

Glass Transition Temperatures of Poly (methyl Vinyl Ether-co-Maleic Anhydride) (PMVEMA) and Poly (methyl Vinyl Ether-co-Maleic Acid) (PMVEMAC) and the Kinetics of Dehydration of PMVEMAC by Thermal Analysis

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Synopsis

Three distinct peaks at 80, 175, and 325°C were identified in the dynamic derivative TGA curves of PMVEMA and PMVEMAC at a 10°C/min heating rate. These peaks were attributed to free water removal, anhydride formation, and polymer degradation, respectively. The kinetics of the anhydride formation were studied by isothermal TGA in the temperature range of 150–200°C. It was found to be an endothermic and first-order intramolecular reaction with an activation energy of 18.8 kcal/mol. It was concluded from FT-IR and DSC results that no intermolecular anhydride structure was present in the dehydration of PMVEMAC. This is different from the cases of the dehydration of poly (acrylic acid) and poly (methacrylic acid) in the literature. The limiting glass transition temperatures of PMVEMA and PMVEMAC were found to be 153 and 144°C, respectively. The higher glass transition temperature in PMVEMA as compared to PMVEMAC is attributed to the increase in stiffness in the main polymer chain by the five-membered ring anhydride structure in PMVEMA.

INTRODUCTION

Poly (methyl vinyl ether-co-maleic anhydride) (PMVEMA) is an alternating copolymer which is produced commercially by free radical polymerization. The anhydride group reacts to form a half-ester with alcohol or hydrolyzes to a diacid in water. This versatile polymer has many applications including use as a thickening agent, film former, dispersing agent, emulsion stabilizer, and denture adhesive.^{1,2}

The glass transition temperature (T_g) of PMVEMA reported in the literature has been variously reported as 153,³ 159,⁴ and 133°C.⁵ No data were reported concerning the molecular weight dependence of the glass transition temperature of PMVEMA.

The hydrolyzed diacid form (PMVEMAC) can revert to the anhydride form upon heating through dehydration. The kinetics of dehydration of other polymeric carboxylic acids have been reported in the literature without agreement.^{6–9} The dehydration of poly (methacrylic acid)⁹ was reported to be a second-order reaction under conditions in which the diffusion of water out of the polymer matrix is not rate-determining. The predominant anhydride structure is a six-membered glutaric anhydride type ring.⁹ For poly (acrylic acid) both first-order⁷ and second-order⁸ reactions have been reported. Intramolecular

(glutaric anhydride type) and intermolecular (isobutyric anhydride type) structures are formed by anhydride formation in poly(acrylic acid).⁶ No report in the literature was found regarding the kinetics of dehydration of PMVEMAC.

The purpose of this investigation was to study the molecular weight dependence of the glass transition temperatures of PMVEMA and PMVEMAC and the kinetics of dehydration of PMVEMAC. Comparison was also made among PMVEMAC, poly(acrylic acid), and poly(methacrylic acid) as to the nature of their dehydration processes.

EXPERIMENTAL

Materials

The PMVEMA and PMVEMAC samples used in this study were commercial grades of Gantrez polymer from GAF Chemicals Corp., which are AN-119 (low molecular weight grade, $0.1 < \eta_{sp} < 0.5$), AN-139 (medium molecular weight grade, $1.0 < \eta_{sp} < 1.4$), AN-149 (medium molecular weight grade, $1.5 < \eta_{sp} < 2.0$), AN-169 (high molecular weight grade, $2.6 < \eta_{sp} < 3.5$), and S-97 (acid form of AN-169). Two extra low molecular weight PMVEMA samples ($\eta_{sp} = 0.069$ and 0.10) were also used. One of the Gantrez AN-119 samples was hydrolyzed in water and freeze-dried for T_g determination.

