

THERMAL DEGRADATION OF LEVAN *

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ABSTRACT

The thermal degradation of the polysaccharide Levan, of various molecular weights, was studied by means of isothermal and dynamic TG, X-ray diffraction, and IR measurements. From dynamic TG traces, two main degradation stages were observed for HL-Levans (hydrolyzed) whereas, three such stages were observed for UL-Levans (unhydrolyzed). These stages were correlated with branching effects, an interpenetrating network, and ring-fragmentation and other reactions in the late stages of the thermal degradation which result in the formation of infusible material that chars on further heating. Isothermal curves obtained for the first stage indicated the possibility of a random type of thermal degradation. Anticipated linear plots were obtained, using expressions from random degradation theory, which added further support for this type of degradation for Levan (stage 1). Various parameters were obtained for the thermal degradation of Levan, e.g., activation energies, and various experimental observations have been correlated in terms of postulated microstructures for Levan and in terms of parameters such as entropy of activation.

INTRODUCTION

Levan is a polysaccharide composed of *D*-fructofuranose units joined by β -2, 6' bonds [1,2]. It is produced in plants [3] and by bacteria that are capable of synthesizing polysaccharides from sucrose or fructose [4,5]. The polyfructoses of plants are generally oligomers with molecular weights below 10 000, whereas bacterial Levans are polymers with molecular weights in the millions [6]. The Levans of interest in this work are of bacterial origin and are branched through β -2, 1' bonds (see Fig. 1). The Levans produced from bacteria in dental plaque have been implicated in dental caries formation and periodontal diseases [7,8]. In this work, the Levans employed were produced by *Streptococcus salivarius*. Recently, Stivala et al. [9–11] investigated the kinetics of the acid hydrolysis of *S. salivarius* Levans under varying conditions of temperature, pH, and Levan concentration. Also, solution properties of fractions of partially hydrolyzed *S. salivarius* Levans were examined. The purpose of this paper is to investigate the thermal degradation of Levan.

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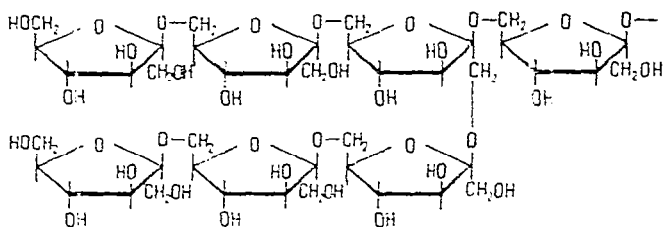


Fig. 1. Structure of Levan.

EXPERIMENTAL

Starting materials

The Levan samples used in this study were the same as those used previously [11,12]. In the following are listed in order, the sample number used in this study, the corresponding sample number used in other papers, and the weight-average molecular weight ($\times 10^{-4}$) of the sample (HL designated hydrolyzed Levan samples while UL designated unhydrolyzed samples): HL-1, E5, 1.81; HL-2, E6, 2.13; HL-3, E7, 2.73; HL-4, F5, 342; UL-12, F12, 1850; UL-14, F14, 2000; UL-18, F18, 2970; UL-19, F19, 3250. (Designations E5, E6, E7, and F5 are mentioned in ref. 11 while F12, F14, F18, and F19 are mentioned in ref. 12.)

Apparatus

A DuPont TGA-950 thermobalance was employed for both dynamic and isothermal TG measurements while a Perkin-Elmer DSC-1B differential scanning calorimeter was used for DSC measurements and for collecting liquid condensates of products of Levan degradation on a sodium chloride disk.

Wide angle X-ray diffractograms of Levan samples were obtained by means of a General Electric XRD-5 diffractometer, equipped with a proportional counter. The X-ray source was a GE evacuated tube with a Cu-target. The diffractograms were used to ascertain peak sharpness (a measure of orientation) of Levan samples of different molecular weights. Powder patterns were recorded with a counter detector as a function of diffraction angle.

Infrared spectral measurements of liquid condensates of degraded products were carried out by means of a Nicolet 7199 Fourier transform IR spectrophotometer.

Procedure

Isothermal TG measurements were carried out on dried Levan samples of about 5 mg at atmospheric pressure using nitrogen at a flow rate of about 25 cc min^{-1} . Rate of weight loss was determined by numerical differentiation of the weight-loss curve according to the forward Gregory-Newton

method. These rate data were used in the following expression for random degradation [13]

$$R_t = 2k(C^{1/2} - C) \quad (1)$$

where, $R_t \equiv dC/dt$; C = conversion; and k = rate constant for bond breakage. In this manner, values of k were estimated for various Levan samples. It should be noted here that eqn. (1) is a special case of random degradation, i.e., it applies when the minimum chain length of non-volatile material (NVM) is 2 ($L = 2$). Further, R_t and C were corrected for non-volatile residue.

