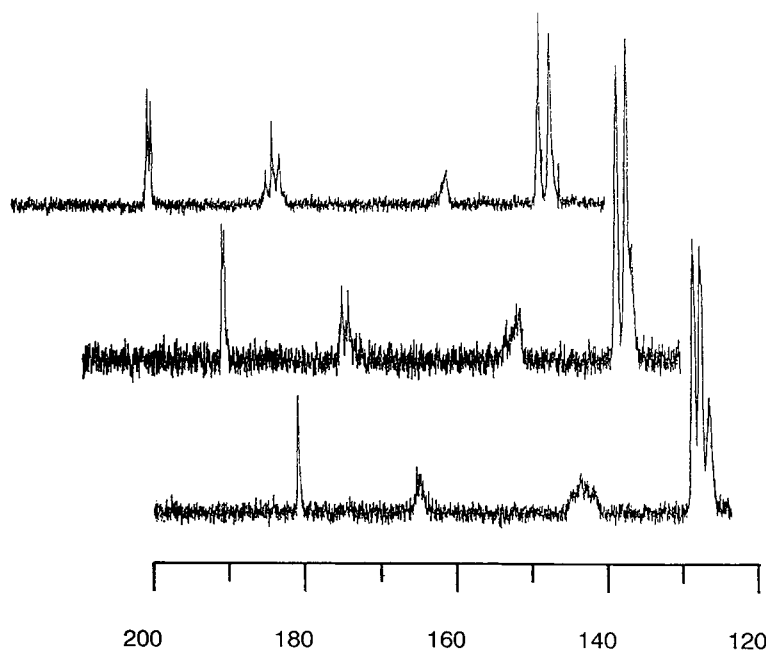


Figure 3. ^{13}C -NMR spectra of VA-St copolymers formed with 80 : 20 (top spectra), 50 : 50 (middle), 20 : 80 (bottom) mole % of VA and St in the feed (upper spectra offset downfield).

multiple peaks in the ^{13}C -NMR spectra, especially for the $\text{C}=\text{N}$ peak at 164 ppm as seen in Figure 3.

^1H -NMR was also used for determining the copolymer compositions. For the VA-EHMA copolymers, the protons on carbons adjacent to the oxygen (a total of 4 protons between 3.2 and 4.5 ppm) in EHMA were integrated with respect to all the other protons in the copolymer. The OH proton was assumed to be undergoing rapid exchange with the trifluoroacetic acid protons, which should cause its peak to broaden and move downfield from this region. The mol % values were then calculated using eq. (4)

Mol % of EHMA

$$= 100(A_1/4) / \{ [A_2 - 5A_1/4]/9 + A_1/4 \} \quad (4)$$

where A_1 = area for the 4 EHMA protons and A_2 = area for all other protons in the copolymer.

Similarly for the VA-St copolymers, the aromatic protons of St were integrated with respect to all other protons. The copolymer compositions were calculated using equation (5)

Mol % of St = $100(A_1/5)/$

$$\{ [(A_2 - 3A_1/5)/9] + A_1/5 \} \quad (5)$$

where A_1 = area for the aromatic protons and A_2 = area for all other protons.

The IR spectra of VA/EHMA homopolymer mixtures were used to find the ratio of absorbances of the carbonyls of VA and EHMA. A straight-line calibration plot was obtained for the ratio of absorbance values versus the mol-ratio of the two monomer units in the polymer mixtures. Using the calibration plot, the mol-ratio of the two monomers in each of the copolymers was obtained from which the mol % was calculated using equation 6

$$\text{Mol \% of VA} = 100X/(1 + X) \quad (6)$$

where X = ratio of molar concentrations of VA and EHMA.

Determination of copolymer composition by UV was attempted since the constituents of the VA-St copolymers have distinct absorptions. A calibration plot was established for the aromatic peak for known concentrations of polystyrene in chloroform. Then the absorbance values of the St component of the copolymers were found and the wt % values of St in the copolymers were calculated. The wt % values were converted to mol % using the molecular weights of the monomers.