Measurements

A Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) was used for the determination of the glass transition temperature (T_g) at a heating rate of $10^\circ\text{C}/\text{min}$ in nitrogen. The first heating for PMVEMA was carried out from -40 to 165°C to eliminate moisture (free water) and other volatiles and T_g was measured from the second heating. The midspan temperature of the step change in heat capacity curve was chosen as T_g . The DSC was calibrated with the melting temperature of indium.

A Perkin-Elmer TGA-7 thermogravimetric analyzer (TGA) was used to study the weight loss of PMVEMAC. For dynamic TGA runs a heating rate of $10^\circ\text{C}/\text{min}$ was used. The isothermal TGA runs were conducted in two steps. The first isothermal stage was applied at 65°C for 1 h to evaporate the free water and volatiles. The temperature was then raised to the desired anhydride formation temperatures at the rate of $100^\circ\text{C}/\text{min}$. In the kinetic study seven different temperatures from 150 to 200°C were used. The isothermal duration time for the second stage is 30 min at each temperature.

A Nicolet model 20 DX Fourier transform infrared spectrometer was used for IR analysis by employing the diffuse reflectance method with diamond as the matrix to eliminate the moisture pickup exhibited by KBr which is more commonly used.

Specific viscosities were determined at 25°C using a Schott Model AVS automated viscometer. The inner diameter of the viscometer capillary used was 0.53 mm. The solutions were prepared as 1% (w/v) in methylethylketone (MEK) for PMVEMA and 0.4% (w/v) in pH 9 buffer (0.1 M phosphate) with 0.2 M LiNO_3 for PMVEMAC. The pH 9 buffer is prepared from phosphoric acid and sodium hydroxide.

RESULTS AND DISCUSSION

Glass Transition Temperatures of PMVEMA and PMVEMAC

The glass transition temperatures and specific viscosities of different grades of PMVEMA and PMVEMAC are shown in Table I. It should be noted that when measuring the T_g of PMVEMAC the maximum temperature of the first heating should not exceed 100°C because higher temperature will make it more susceptible to anhydride formation.

The results showed that within experimental error the T_g 's of PMVEMA increase with molecular weight and level off at about 153°C. The T_g 's of PMVEMAC (hydrolyzed AN-119 and S-97) are about 10°C less than the anhydride from PMVEMA. This can be explained by the fact that the anhydride form has a five-membered ring including two carbon atoms in the polymer backbone which increases its stiffness vis-à-vis the hydrolyzed form. However, this difference (about 10°C) is much less than the difference in T_g between poly(acrylic acid) (about 103°C) and its anhydride (about 140°C).⁷ This is probably due to the fact that in poly(acrylic acid) (a homopolymer) every monomer unit can contribute to form the six-membered (anhydride) ring structure whereas in PMVEMA only the succinic acid comonomer portion can form the five-membered ring structure and contribute to chain stiffness. Furthermore, dehydration in poly(acrylic acid) can occur by intra- and intermolecular structures,⁸ whereas, in the PMVEMAC case, only intramolecular dehydration was observed, contributing to increased stiffness in the former (as discussed in the next section).

The Nature of the Dehydration Process of PMVEMAC

A typical dynamic TGA run of PMVEMAC (S-97) is shown in Figure 1. Three distinct regions of weight loss (up to 400°C) was observed. This is more evident from the derivative curve (dotted curve in Fig. 1). The first peak (around 80°C) corresponds to the evaporation of free water and other volatiles. The second peak (around 175°C) can be attributed to the dehydration of the diacid groups. The third peak is due to decarboxylation and other degradation reactions.