Dynamic TG measurements were carried out on dried Levan samples using a flow rate of nitrogen of about 25 cc min⁻¹ and samples of about 5 mg. In order to estimate activation energy (E), irrespective of mechanism, four different heating rates were used: 1.25, 2.5, 5.0, 10.0 and/or 20.0°C min⁻¹. The following expression was used [13–15]

$$\frac{-d \log(\text{RH})}{d(1/T)} = \frac{0.457E}{R} \quad (2)$$

where, RH = rate of heating; and R = gas constant. From eqn. (2), a plot of $\log(\text{RH})$ vs. $1/T$ (at a constant conversion and for several heating rates) should yield a linear relationship whose slope affords the value of E . (The value of E/RT should lie in the range 20–60.) Further, the following random degradation equations were employed to estimate the values of L and E , using a computer [13]

$$\frac{(1 - C)}{1 - \alpha(L - 1)} = (1 - \alpha)^{L-1} \quad (3)$$

$$R_T \equiv \frac{dC}{dT} = A'(L - 1)[(1 - C) - (1 - \alpha)^L] e^{-E/RT} \quad (4)$$

and

$$\ln \left\{ \frac{R_{T,1}[(1 - C) - (1 - \alpha)^L]_2}{R_{T,2}[(1 - C) - (1 - \alpha)^L]_1} \right\} = -\frac{E}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (5)$$

where, α = fraction of bonds broken in original polymer chain at any particular time; A = frequency factor; and $A' = A/(\text{RH})$. Equations (3)–(5) are valid for random degradation when the degree of polymerization of the original chain is much greater than L . Values of L and E were estimated as follows. From TG traces, T and corresponding values of C and R_T were determined. Then, for various values of C and assumed values of L (1, 2, ...), values of α were determined from eqn. (3) by means of a computer (using an iteration procedure). Thus, for any particular value of L , corresponding values of C , α , T , and R_T for various sets of data could be estimated. Then a plot of the left-hand side of eqn. (5) vs. $1/T$ was carried out to afford values of E/R and intercept, determined by a least-squares treatment. Those values of L and E/R were found acceptable when the corresponding value of intercept was closer to zero than intercepts determined using other L and E/R values and when the E/R values were in reasonable agreement with similar values estimated from eqn. (2).

RESULTS AND DISCUSSION

From TG traces of Levans HL-1, HL-3, UL-12, and UL-19, there appears to be two degradation stages for the HLs and three for the ULs. For the HLs there are relatively smooth TG traces until about 40–50% weight loss, after which a relatively slow weight loss occurs. For the ULs, there are relatively smooth TG traces up to about 30% weight loss, after which a slower rate of weight loss occurs and after about 50% weight loss an even slower weight-loss rate sets in. This paper is concerned mainly with the first stage of degradation for the various Levans studied.

Recently [10,11,16], solution properties of Levan have been examined. Thus, a log–log plot of intrinsic viscosity vs. weight-average molecular weight (M_w) indicated that the Mark–Houwink coefficient (MHC) was about 0.15 for M_w above about 6×10^6 , whereas $MHC = 0.49$ below about 6×10^6 . This suggested that a spherically branched structure is maintained down to $M_w = 6 \times 10^6$ (the UL-Levans) whereas, below this value, the Levan structure is hydrodynamically approaching a random coil (the HL-Levans). When UL-Levans are precipitated from solution, the solid is now presumed to consist of a relatively disoriented, interpenetrating network from which protrude relatively long branches. In contrast, the HL-Levans precipitate from solution to form a rather disoriented, interpenetrating network consisting primarily of random coils with short, if any, branches. Such structures can explain many of the observations noted during the thermal degradation of Levan. Thus, in regard to TG traces, the relatively uniform network of the HL-Levans allows for a relatively uniform rate of weight-loss via a random degradation mechanism. Then, due to ring fragmentation and other reactions (stage 2), a relatively infusible residue results which degrades very slowly and chars upon further heating. In the case of the UL-Levans, the branch points are presumed to break relatively easily [$\beta(2 \rightarrow 1')$ bonding is involved as compared with $\beta(2 \rightarrow 6')$ bonding for the main chain]. Thus, weight loss for the ULs is visualized as occurring mainly by breakage of branch points and subsequent breakdown (via a random method) of these branch-chains. After much of the branches have thermally degraded, the more thermally-resistant interpenetrating network causes a slower weight loss to ensue. Finally, as for HLs, ring fragmentation and other reactions result in the formation of a relatively infusible residue which degrades slowly and chars upon further heating.