Table I gives the VA-EHMA copolymer compositions determined with the various techniques along with the conversions obtained for each copolymerization. Table II shows the same for the VA-St copolymers. The compositions of VA-EHMA co-

Table I. Copolymer Compositions and Yields for VA-EHMA Copolymers; Values in Parentheses Not Used in Tables III and IV

VA mol % in Feed	VA mol % in Copolymer Determined by:			Yield (wt %)
	¹³ C-NMR ^a	¹ H-NMR ^b	IR ^c	
10.95	15.06	(23.94)	12.52	8.22
18.74	19.84	(30.90)	17.85	9.45
29.91	33.34	(39.64)	21.30	6.31
50.96	44.20	(49.10)	43.16	8.30
71.18	54.35	(56.82)	62.20	6.75
77.38	64.28	(72.11)	66.67	9.90
89.95	86.40	(82.00)	73.62	7.72

^a In HFIP.^b In trifluoroacetic acid.^c KBr pellets.

polymers calculated from ¹H-NMR data were somewhat different from those obtained with the other two techniques. This may be due to contaminants possessing exchangeable hydrogens or the presence of the exchangeable alcohol peak being partially counted causing errors in one of the peak areas integrated. The values of compositions from the other two techniques were therefore used for further calculations. Similarly, the copolymer compositions of VA-St copolymers determined by UV were also suspect in that overlap of the trailing edge of the carbonyl band of azlactone units with the styrene peak made quantitation unreliable; the values determined disagreed with those obtained from ¹³C- and ¹H-NMR integrations. Thus, the values of the latter two were used for determining the reactivity ratios. While a third analytical method for both systems would be desirable, such methods as elemental analysis are not available on our campus.

Figure 4 shows the dependence of instantaneous copolymer compositions on the comonomer feeds for both VA-EHMA and VA-St copolymerizations and indicates essentially random copolymer formation for both systems. The reactivity ratios were calculated using the extended Kelen-Tüdös method which has been found to yield results as good as the nonlinear least squares analysis.⁸ Kress et al. reported that the extended Kelen-Tüdös technique can be used with confidence even at relatively high conversions (> 10%).⁴ The MRR values were calculated individually from the copolymer compositions obtained with each technique for both polymers and are given in Table III. The average MRR values from the two techniques giving comparable composition values for VA-EHMA polymerization at 65°C and photopolymerization were (*r*₁ and *r*₂) 0.24 and 0.73, and 0.20 and 0.53, respectively, with monomer 1 being VA. While essentially random in

Table II. Copolymer Compositions and Yields for VA-St Copolymers; Values in Parentheses Not Used in Tables III and IV

VA mol % in Feed	VA mol % in Copolymer Determined by:			Yield (wt %)
	¹³ C-NMR ^a	¹ H-NMR ^a	UV ^b	
10.08	30.80	21.40	(18.35)	6.23
20.18	32.56	32.45	(39.06)	9.08
40.09	51.46	54.14	(66.06)	10.98
50.06	51.15	49.65	(72.31)	16.88
59.94	53.44	57.74	(77.26)	9.82
79.64	69.04	72.72	(88.60)	15.78
90.05	72.90	76.90	(90.05)	5.82

^a In CDCl₃.^b In CHCl₃.

