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Thermogravimetric Analysis of Vinyl Chloride/Acrylonitrile Copolymers

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ABSTRACT

The dehydrohalogenation of several alternating and random vinyl chloride/acrylonitrile copolymers was characterized by thermogravimetry. The polymers were made in solution, and the conversions were kept below 5% to insure uniform sequence distributions. Hydrogen chloride was generated within a relatively narrow temperature range somewhere between 200 and 300°C depending on the sequence distribution, relative viscosity, and composition. The weight-loss during the dehydrohalogenation could be attributed completely to the hydrogen chloride available in the copolymer. Alternating copolymers were significantly more stable than random copolymers at the same relative viscosity. For a given sequence distribution or composition, stability decreased with decreasing relative viscosity. The stability decreased as acrylonitrile content was increased from 23 to 57%.

The thermogravimetric analyzer was interfaced with a digital computer. The digitized data were smoothed and differentiated by convoluted integers. The differentiated data provided rates for a qualitative discussion of dehydrohalogenation kinetics.

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INTRODUCTION

Vinyl chloride/acrylonitrile copolymers are interesting candidates for studying dehydrohalogenation. They are easily polymerized. In contrast to the vinyl acetate unit in vinyl chloride/vinyl acetate copolymers, the acrylonitrile unit in vinyl chloride/acrylonitrile copolymers is not expected to generate volatile fragments at the temperatures where dehydrohalogenation occurs in polyvinyl chloride. If so, vinyl chloride/acrylonitrile copolymers would provide an opportunity to study dehydrohalogenation in different molecular environments (e.g., by changing sequence distribution) without interference from other volatile fragments. Alternating copolymers are known to have different mechanical properties than corresponding random copolymers [1, 2], so it is of interest to know how sequence distribution affects thermal stability.

EXPERIMENTAL

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An alternating copolymer of vinyl chloride/acrylonitrile (VCl/AN) was prepared using a 1:1 molar ratio of ethyl aluminum dichloride (EADC) to AN and a 15:1 molar ratio of VCl to AN. This mixture was polymerized in toluene at -78°C under N_2 atmosphere and yielded a polymer with an RV of 0.38 in acetone. N, C, and Cl analysis indicated the polymer (A-1) to be 47 mole % or 43 wt% AN. A higher molecular weight alternating copolymer of VCl/AN was prepared using a 1.2:1 molar ratio of EADC to AN and a 5:1 molar ratio of VCl to AN. This mixture was polymerized in toluene at -78°C under N_2 atmosphere and yielded a polymer with an RV of 1.10 in acetone.

Several random VCl/AN copolymers were prepared by azobisisobutyronitrile (AIBN) initiation in 2-butanone at 65°C. Reaction times and AIBN concentration were varied to obtain various molecular weights. Polymerization data on the alternating and random copolymers are listed in Table 1. All conversions were kept below 5% in order to insure that all polymers had uniform sequence distributions.

THERMAL STABILITY MEASUREMENTS

Thermal stability was determined by thermogravimetric analysis (TGA) or thermogravimetry using a Perkin-Elmer TGS-1 Thermobalance. The TGS-1 incorporates a Cahn electrobalance to measure the weight of a sample continuously as it is heated according to some selected thermal program. The sample is heated by a microfurnace that is calibrated with a set of magnetic metals which lose their magnetism at well-defined temperatures [3]. The magnetic metals are heated under the same conditions as the sample to obtain a set of corrections to the

TABLE 1. VCl/AN Copolymers Polymerization

No.	Polymerization technique	VCl (wt%) Feed	VCl (wt%) Copolymer	RV
A-1	EADC	97	57	0.38
A-2	EADC	86	55	1.10
R-1	AIBN	78	43	0.71
R-2	AIBN	90	57	0.38
R-3	AIBN	90	60	0.24
R-4	AIBN	96	74	0.30
R-6	AIBN	98	77	1.20

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temperature indicated on the programmer dial. The set of corrections is fitted by least squares polynomials to a quadratic expression to obtain the corrections at any other temperature.