In Figs. 2 and 3 are depicted isothermal (205°C) studies of rate of weight loss vs. conversion for various Levan samples. These values are not corrected for non-volatile material (NVM) after stage 1. Upon correction (using extrapolated values from the various curves), the following approximate conversions (%) were obtained at the maximum rate for the corresponding Levan samples: 34, HL-1; 29, HL-2; HL-3; 27, HL-4; 29, UL-12, 32, UL-14; 31, UL-18; 34, UL-19. For purely random degradation, the theoretical value of conversion at the maximum rate should be about 26–27%. Aside from HL-3, the values for the other Levans are in reasonably good agreement with the theoretical values. Further, theoretical curves for random degradation (rate vs. conversion) generally rise rapidly and, after attaining a maximum rate,

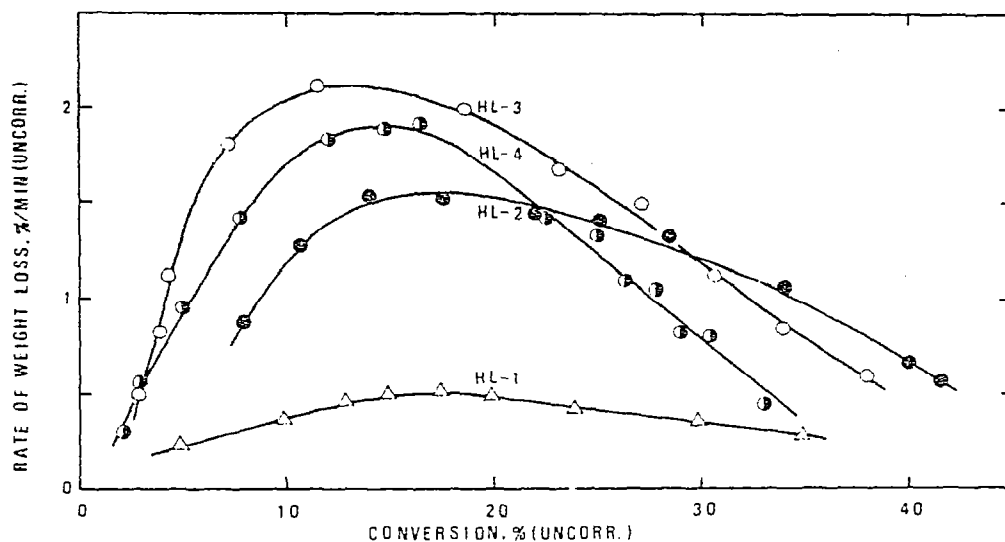


Fig. 2. Rate of weight loss vs. conversion for HL-Levans at 205°C.

they generally gradually decrease to a zero rate. At low values of L , this decrease may resemble a linear decrease in rate. Because of the preceding, it was postulated that the Levan samples tested undergo random thermal degradation to a large extent during stage 1. Further evidence for the postulation is presented in the following.