TABLE I
Glass Transition Temperatures and Specific Viscosities of PMVEMA and PMVEMAC

Sample	Specific viscosity	Glass transition temperature (°C)
Extra low molecular weight PMVEMA	0.069	132
	0.100	133
AN-119	0.31	152
AN-139	1.10	151
AN-149	1.76	153
AN-169	2.67	154
S-97	6.23	144
Hydrolyzed and freeze dried AN-119	0.93	143

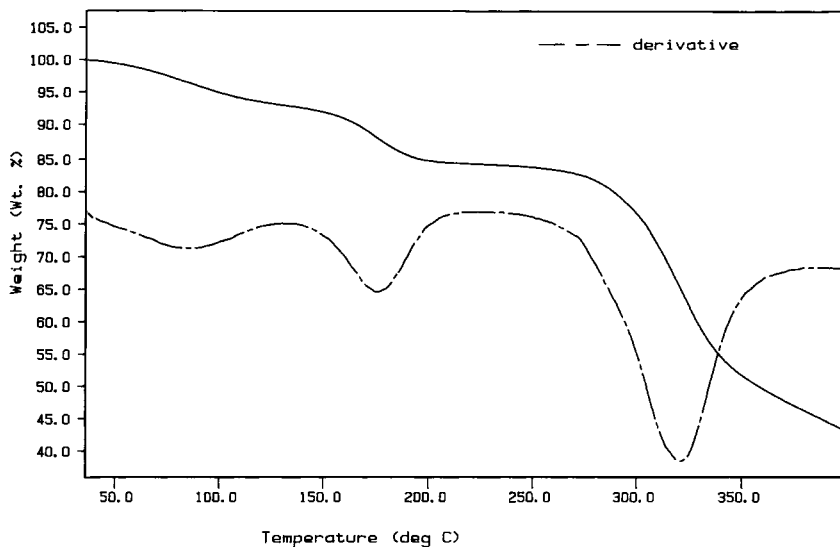


Fig. 1. TGA curve of PMVEMAC (S-97).

The fact that the second peak corresponds to anhydride formation was confirmed by FT-IR. Figure 2 shows the IR spectrum of untreated PMVEMAC while Figure 3 shows the spectrum of PMVEMAC which was heated isothermally for 1 h at 185°C. The characteristic absorption bands of carboxylic acid

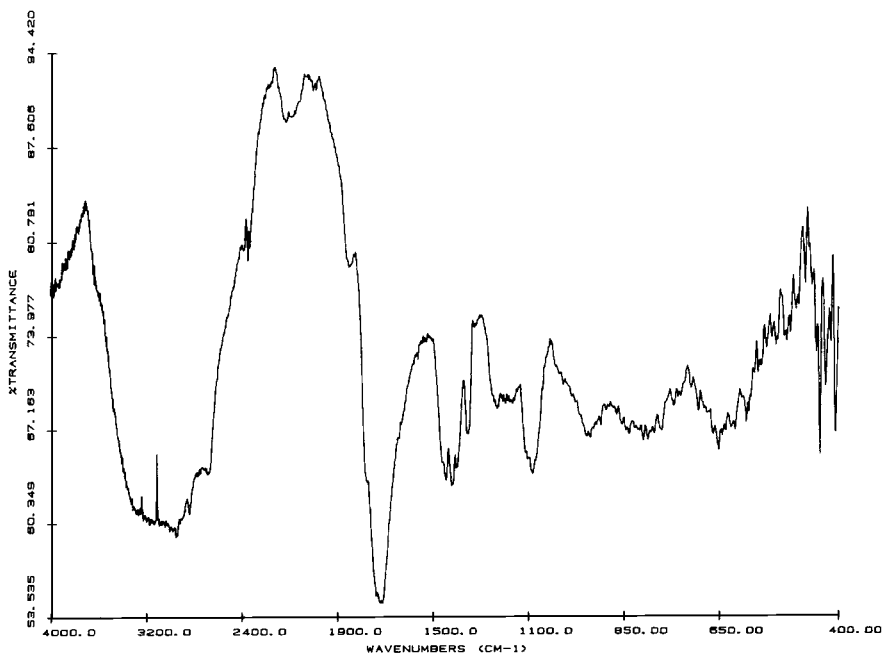


Fig. 2. FT-IR spectrum of PMVEMAC (S-97).