Approximately 2 mg of polymer were cut from pellets which were compacted at room temperature. After purging the sample environment with nitrogen for 20 to 30 min, the sample was heated at 10°C/min in nitrogen.

The TGS-1 was interfaced to an 1130 IBM computer with a Perkin-Elmer ADS-VI Analytical Data System. The ADS-VI provides a digital record of the TGA data via a shaft encoder on a Leeds and Northrup Model "W" Potentiometric Recorder. The digital record provides the computer input which can be analyzed and replotted versus corrected temperature.

RESULTS AND DISCUSSION

Figure 1 shows a typical weight-loss curve of a vinyl chloride/acrylonitrile copolymer when heated in nitrogen at 10°C/min. The first step of the weight-loss curve represents dehydrohalogenation. The residue at the first plateau does not contain any chlorine. By assuming that the first step of the weight loss represents the quantitative generation of HCl and nothing else, the VCl content of the copolymer can be calculated from

$$\%\,\mathrm{VCl} = \%\,\mathrm{HCl} \times (62.5/36.5) \qquad (1)$$

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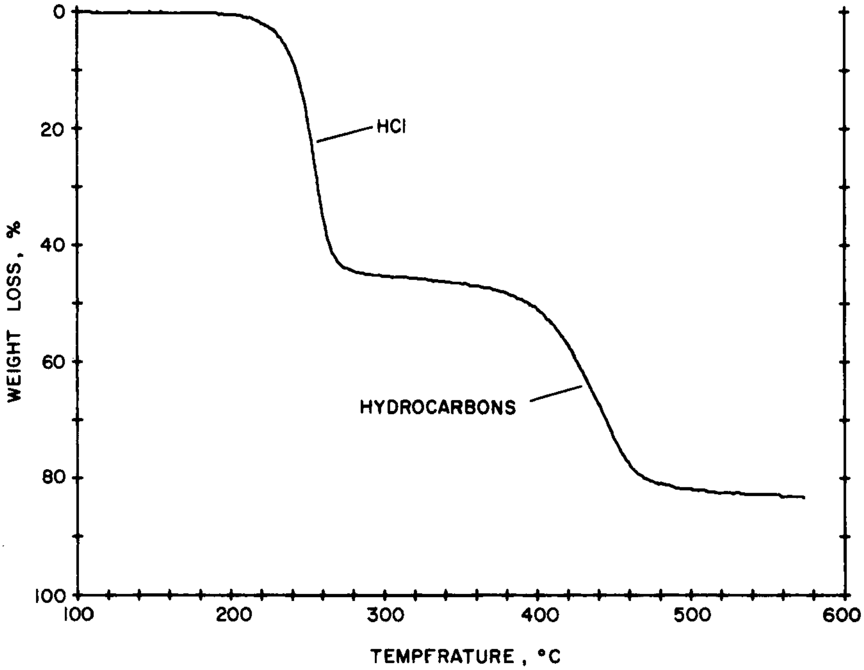

FIG. 1. Weight-loss of typical vinyl chloride/acrylonitrile copolymer heated at 10° C/min in nitrogen.

TABLE 2. VCl Content of VCl/AN Copolymers by TGA

		VCl (wt%)	
Sample	TGA	Cl	C
A-1	56.3	57.1	56.6
A-2	50.5	53.9	55.9
R-1	39.0	41.1	42.8
R-2	54.6	56.0	57.3
R-3	56.2	55.9	59.6
R-4	76.4	76.1	73.7
R-6	78.8	79.3	77.1

Table 2 compares the results of determining the vinyl chloride content from Eq. (1) with the results of chlorine or carbon analysis. With the exception of A-2, the agreement between the TGA results and chlorine analysis is at least as good as the agreement between chlorine analysis and carbon analysis. Therefore, the weight loss in the first step can be completely accounted for by the HCl available in the copolymer. This behavior differs from that of polyvinyl chloride which generates benzene during dehydrohalogenation [4].