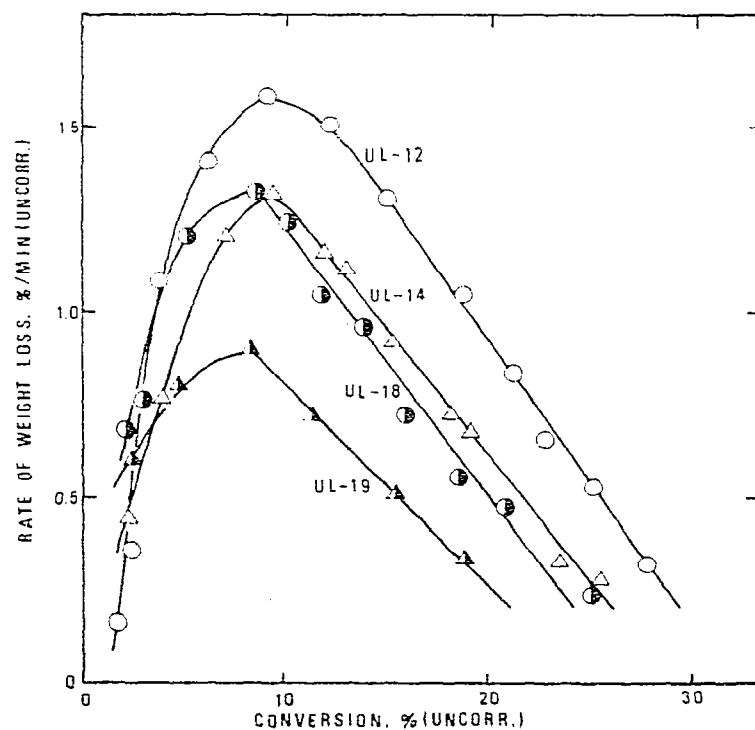


Fig. 3. Rate of weight loss vs. conversion for UL-Levans at 205°C.

As mentioned in the Procedure, values of L and E/R can be determined from eqns. (3)–(5) using a computer. Thus, using TG data for HL-1 (correcting for NVM and using a temperature range of 220–245°C), the following values of L , intercept, and E/R (kcal mole⁻¹) were obtained, respectively: 2, -0.124, 22.3; 3, -0.129, 21.2; 4, -0.130, 20.8; 5, -0.131, 20.7. Values of L up to 10 showed similar gradations for values of intercept and E/R , i.e., the absolute value of intercept increased and E/R decreased. Thus, the value of intercept closest to zero corresponded to $L = 2$ and $E/R = 22.3$. In Fig. 4 can be seen a plot of eqn. (2) for Levan sample HL-1. Aside from the 5% conversion, the other conversions from 10–40% afforded a value of E/R of about 22.1 kcal mole⁻¹, which is in excellent agreement with the value of E/R obtained previously for $L = 2$. Another Levan sample, chosen at random, HL-3, afforded the following values of L , intercept, and E/R (kcal mole⁻¹) (after correction for NVM and over a temperature range of 245–268°C): 2, -0.0470, 14.0; 3, -0.0484, 12.8; 4, -0.0488, 12.5; 5, -0.0490, 12.4. Thus, the favorable values are $L = 2$ and $E/R = 14.0$. In Fig. 5 is depicted a plot of eqn. (2) for HL-3. Over a conversion of 10–30%, $E/R = 14.2$ kcal mole⁻¹, which is in excellent agreement with $E/R = 14.0$ and the corresponding value of $L = 2$. Thus, in the two samples of Levan tested, there is good agreement with E/R -values obtained from random degradation

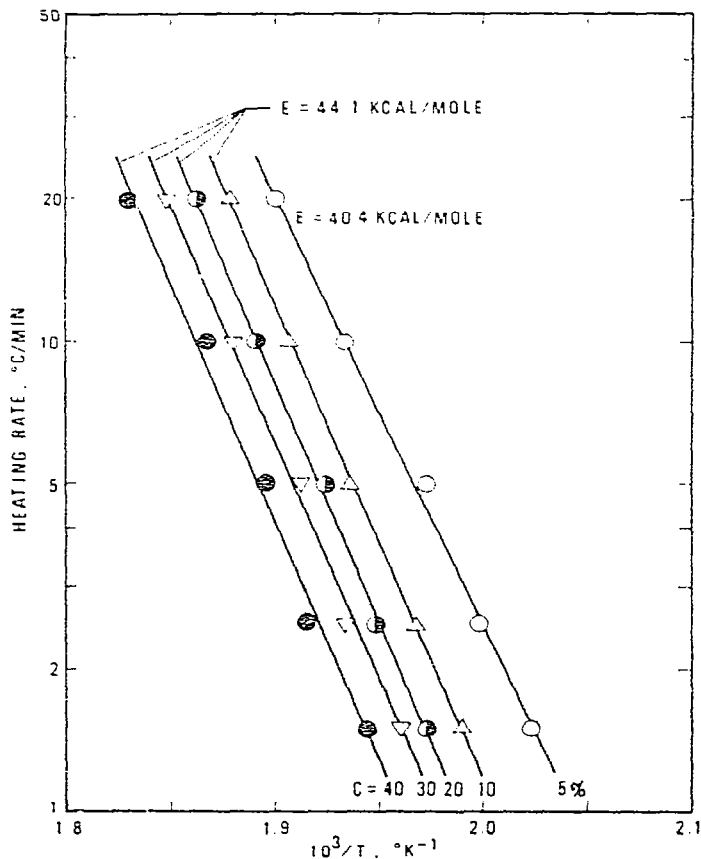


Fig. 4. Log of heating rate vs. $1/T$ for HL-1 Levans.