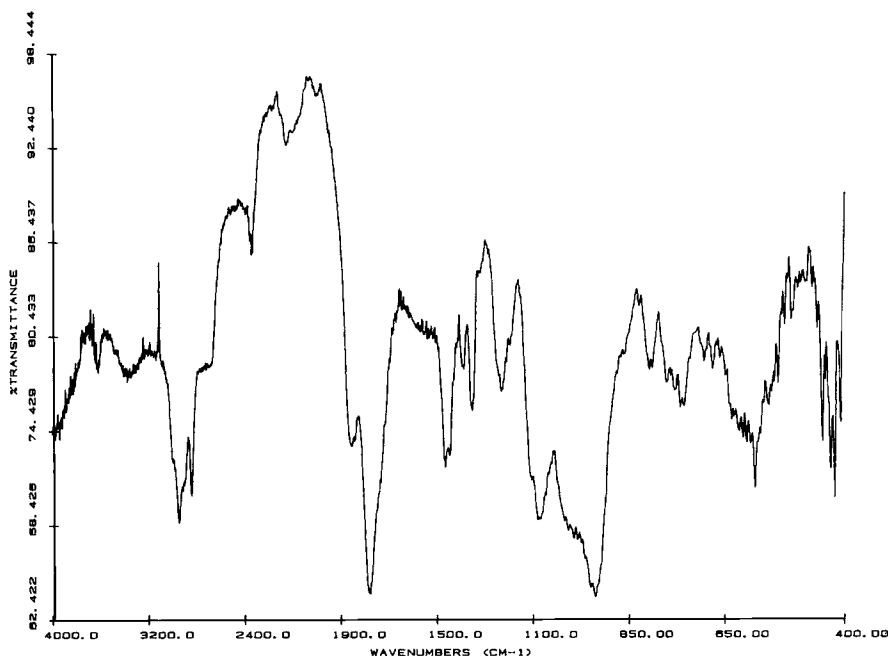


Fig. 3. FT-IR spectrum of PMVEMAC (S-97) which was held for 1 h at 185°C.

at 1712 and 1738 cm^{-1} in Figure 2 were virtually completely replaced by the succinic anhydride bands at 1780 and 1854 cm^{-1} in Figure 3. It should be pointed out that no other anhydride band is noticeable in this region, which may be indicative of the existence of isobutyric type anhydride structure (1743 and 1803 cm^{-1}).⁹ This indicates that PMVEMAC forms only the succinic anhydride structure by an intramolecular dehydration process. No intermolecular structure (isobutyric type anhydride) was formed. This is very different from the dehydration processes of poly(acrylic acid) and poly(methacrylic acid) where both inter- and intramolecular dehydrations occur.⁶⁻⁹

The progress of anhydride formation at 165°C by intramolecular reaction also can be followed by DSC analysis of a PMVEMAC sample which was heated to 165°C and held for 0, 1, 2, 5, and 30 min in the first heating. T_g 's, which were subsequently measured from the second heating, are listed in Table II. The results indicate that T_g continuously increased to 153°C after a 2-min time duration at 165°C and stayed constant at 153°C, which is the same as the T_g of the equivalent anhydride. Any intermolecular (crosslinking) anhydride structures formed during the dehydration process would cause the T_g to be much higher than the T_g of the linear polymer. The dehydration reaction is an endothermic reaction as evidenced by the endothermic peak between 150 and 200°C in the DSC curve of a PMVEMAC sample, which was held for 20 min at 85°C to remove free water in the first heating in Figure 4. This endothermic peak decreased as the dwell time increased at 165°C in the first heating. After 5 min dwell time this endothermic peak disappeared completely as shown in Figure 5.