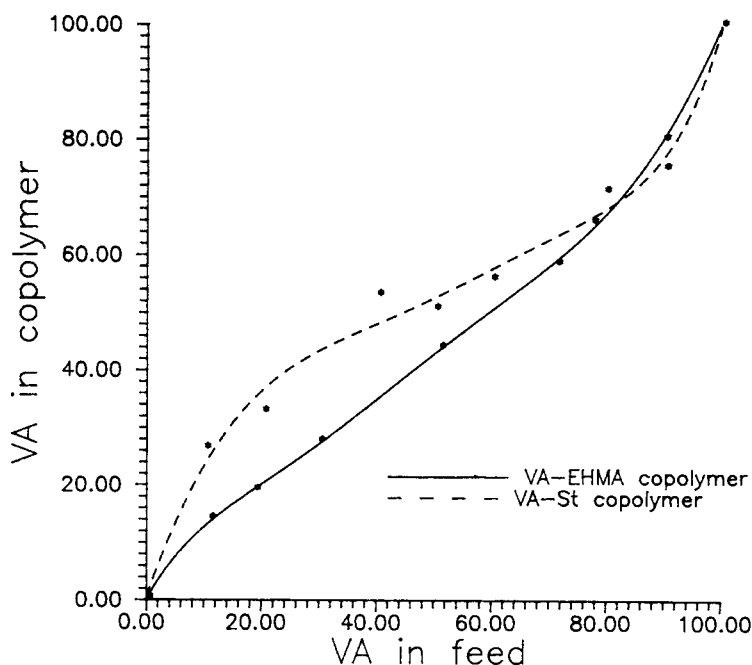


Figure 4. Plots of average copolymer compositions versus monomer feeds (mol %) for VA-St (dashed line) and VA-EHMA (solid line).

reactivity, the copolymerization favors alternation. There is also a slightly greater tendency for the EHMA radical to react with another EHMA than for the VA radical to add to another VA monomer. Surprisingly, this selectivity appears to be somewhat reduced with photopolymerization, perhaps due to a large temperature increase with the uv light source used leading to a decrease in the differences in energies of activation for the propagation steps. For the VA-St copolymerization, the obtained reactivity ratios of 0.16–0.24 for both monomers indicate formation of a random copolymer favoring alternation even more than the EHMA system.

Thermolysis and Crosslinking Reactions

T_g 's of VA-EHMA and VA-St copolymers varied between 100 and 136°C, and 96 and 117°C, respec-

tively. The individual values are given in Table IV and are the result of multiple DSC scans on the same sample to eliminate sample history artifacts. For reference, the T_g 's of the homopolymers of VA, EHMA, and St are 96, 97 and 100°C, respectively. The VA-EHMA copolymers containing low amounts of VA gave higher T_g 's both in the first heating cycle from 20 to 150°C and in the second cycle of 20–300°C. T_g values after the first cycle were increased by 20–30°C due to crosslinking. The high concentration of OH groups in copolymers containing low amounts of VA enhanced the rapid crosslinking reaction, even during the first DSC run. The copolymer containing 65.5% of VA gave two transitions in the second run possibly due to inhomogeneous crosslinking.

The thermal behavior of the VA-EHMA copoly-

Table III. Monomer Reactivity Ratios Calculated for VA Copolymerizations with EHMA and St; Monomer 1 (r_1) is VA

VA-EHMA Copolymerization			VA-St Copolymerization	
Determination of Composition	Polymerization at 65°C	Photopolymerization	Determination of Composition	Polymerization at 65°C
^{13}C -NMR	$r_1 = 0.27$ $r_2 = 0.62$	$r_1 = 0.20$ $r_2 = 0.68$	^{13}C -NMR	$r_1 = 0.19$ $r_2 = 0.16$
IR	$r_1 = 0.21$ $r_2 = 0.83$	$r_1 = 0.19$ $r_2 = 0.37$	^1H -NMR	$r_1 = 0.24$ $r_2 = 0.21$