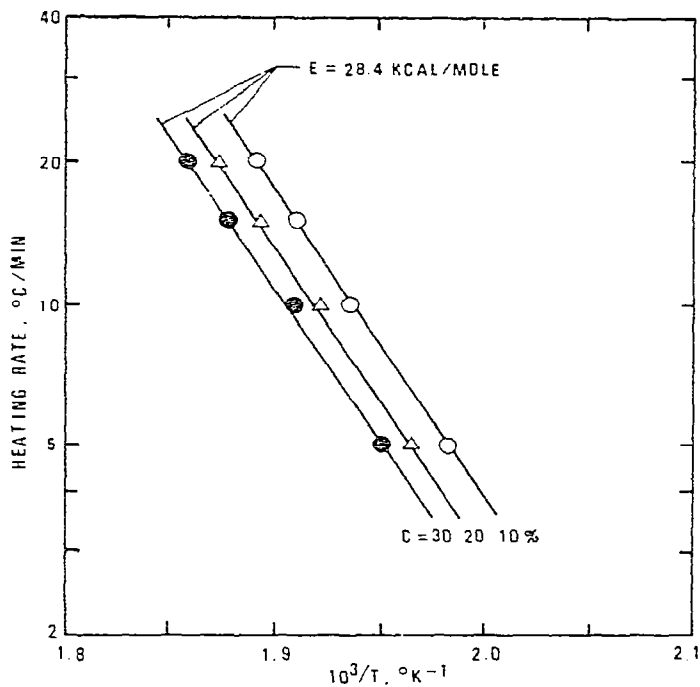


Fig. 5. Log of heating rate vs. $1/T$ for HL-3 Levans.

theory and from eqn. (2), which is independent of mechanism.

When $L = 2$, it can be shown [13] that eqn. (1) is valid for random thermal degradation. In Fig. 6 are depicted typical plots of R_t vs. $C^{1/2} - C$ (corrected for NVM) for three Levan samples, HL-1, HL-4, and UL-19. In

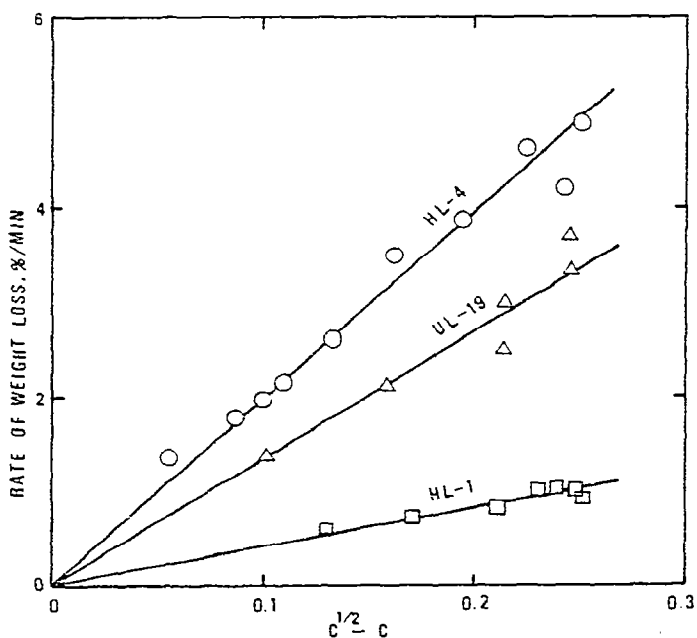


Fig. 6. Rate of weight loss vs. $C^{1/2} - C$ for various Levans.

these plots, the initial points were usually neglected since during an isothermal TGA run, the initial points will probably not have attained thermal equilibrium conditions. Further, from such plots, values of k could be estimated at the isothermal temperature used, i.e., 478 K. Then values of frequency factor could be calculated from

$$A = k/e^{-E/RT} \quad (6)$$

and values of entropy of activation, S^* , from

$$S^* = R \left[\ln \frac{ANh}{RT} - 1 \right] \quad (7)$$

where, N = Avogadro's constant; and h = Planck's constant. In this manner, Table 1 was constructed, in part. These tabulated values will be utilized in attempts to explain other experimental observations to be noted subsequently.