TABLE II
Glass Transition Temperatures of PMVEMAC Samples with Different Dwell Time
at 165°C in the First Heating

Dwell time at 165°C in the first heating (min)	T_g from second heating (°C)
—	144 (PMVEMAC) from Table I
0	147
1	151
2	154
5	153
30	153

Kinetics of Dehydration of PMVEMAC

Information about the kinetics of dehydration of PMVEMAC can be obtained from the weight loss in the second stage of isothermal TGA runs performed at various different temperatures: 150, 155, 160, 165, 175, 185, and 200°C. A typical isothermal TGA curve at 175°C (second stage temperature) is shown in Figure 6. The starting reaction time ($t_0 = 61.04$ min) and initial weight ($Y_0 = 94.02\%$) were determined by linear extrapolation of the tangent of the maximum slope as indicated in Figure 7. The degrees of conversion (p) based upon the theoretical weight loss of 10.35% at 100% conversion can then be calculated and are shown in Table III for the 175°C run as a typical example.

A plot of $\ln[1/(1-p)]$ vs. time at each temperature yielded a set of initial straight lines, indicating first-order kinetics in the initial stage of the dehydration process as shown in Figure 8. This first-order kinetics confirms that the mechanism for dehydration of PMVEMAC is a simple intramolecular reaction.

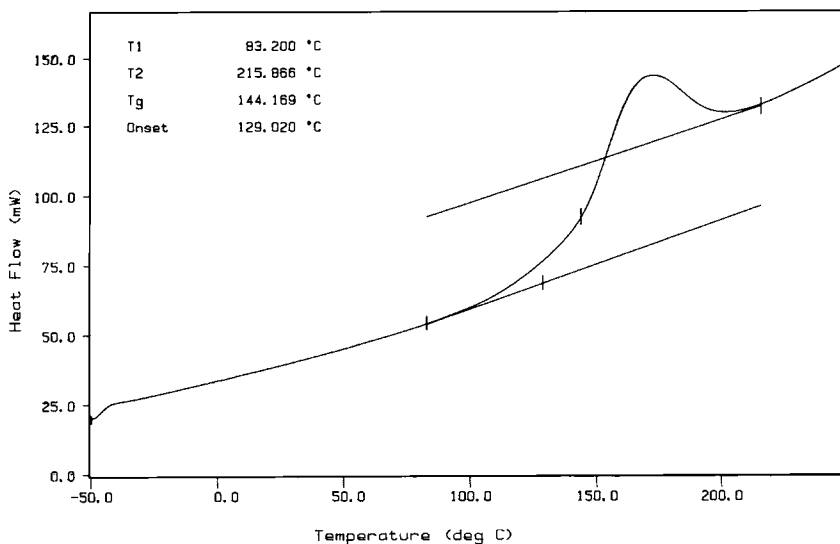


Fig. 4. DSC curve of PMVEMAC (S-97) sample which was held for 20 min at 85°C in the first heating.