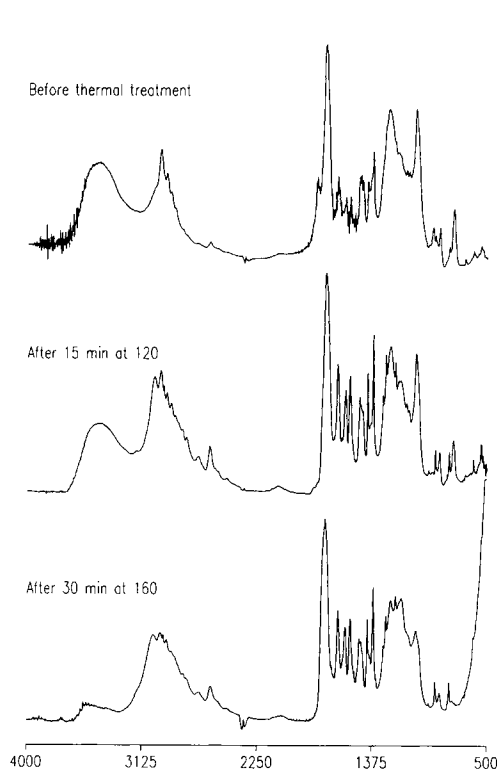
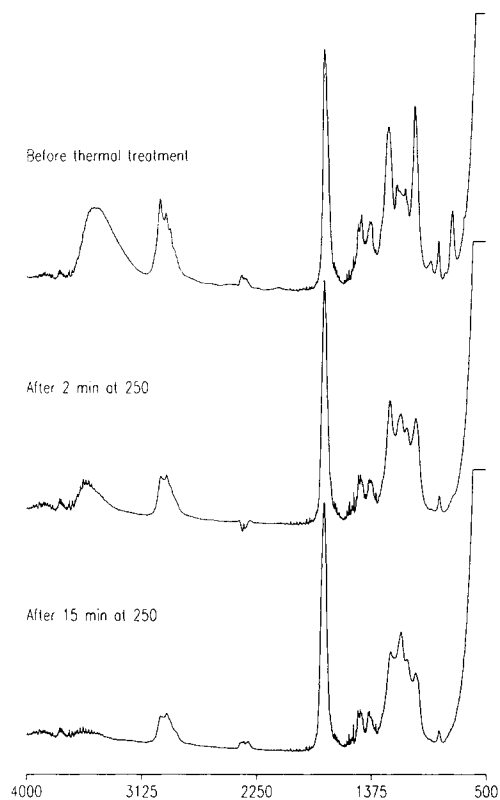
Table IV. T_g 's of VA-EHMA and VA-St Copolymers (in °C)

VA-EHMA Copolymers			VA-St Copolymers	
VA mol % in Copolymer	First Cycle, 20–150°C	Second Cycle, 20–300°C	VA mol % in Copolymer	First Cycle, 20–150°C
13.79	136	152	26.10	96
18.85	132	143	32.50	105
27.32	111	141	52.80	— ^a
43.68	— ^a	148	50.40	117
58.28	98.8	134	55.59	116
65.48	— ^a	133 ^b	70.88	98.1
80.01	131	138	74.90	104

^a T_g not distinct.^b A second transition was observed at higher temperature.

mers was further analyzed by IR with observation of the conversion of the ring carbonyl of VA (peak at 1819 cm^{-1}) to ester $\text{C}=\text{O}$ (at 1730 cm^{-1}). This is shown in Figure 5 for the 20 : 80 VA-EHMA copolymer. A competitive reaction involves transesterification of the pendent OH groups with the ester moieties with resulting loss of ethanol.³ The vinyl

azlactone ring-opening reaction is much more facile and occurs readily at 120°C , followed by transesterification beginning at 160°C . This shows that the process of crosslinking can be sequentially controlled to involve just ring-opening of VA heterocycles or both ring-opening and transesterification of EHMA units.

**Figure 5.** IR spectra of VA-EHMA copolymer (20 : 80 VA and EHMA mol % in feed) obtained at room temperature (top trace), after 15 min at 120°C (middle), and after 30 min at 160°C (bottom).**Figure 6.** IR spectra of poly(EHMA) before thermal treatment (top trace), after 2 min at 250°C (middle), and after 15 min at 250°C (bottom).