The weight-loss data of a random copolymer and an alternating copolymer of the same relative viscosity are compared in Fig. 2. These two copolymers also have approximately the same composition, which is nearly 1 to 1 on a molar basis. The alternating copolymer is considerably more stable than the random copolymer, since it loses weight rapidly about 40° higher than the random copolymer. The improved thermal stability of alternating over random VCl/AN copolymers was briefly noted by Furukawa et al. [5] but no additional data were presented.

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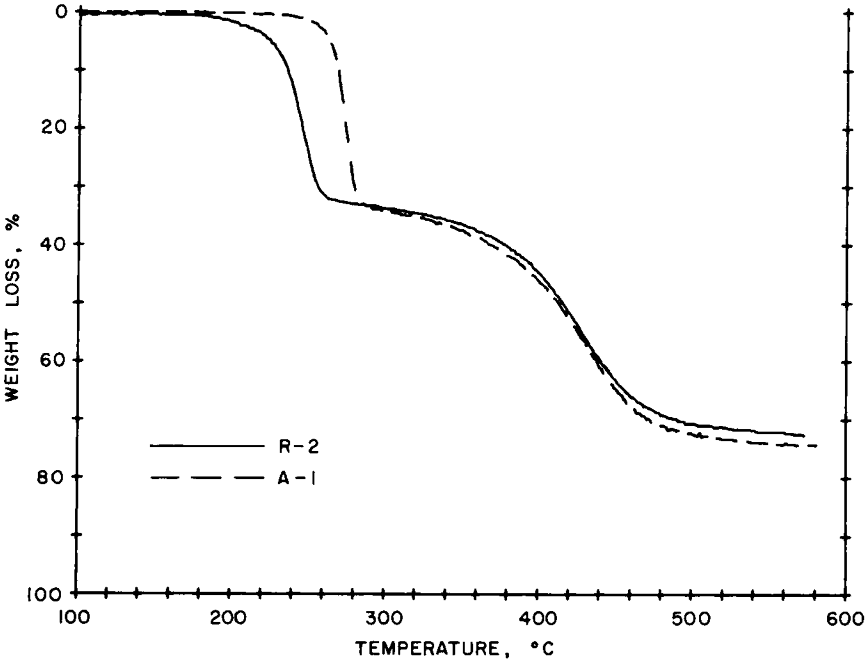

FIG. 2. Effect of sequence distribution on weight-loss of vinyl chloride acrylonitrile copolymers.

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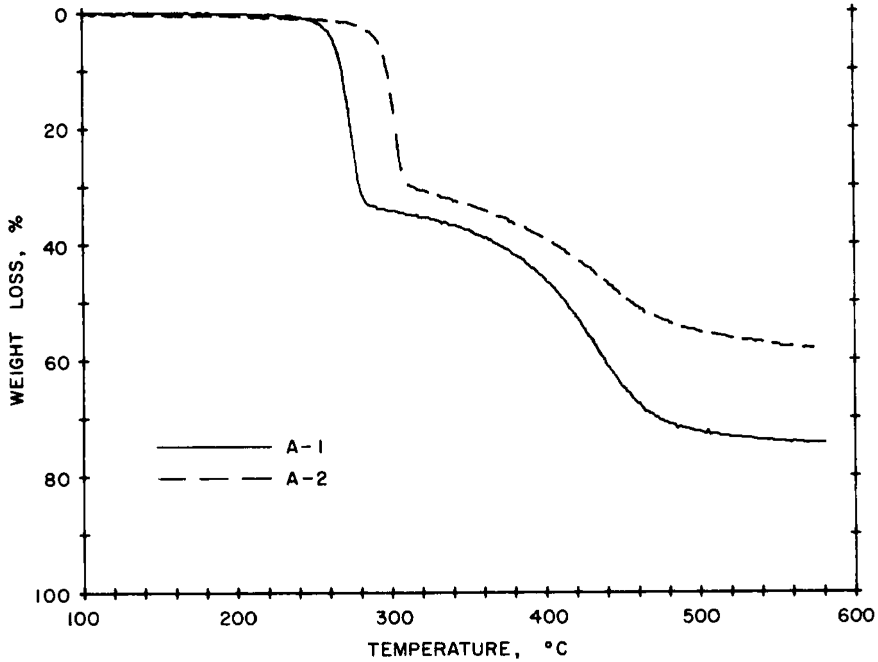

FIG. 3. Effect of relative viscosity on weight-loss of alternating vinyl chloride acrylonitrile copolymers.