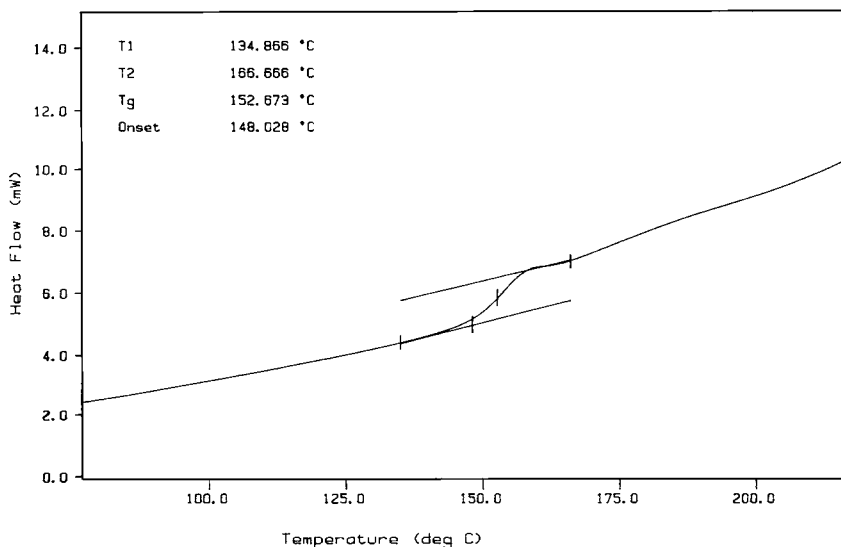


Fig. 5. DSC curve of PMVEMAC (S-97) sample which was held for 5 min at 165°C in the first heating.

At a later stage, deviation from linearity was noticed particularly for the high temperatures. The exact cause for the deviation is not known at this time. The formation of isobutyric anhydride type structure, which stiffens the chain to slow down the succinic anhydride formation, is possibly not the main cause for deviation. As indicated earlier, no isobutyric anhydride structure was noticed in IR spectra and DSC results. If the deviation is due to the interference of main chain degradation, then it should be in the increasing slope direction,

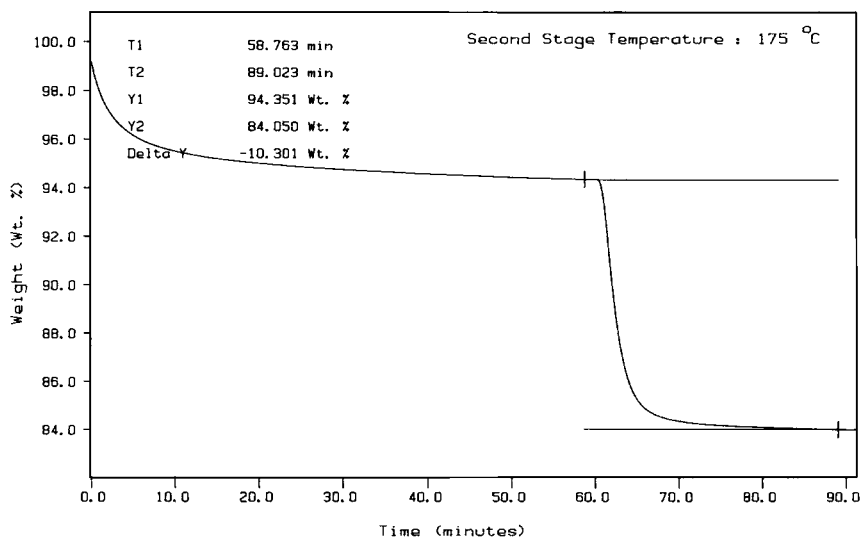


Fig. 6. Isothermal TGA curve for PMVEMAC (S-97) at 175°C second stage temperature.

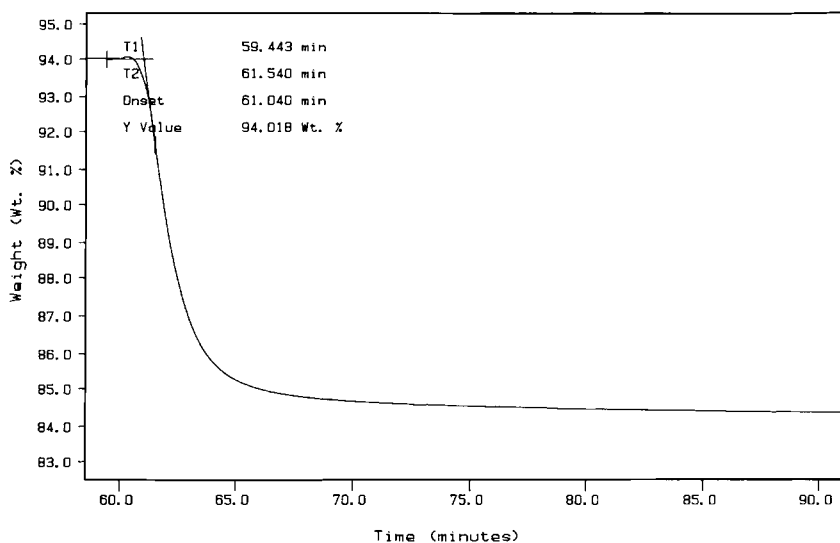


Fig. 7. Linear extrapolation to determine the initial time and weight for PMVEMAC (S-97).