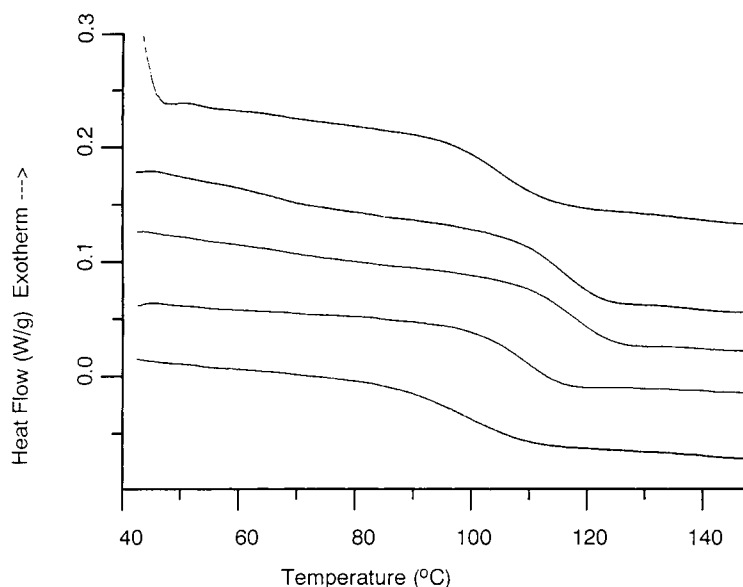


Figure 7. DSC thermogram of VA-St copolymers; traces from top to bottom correspond to VA and St mol % in monomer feed of 90/10, 60/40, 50/50, 80/20, and 10/90, respectively.

The transesterification can be driven to completion even for the homopolymer of EHMA as shown by a 25°C-wide TGA plateau beginning at 250°C. The 35% weight loss accounts for 100 mol % loss of ethanol. This process was monitored by IR at 250°C for different reaction times; representative spectra are shown in Figure 6. The reduction in intensity of peaks at 1226 and 1032 cm^{-1} and the increase in the peak at 1152 cm^{-1} are due to transesterification. The disappearance of the OH peak at 3520 cm^{-1} confirms complete reaction. Similar changes in various peak intensities were observed during thermolysis of the copolymers as shown in Figure 5 at 160°C for which both azlactone ring-opening and transesterification were observed.

Crosslinking does not occur for the VA-St copolymers in the absence of added reactants. The T_g 's of VA-St copolymers were consistent with what would be expected based on the T_g 's of the homopolymers of VA and St of 96 and ca. 100°C, respectively. The DSC thermograms of VA-St copolymers

obtained in the second heating cycle from 20 to 150°C is given in Figure 7.

Dimer Formation and Crosslinking

The dimer of VA and EHMA was formed in the presence of DBU as catalyst (Fig. 8). This dimer was formed in good yields as seen by GC and FT-IR analysis. Figure 9 shows the complete disappearance of the OH peak in the IR spectrum of EHMA and the carbonyl of VA starting materials and the appearance of new peaks for the amide carbonyl and NH groups of the product. The formation of the dimer was also confirmed by ^{13}C -NMR.

The dimer was found to be an efficient crosslinking agent at the 5 mol % level for St and MMA as evidenced by swelling studies of the crosslinked polymers and spectral analysis. For example, solid-state ^{13}C -NMR spectra of styrene and MMA crosslinked with the dimer are given in Figure 10, with peaks at 173.7, 165.2, and 14.7 showing incorporation

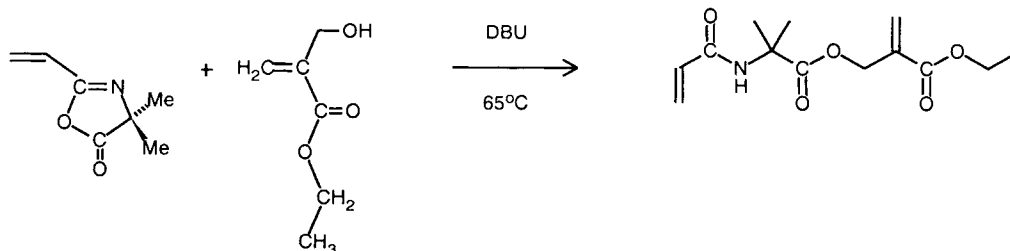


Figure 8. Reaction scheme for dimer formation from VA and EHMA at 65°C.