The random and alternating copolymers have different sequence distributions. The alternating copolymer should not have any VCl-VCl or AN-AN dyads and, therefore, cannot form allyl chlorides or cyclic nitriles. Copolymer R-2 is a random copolymer and has a predicted sequence distribution [6] of 22% VCl-VCl, 10% AN-AN, and 68% VCl-AN. Films of A-1 and R-2 pressed at the same temperature show A-1 to be colorless and clear while R-2 is yellow-brown.

Figure 3 illustrates the effect of relative viscosity on the stability of the alternating copolymers. The evolution of HCl was delayed about 30° by increasing the relative viscosity from 0.38 to 1.1. The effect of relative viscosity on stability was also observed for random copolymers. Therefore, molecular weight and/or molecular weight distribution also affect the dehydrohalogenation, which suggests that initiation might occur at end groups. A similar effect has been reported for polyvinyl chloride [7].

Based on the chlorine and carbon analysis, A-1 and A-2 have more nearly the same composition than what is suggested by the weight loss in

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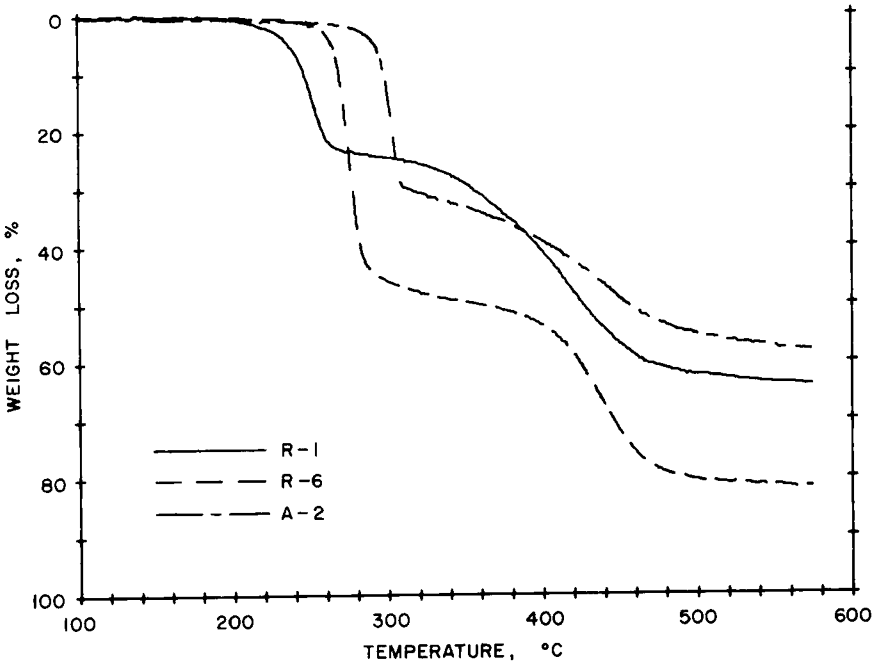

FIG. 4. Effect of composition on weight-loss of vinyl chloride/acrylonitrile copolymers.

the first step. Recall that A-2 was the exception to the otherwise good agreement among the three methods for determining vinyl chloride content. There are evidently some VCl units in A-2 from which HCl is not eliminated.