which is contrary to the direction of the curves at high temperature in Figure 8. It is possible that this deviation is due to the slowdown in the diffusion of water (formed in the dehydration reaction) out of the polymer matrix. The rate of diffusion is proportional to the concentration gradient of water in the polymer matrix. At a later stage of the dehydration reaction, the rate of formation of water slows down which in turn slows down the diffusion process.

The rate constant K determined from the slope of the straight line in Figure 7 at each temperature can be used to calculate the activation energy of the first-order dehydration reaction according to the Arrhenius equation

$$k = Ae^{-E/RT}$$

where k = rate constant, A = frequency factor, E = activation energy (cal/mol⁻¹), R = gas constant (cal K⁻¹ mol⁻¹), and T = absolute temperature (K). The Arrhenius plot for the first-order dehydration reaction is shown in Figure 9. The activation energy calculated from the slope ($-E/R$) by linear regression is 18.8 kcal/mol. The correlation coefficient of linear regression is 0.997. The Arrhenius equation for this dehydration reaction can be simplified to $\ln k = 20.44 - 9.5 \times 10^3/T$. In contrast, the activation energy reported for the dehydration of poly(acrylic acid) is much higher at 26 kcal/mol⁷ for a first-order mechanism or 38 kcal/mol⁸ for a second-order mechanism. The formation of the five-member-ring succinic-type anhydride in PMVEMAC is a more favorable process than the formation of six-member-ring glutaric-type anhydride or the intermolecular isobutyric-type anhydride in poly(acrylic acid).

CONCLUSIONS

Three distinct peaks at 80, 175, and 325°C were identified in dynamic derivative TGA curves of PMVEMA and PMVEMAC and were attributed to free

TABLE III
Kinetics Data for Dehydration of PMVEMAC (S-97) at 175°C

Run time t	Reaction time $t - t_0$	Sample weight (%) Y	Weight loss (%) $Y_0 - Y$	Degree of conversion, $P = [(Y_0 - Y)/10.35] \times 100\%$	$1/(1 - p)$	$\ln 1/(1 - p)$
61.31	0.27	92.65	1.37	13.2	1.15	0.142
61.43	0.39	92.17	1.85	17.9	1.22	0.197
61.54	0.50	91.63	2.39	23.1	1.30	0.263
61.65	0.61	91.09	2.93	28.3	1.39	0.333
61.77	0.73	90.58	3.44	33.3	1.50	0.405
61.88	0.84	90.08	3.94	38.1	1.62	0.480
61.99	0.95	89.64	4.38	42.3	1.73	0.550
62.11	1.07	89.21	4.81	46.5	1.87	0.625
62.22	1.18	88.83	5.19	50.2	2.01	0.697
62.33	1.29	88.47	5.55	53.7	2.16	0.770
62.56	1.52	87.85	6.17	59.6	2.48	0.906
62.90	1.86	87.10	6.92	66.9	3.02	1.11
63.35	2.31	86.38	7.64	73.9	3.83	1.34
64.26	3.22	85.58	8.14	81.6	5.43	1.69
65.17	4.13	85.18	8.84	85.5	6.90	1.93
67.89	6.85	84.77	9.25	89.4	9.43	2.24
69.70	8.66	84.66	9.36	90.5	10.5	2.35
73.33	12.29	84.54	9.48	91.6	11.9	2.48
78.77	17.73	84.45	9.57	92.5	13.3	2.59
84.21	23.17	84.39	9.63	93.1	14.5	2.67