The value of $L = 2$ indicates that the main volatile product from random thermal degradation of Levan should be fructose. However, under the experimental conditions employed, fructose itself degrades further. Thus, we should anticipate at best, volatile condensates of Levan which should be similar in structure to volatile condensates from fructose itself. In Fig. 7 are shown IR spectra of the liquid condensates of both fructose and HL-4 volatile products. From Fig. 7, it can be seen that the IR spectra of condensates from both materials are very similar. On standing for about 1 week in a desiccator, several absorption peaks of the Levan liquid condensate disappeared. This indicates the presence of relatively low molecular weight material in the condensate, which would be anticipated if the fructose moiety itself degraded prior to or during volatilization.

In Fig. 8 (cf. Table 1), it can be observed that as we proceed from HL-1 to HL-3, the value of E decreases from 44 to about 28 kcal mole⁻¹. From HL-3 to UL-19, E remains approximately constant, 28–33 kcal mole⁻¹. In light of what has been mentioned previously in regard to Levan microstructure, such behavior may be explained as follows. Levans HL-1 to HL-4 possess values of M_w below 6×10^6 ; UL-12 to UL-19 possess values above 6×10^6 .

TABLE 1

Summary of various parameters for various Levans

Levan	k (min ⁻¹) at 205°C	E (kcal mole ⁻¹)	A (min ⁻¹)	S^* (cal deg ⁻¹ mole ⁻¹)
HL-1	0.020	44	2×10^{18}	+15
HL-2	0.064	37	4×10^{15}	+2
HL-3	0.14	28.5	1×10^{12}	-14
HL-4	0.093	31	1×10^{13}	-9
UL-12	0.095	32.5	6×10^{13}	-6
UL-14	0.082			
UL-18	0.090			
UL-19	0.070	33	7×10^{13}	-6

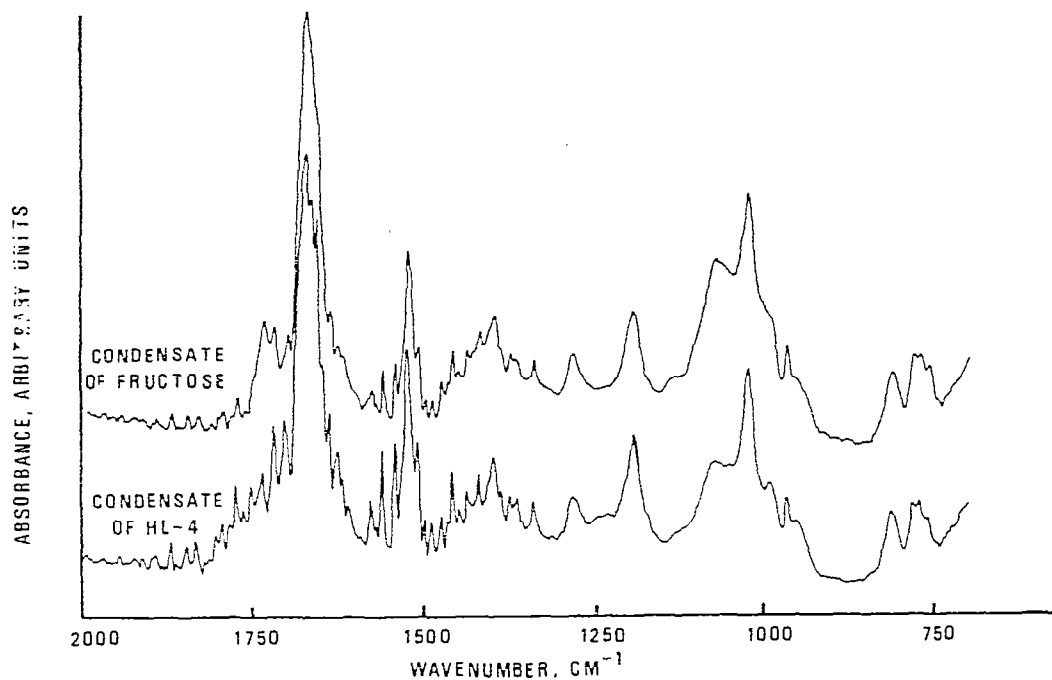


Fig. 7. FT-IR absorbance vs. wave number for condensates of fructose and HL-4.