Figure 4 illustrates the effect of composition on dehydrohalogenation. The thermal stability of the random copolymer having 57% AN (R-1) was less than that of the copolymer having 23% AN (R-6). That is, between 23 and 57% AN, the thermal stability of random copolymers decreases as the amount of AN increases. However, the deleterious effect of the AN units can be circumvented if they alternate with VCl units (A-2).

The weight-loss of A-2 and R-6 is compared with that of a polyvinyl chloride suspension resin (0.85RV) in Fig. 5. Based on this comparison the alternating copolymer is probably at least as stable as PVC, and perhaps more stable, depending on how much the stability of PVC is affected by relative viscosity.

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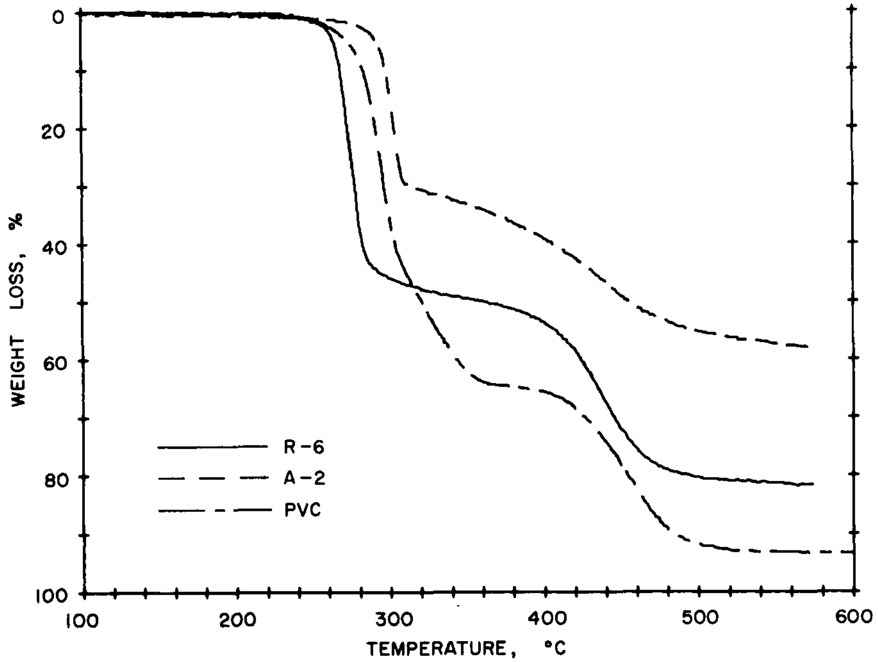

FIG. 5. Weight-loss of vinyl chloride/acrylonitrile copolymers compared to weight-loss of polyvinyl chloride.

KINETICS

The rate of weight loss is plotted versus temperature for the random (R-2) and alternating (A-1) copolymers of 0.38 RV in Fig. 6. The rate of weight loss was calculated at each point by using convoluted integers [8]. The use of convoluted integers is equivalent to smoothing and differentiating by least squares polynomials. For the rates in Fig. 6, 9-point quadratic convoluted integers were used. That is, each rate is equivalent to fitting a quadratic expression through 9 points (4 points on each side of the point of interest) and evaluating the derivative of the quadratic expression at that point.

The maximum rate of weight loss is lower and the decomposition is distributed over a broader temperature range for the random copolymer than for the alternating copolymer. The difference in the shape of the weight-loss curve suggests that the mechanism of dehydrohalogenation is different in the random than in the alternating copolymer. As might be expected from the differences in sequence distribution, the relative contributions of initiation and propagation to the weight loss are probably different in the two copolymers.