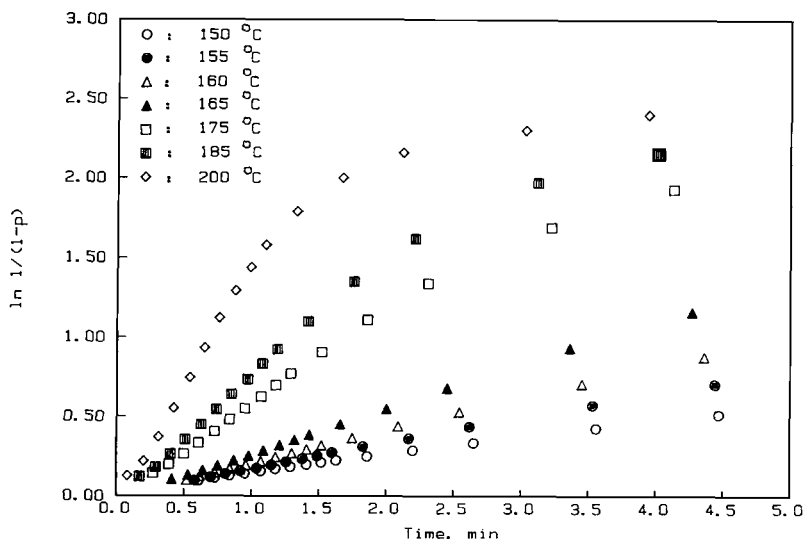


Fig. 8. First-order plot of dehydration reaction of PMVEMAC (S-97).

water removal, anhydride formation, and polymer degradation, respectively. The anhydride formation reaction was found to be an endothermic and first-order intramolecular reaction with an activation energy of 18.8 kcal/mol. This is different from the anhydride formation reactions of poly(acrylic acid) and poly(methacrylic acid). The glass transition temperature of PMVEMA was found to increase with molecular weight and levels off at 153°C. The glass transition temperature of PMVEMAC was found to be 144°C. The higher glass transition temperature of PMVEMA when compared to PMVEMAC is attrib-

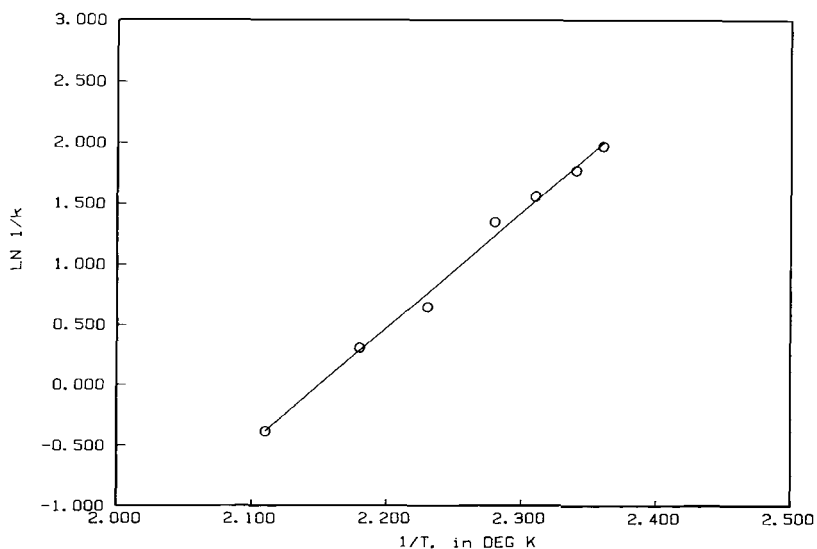


Fig. 9. Arrhenius plot for the first-order dehydration reaction of PMVEMAC (S-97).

uted to the increase in stiffness of the polymer chain resulting from the five-member-ring anhydride structure in PMVEMAC.

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