Further, noting the positive S^* -values for HL-1 and HL-2, we can postulate an interpenetrating and disoriented network for these Levans, which restricts rotational and/or vibrational degrees of freedom. Thus, in order to degrade such Levans, higher E -values and positive S^* -values would be anticipated. Bond breakage would presumably involve $\beta(2 \rightarrow 6')$ bonds. As the molecular

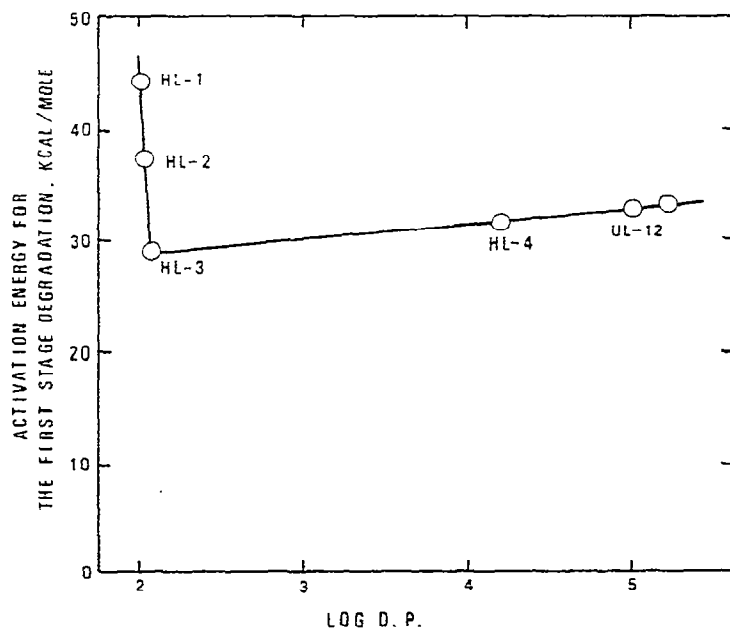


Fig. 8. Activation energy vs. degree of polymerization (DP) for various Levans.

weight increases, branching effects increase (UL-Levans) and it is assumed that a more oriented (S^* becomes negative) less densely packed network results for HL-3 to HL-4 so that the E -values for these HLs are similar and lower than for HL-1 and HL-2. In the case of the ULs, branches can align to an extent causing negative S^* -values. Further, branch points [$\beta(2 \rightarrow 1')$ bonds] are presumed to break initially and the resulting chains then degrade preferentially (via a random method) so that lower E -values, 29–33 kcal mole⁻¹, than for HL-1 and HL-2 result. Also, as more and more branches degrade, e.g., as in the case of UL-19, the remaining relatively refractory network should resist further degradation. Thus, for UL-19, E -values should begin to increase after a certain conversion, as depicted in Fig. 9. For HL-1, the relatively uniform refractory network initially present degrades slowly and rather uniformly so that little change in E -value should be expected with conversion (cf. Fig. 9). For HL-3, a more oriented “looser” network is initially present which degrades rather uniformly so that E -values also do not change much as conversion increases.

In Fig. 10 is depicted a plot of peak sharpness (PS), from X-ray diffractograms, vs. degree of polymerization (DP) for several Levans. (Values of PS were estimated as shown in Fig. 11.) As DP increases, PS increases from HL-1 to HL-3, remains nearly constant for HL-3 and HL-4, rises sharply for UL-12 and then decreases for UL-19. The disoriented, interpenetrating network of random coils assumed for HL-1 and HL-2 can explain the low PS-value for HL-1. As DP increases further, a more oriented, less interpenetrating network obtains for HL-3 and HL-4, thereby causing a larger value of PS for these HLs than for HL-1. The UL-Levans are more highly branched (and therefore oriented) than the HL-Levans so that the former should possess larger values of PS, as observed. The larger value of PS for UL-12 than for UL-19 is attributed to a greater degree of symmetrical branching for UL-12. As branches degrade more and more, e.g., as for UL-19, a relatively disoriented, interpenetrating network remains so that PS should decrease

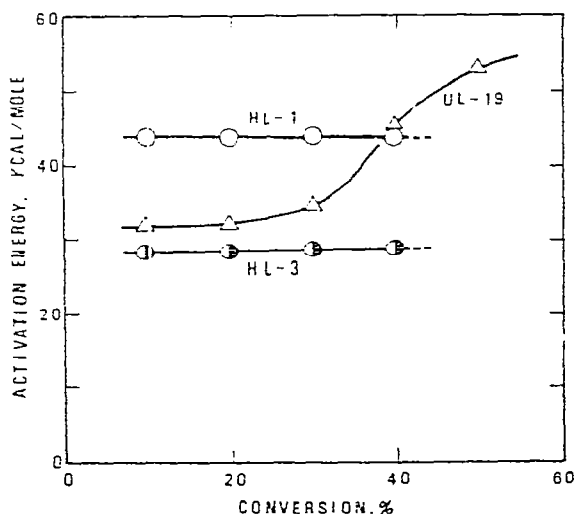


Fig. 9. Activation energy vs. conversion for HL-1, HL-3, and UL-19 Levans.

