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Hydrogenation of Polybutadienes. Microstructure and Thermal Properties of Hydrogenated Polybutadienes

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ABSTRACT: Hydrogenations of 1,4-, atactic 1,2-, and syndiotactic 1,2-polybutadienes have been conducted at 100 °C under 50 bar of H_2 in the presence of soluble $(PPh_3)_3RhCl$ catalyst, and completely hydrogenated polybutadienes (HPB) of different molecular weights have been prepared. The chain microstructure of HPB samples has been well characterized by their ^{13}C NMR spectra. The melting temperature of quenched HPB samples with ~10% 1,2 addition decreases with an increase in $\bar{M}_n$, which is associated with a decrease in the crystallinity. The glass transition temperature of syndiotactic HPB with nearly 100% 1,2 addition is higher by ~9 °C than the value of isotactic poly(1-butene). It is concluded that the isotactic sequences of 1-butene units possess a less restricted segmental mobility than do the syndiotactic sequences.

Introduction

Hydrogenation of polybutadienes to prepare well-defined polyolefins and their copolymers is of both academic and commercial interest.[1,2] The methods for hydrogenating polybutadienes involve catalytic hydrogenation by soluble and insoluble transition-metal compounds[3-6] and stoichiometric hydrogenation with diimide.[7,8] The microstructure of parent polybutadienes is known to vary from 1% to 99% in 1,2-unit content, depending on polymerization conditions.[9] The completely hydrogenated polybutadienes are structurally equivalent to copolymers of ethylene with 1–99% 1-butene. On the other hand, atactic and syndiotactic forms of poly(1-butene) can be obtained by the hydrogenation of atactic and syndiotactic 1,2-polybutadienes with nearly 100% 1,2 addition, respectively. At the present stage of polymerization technology, Ziegler–Natta catalysts copolymerize ethylene with 1-butene to give copolymers of rather broad molecular weight distribution ($\bar{M}_w/\bar{M}_n \geq 2.0$), and the homopolymerization of 1-butene produces solely isotactic poly(1-butene).[10] Recently, Graessley et al.[11] prepared a series of monodisperse copolymers of ethylene with 4–99% 1-butene by the hydrogenation of polybutadienes in the presence of an insoluble $Pd/CaCO_3$ catalyst and studied the effects of chain structure (mole fraction of 1,2 unit) on physical properties such as density, melting temperature, glass transition temperature, and crystalline morphology.

In this paper we prepare syndiotactic and atactic forms of poly(1-butene) by hydrogenating 1,2-polybutadienes by a soluble $(PPh_3)_3RhCl$ catalyst and examine the effect of stereoregularity on the glass transition temperature. In addition, the effects of chain length on melting temperature and crystalline morphology are studied for almost monodisperse hydrogenated polybutadienes with ~10% 1,2 addition.

Experimental Section

Polymerization. We prepared ten polybutadiene samples (PB 1 to PB 10) of varying molecular weight, 1,2 unit content, and stereoregularity. A series of four samples (PB 1 to PB 4) with nearly 10% 1,2 addition was prepared by anionic polymerization of butadiene in a heptane solution of *n*-butyllithium as initiator at 30 °C, and their molecular weights were as follows: PB 1, $\bar{M}_n = 99\,000$, $\bar{M}_w/\bar{M}_n = 1.1$; PB 2, $\bar{M}_n = 66\,000$, $\bar{M}_w/\bar{M}_n = 1.1$; PB 3, $\bar{M}_n = 57\,000$, $\bar{M}_w/\bar{M}_n = 1.1$; PB 4, $\bar{M}_n = 25\,000$, $\bar{M}_w/\bar{M}_n = 1.1$. Atactic 1,2-polybutadiene sample PB 5 with 96% 1,2 addition was obtained by anionic polymerization of butadiene by *n*-butyllithium modified with dipiperidinoethane in heptane at 30 °C. Syndiotactic 1,2-polybutadiene samples PB 6 to PB 10 with nearly 100% 1,2 addition were prepared by coordination polymerization of butadiene in a toluene solution of the $Co(acac)_3/CS_2/Al(C_2H_5)_3/H_2O$ catalytic system[12] at temperatures of 0–50 °C. For comparison, two samples P1B 1 and P1B 2) of isotactic poly(1-butene) were prepared by coordination polymerization of 1-butene with the $Ti(OC_4H_9)_4/MgCl_2/Al(C_2H_5)_2Cl$ catalytic system in heptane at 20 °C.