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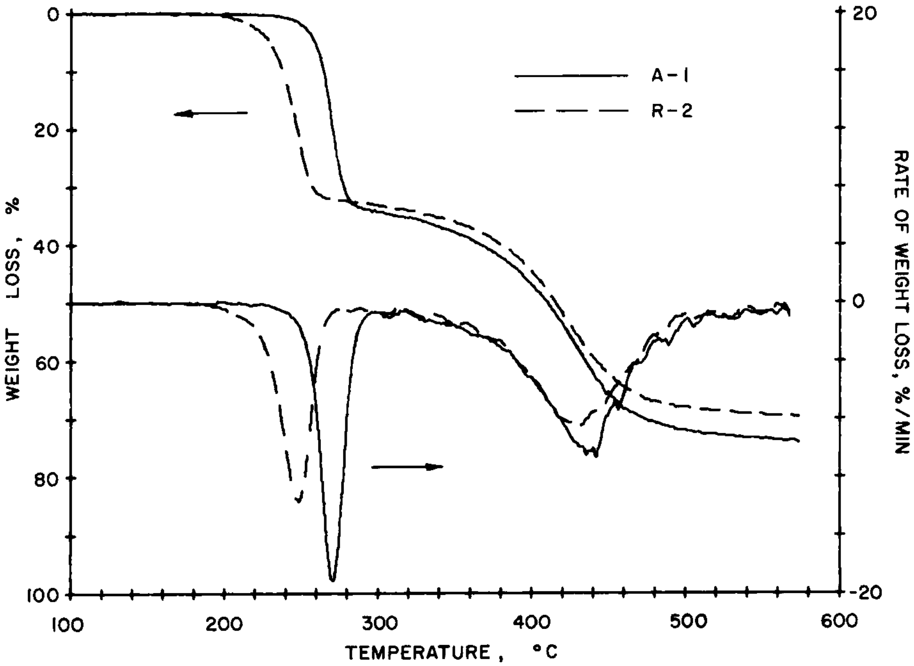

FIG. 6. Rate of weight-loss vs temperature for random (R-2) and alternating (A-1) vinyl chloride/acrylonitrile copolymers.

Figure 7 illustrates that the maximum rate occurs at a lower conversion for the alternating copolymer than for the random copolymer. The conversion was calculated as the ratio of the weight loss at each temperature to the total weight loss attributable to generation of HCl. Assuming that the weight-loss can be described by

$$dW/dt = (dW/dT)r = Ze^{-E/RT}W^n \tag{2}$$

Flynn and Wall [9] found that the maximum rate shifts toward lower conversion as the reaction order, n, increases. Therefore the results in Fig. 7 suggest that the order of the reaction is higher for the alternating copolymer than for the random copolymer. That is, the concentration of some reactant controls the decomposition of the alternating copolymer more strongly than that of the random copolymer. For example, the elimination of HCl might be expected

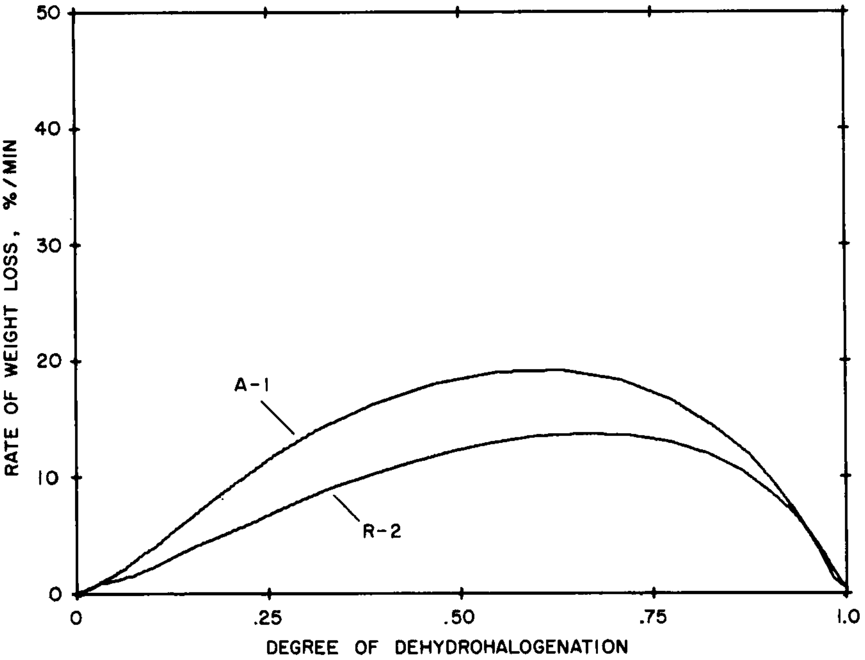

FIG. 7. Rate of weight-loss vs degree of dehydrohalogenation for R-2 and A-1.