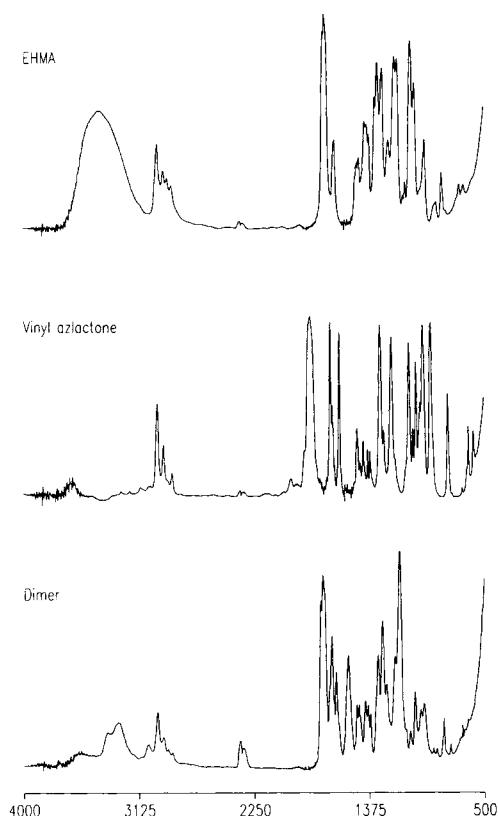


Figure 9. IR spectra of EHMA (top spectra), VA (middle), and dimer (bottom).

of the dimer into the polymer. In the styrene system the polymerization did not go to completion, and excess monomer was removed by swelling in CHCl_3 . No evidence of unreacted vinyl groups of the crosslinking agent was observed, indicating good crosslink efficiency.

CONCLUSIONS

The MRR values for the VA-EHMA copolymerization show that EHMA is slightly more reactive than VA but with a tendency to alternation for both monomers. Overall, however, essentially random copolymers were formed. The VA-St copolymerizations proceeded with a tendency to form random copolymers favoring alternation more strongly than for VA-EHMA. Thermolysis of the VA-EHMA copolymers resulted in the ring-opening reaction of VA groups with EHMA alcohol moieties followed at higher temperature by transesterification involving EHMA units. The overall process leads to a highly crosslinked structure. Preformed dimer of EHMA and VA was also readily synthesized in bulk and shown to be an effective crosslinking agent for St and MMA.

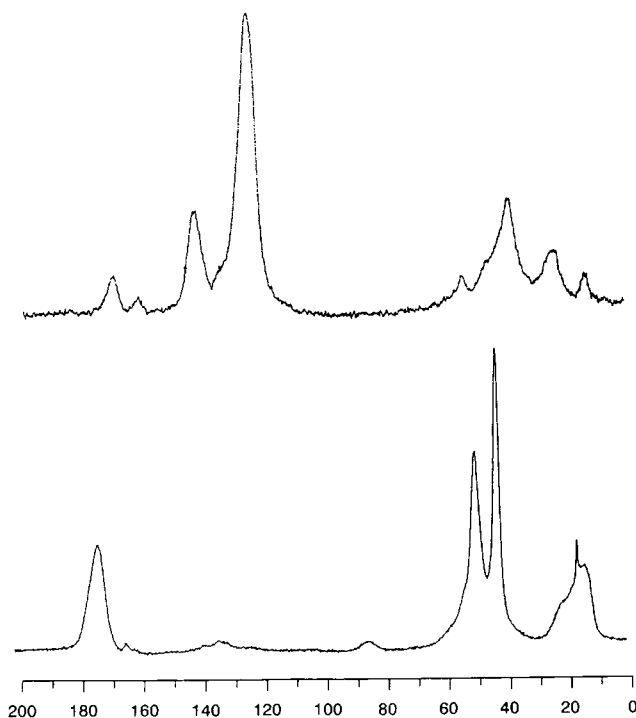


Figure 10. ^{13}C -CP/MAS of polystyrene (top spectrum) and PMMA (bottom) crosslinked through dimer.

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