Hydrogenation. All PB samples were hydrogenated in a toluene solution of tris(triphenylphosphine)rhodium chloride ($(PPh_3)_3RhCl$)[13] and triphenylphosphine (PPh_3) under a hydrogen pressure of 50 bar at 100 °C. A high-pressure reactor (100 cm^3) equipped with a magnetic stirrer was used as a reactor. A 500-mg sample of PB was added to 50 cm^3 of toluene in the reactor, 0.02 mmol of $(PPh_3)_3RhCl$ and 0.38 mmol of PPh_3 were admitted under a nitrogen stream (450 mol of carbon–carbon double bonds per mol of Rh), and the reactor was purged with hydrogen. Then the reactor was pressurized to 50 bar with hydrogen and kept at 100 °C for 24 h. After the hydrogen was removed, the hydrogenated polybutadiene (HPB) was precipitated in methanol, washed with methanol, and finally dried under vacuum at room temperature.

Analysis. The microstructure of the polymers was analyzed by FT-IR and ^{13}C NMR spectroscopy. IR spectra of the polymer films were recorded at room temperature on a JASCO FT/IR-3 spectrometer. The contents of 1,2, 1,4-trans, and 1,4-cis additions in PB samples were determined from the absorption bands at 912, 967, and 734 cm^{-1}, respectively, according to the method of Morero et al.[14] The ^{13}C NMR spectra of HPB samples were recorded on a JEOL FX-200 spectrometer operating at 50 MHz under proton decoupling in the Fourier transform (FT) mode. The polymer solutions were prepared at a concentration of 0.2 g/cm^3 in a 9:1 *o*-dichlorobenzene–perdeuteriobenzene mixture without degassing, and the temperature for measurement was 100 °C. Tetramethylsilane (Me_4Si) was used as an internal reference. As reported previously,[15] carbon-13 spin–lattice relaxation times (T_1's) of methine and methylene carbons in an isotactic poly(1-butene) are in the range 0.19–0.45 s at 50 MHz in *o*-dichlorobenzene–perdeuteriobenzene mixture at 100 °C. Therefore, spectra were recorded with a 4000-Hz window, 16K data points, a 90° sampling pulse, a repetition time of 2.0 s, and 8000–12 000 accumulations.

The molecular weight distributions of PB and HPB samples were measured at 140 °C with a Shodex LCHT-3 gel permeation chromatograph fitted with a Shodex 80 M column, using *o*-dichlorobenzene as solvent. The number-average molecular weight ($\bar{M}_n$) and weight-average molecular weight ($\bar{M}_w$) of the HPB samples with low contents (9–10%) of 1,2 addition were obtained on the basis of the molecular weight calibration curve of polyethylene, and those of the HPB samples with high contents (96–99%) of 1,2 addition were estimated by using the molecular weight calibration curve of poly(1-butene). The correction of GPC peak spreading (zone spreading) for the polydispersity ($\bar{M}_w/\bar{M}_n$) was not made.

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Table I
Molecular Weight, Microstructure, and Calorimetric Characterizations of Hydrogenated Polybutadienes

	molecular weight		units		calorimetric data			
					as hydrogenated		after quench[c]	
sample	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	x_{12}[a]	x_B[b]	T_m, °C	ΔH_m, cal/g	T_m, °C	ΔH_m, cal/g
HPB-1	100 000	1.1	0.09	0.047	114	39	109	22
HPB-2	71 000	1.1	0.10	0.052	113	33	110	23
HPB-3	52 000	1.1	0.09	0.047	112	35	110	27
HPB-4	25 000	1.2	0.10	0.052	113	32	113	30

[a] Mole fraction of 1,2 units. [b] Mole fraction of 1-butene units in the equivalent ethylene–1-butene copolymer. [c] Samples quenched initially at 320 °C/min from 187 °C.

Thermal measurements were made on a Perkin-Elmer DSC-2C instrument equipped with a liquid nitrogen subambient accessory. The temperature scale was calibrated at 20 °C/min against indium (156.6 °C), water (0.0 °C), and mercury (−38.9 °C). The heat of fusion of indium (6.80 cal/g) was used as a calorimetric calibration. Polymer samples of 5–10 mg were encapsulated in aluminum pans. Samples were heated at 20 °C/min up to 187 °C, quenched at 320 °C/min to −80 °C, and scanned again at 20 °C/min. Glass transition temperatures, melting temperatures, and heats of fusion were calculated with the Perkin-Elmer standard TADS program.