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to be controlled by the concentration of initiation sites in the alternating copolymer because propagation cannot occur along runs of VCl units.

Figure 8 compares the rates of weight loss calculated from the dynamic data with the rates of weight loss measured at constant temperature near the threshold of weight loss for R-2 and A-1. Even after smoothing the dynamic data to 25 points, there is still considerable scatter in the data at low conversion, so that the dynamic rates and isothermal rates are only approximately in agreement. This illustrates the difficulty in using dynamic data for kinetic studies at low conversions. For the isothermal rates included in Fig. 8, the rates were constant for at least 30 min. Based on the isothermal data, the activation energy which could be calculated from Eq. (2) would be approximately the same for the two copolymers, but the frequency factor would be considerably less for the alternating copolymer than for the random copolymers.

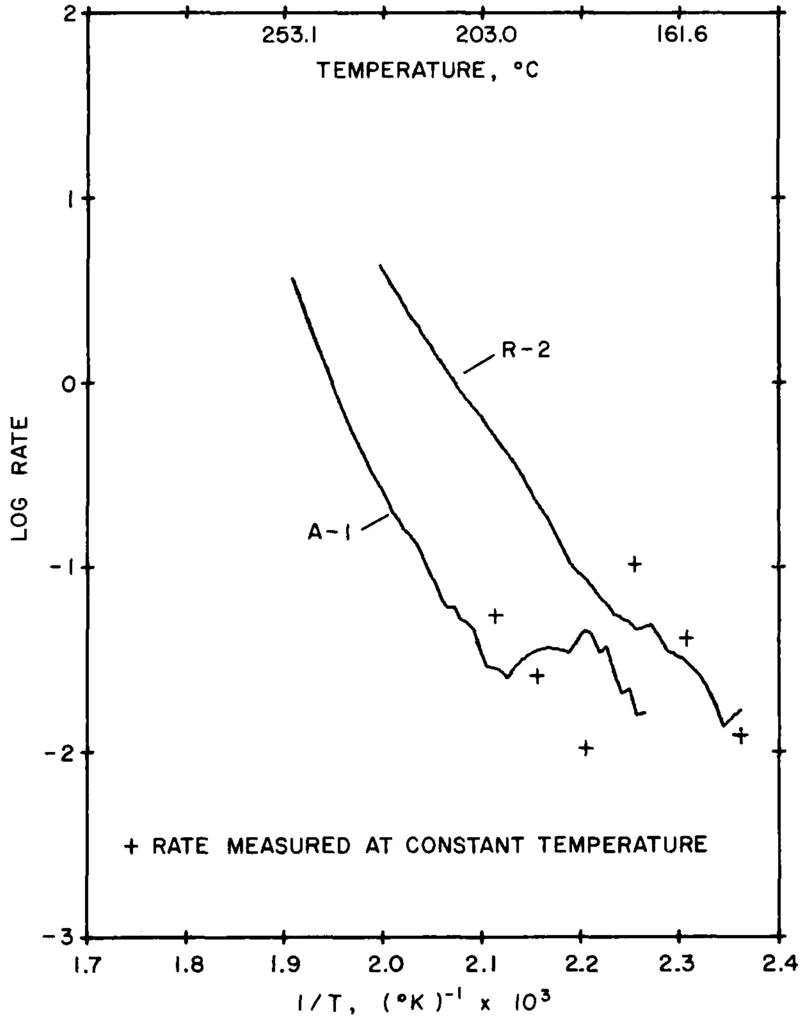

FIG. 8. Logarithm of rate of weight-loss vs reciprocal of absolute temperature for R-2 and A-1.

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