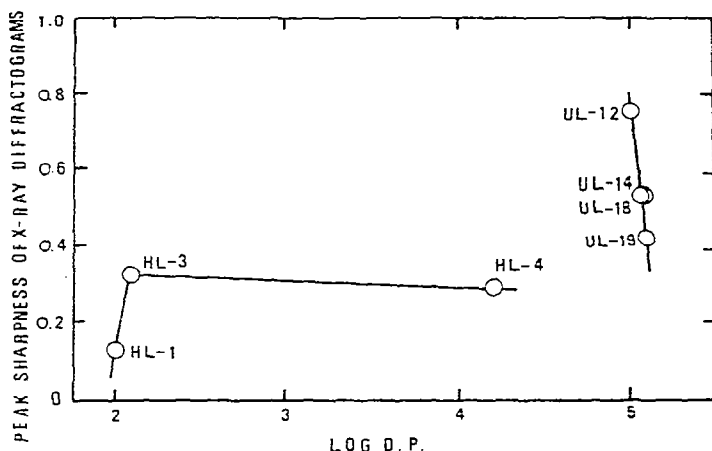


Fig. 10. Peak sharpness from X-ray diffractograms for various Levan samples vs. degree of polymerization (DP).

rapidly with conversion, as observed in Fig. 12. The relatively constant PS for HL-3 with conversion may be explained based on its microstructure mentioned earlier. Thus, the HL-3 randomly coiled network is more oriented and less interpenetrating than HL-1 or HL-2, and this relatively homogeneous network degrades uniformly and the PS-value remains fairly constant with conversion and is higher than the PS-value for HL-1.

Based on the preceding, the k -value of HL-3 should be greater than those for HL-1 or HL-2 (cf. Table 1). Since HL-4 represents a marginal case of branching, its k -value during the initial degradation stage may be of an order of magnitude similar to the ULs, as can be seen from Table 1. As anticipated, the k -values (205°C) for UL-12, UL-14, and UL-18 are similar, if the initial stage involves mainly random degradation of cleaved branches. However, it is not clear at the present time, why the k -value for UL-19 should be so low (or why HL-3 should possess such a relatively high k -value).

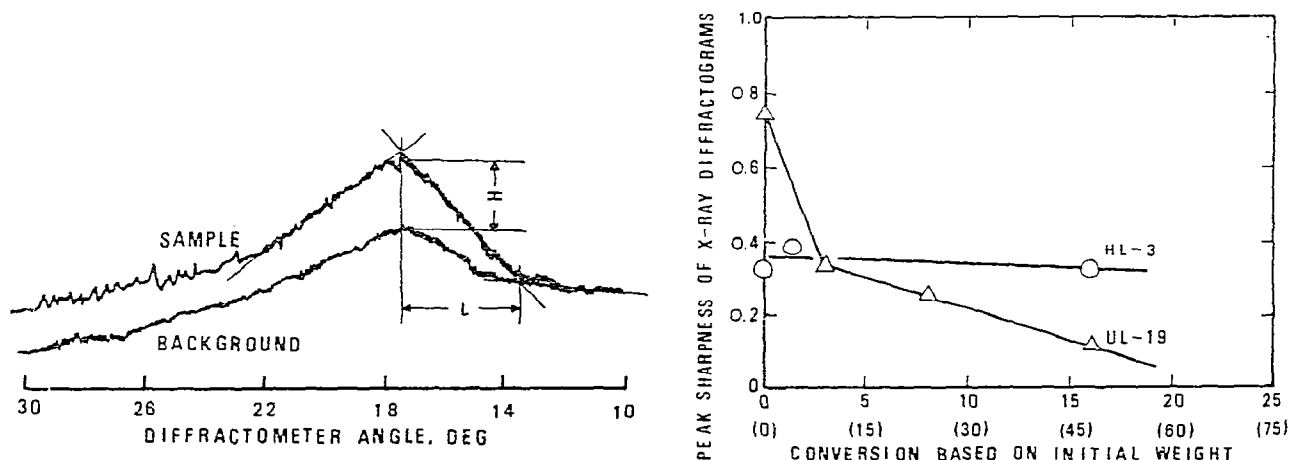


Fig. 11. Method used for estimation of peak sharpness from X-ray diffractograms.

Fig. 12. Peak sharpness from X-ray diffractograms for HL-3 and UL-19 vs. conversion.

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