Results and Discussion

Hydrogenation of Polybutadienes. All polybutadiene hydrogenations were conducted at 100 °C under a hydrogen pressure of 50 bar in a toluene solution of $(PPh_3)_3RhCl$ and PPh_3 (450 mol of double bonds per mol of Rh). Figure 1 shows IR spectra of PB sample 1 ($\bar{M}_n$ = 99 000, $\bar{M}_w/\bar{M}_n$ = 1.1) of 9% 1,2, 51% cis-1,4, and 40% trans-1,4 additions obtained at different times of hydrogenation. After 15 min of hydrogenation the absorption band at 912 cm^{-1} due to the vinyl group of 1,2 addition disappeared. The broad absorption band at 734 cm^{-1} due to the double bond of cis-1,4 addition disappeared after 30 min of hydrogenation, and new absorption bands appeared at 728 and 720 cm^{-1}, being attributable to the CH_2-rocking vibrations in crystalline and amorphous fractions of poly(methylene)segments, respectively. The absorption band at 967 cm^{-1} due to the double bond of trans-1,4 addition completely disappeared after 24 h of hydrogenation. Thus, the double bonds of 1,2 and cis-1,4 additions were hydrogenated faster than the trans-1,4 double bond in the presence of a soluble Rh catalyst. The average molecular weights ($\bar{M}_n$ = 100 000, $\bar{M}_w/\bar{M}_n$ = 1.1) of hydrogenated sample HPB 1 were consistent with the values of parent polybutadiene sample PB 1, which indicates that chain scission due to hydrogenolysis does not take place during the course of catalytic hydrogenation.

All hydrogenated samples of HPB 1 to HPB 10 in this study were obtained after hydrogenation for 24 h at 100 °C and were examined for residual unsaturation by IR and ^{13}C NMR spectroscopy. No trace of residual double bonds was detected by either spectroscopic method.

Microstructure of Hydrogenated Polybutadienes. The microstructure of the HPB samples was determined from their ^{13}C NMR spectra. The ^{13}C NMR spectra of HPB 1 to HPB 4 with low contents (9–10%) of 1,2 addition showed that every single 1,2 unit is isolated in a long sequence of 1,4 units. The fraction of 1,2 units, x_{12}, was determined from the relative peak areas of main-chain methylene carbon resonances in the ^{13}C NMR spectra. The result is listed in Table I, together with the average molecular weights of HPB samples and the mole fraction of 1-butene units, x_B, in the equivalent ethylene–1-butene copolymer, calculated from the relation $x_B = x_{12}/(2 - x_{12})$.

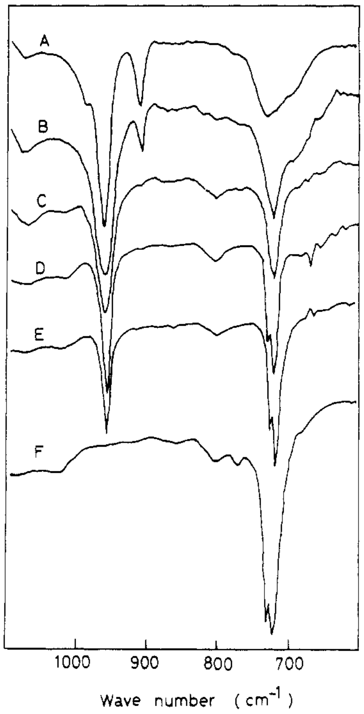
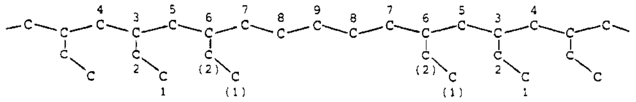


Figure 1. IR spectra of PB sample 1 with 9% 1,2, 51% cis-1,4, and 40% trans-1,4 additions obtained at different times (A, 0 min; B, 5 min; C, 15 min; D, 30 min; E, 1 h; F, 24 h) of hydrogenation. Hydrogenation conditions: 100 °C, 50 bar of initial H_2 pressure, 500 mg of PB 1 sample, 0.02 mmol of $(PPh_3)_3RhCl$, 0.38 mmol of PPh_3, and 50 cm^3 of toluene.

Figure 2 shows typical ^{13}C NMR spectra of hydrogenated syndiotactic 1,2-polybutadiene (HPB 7) and hydrogenated atactic 1,2-polybutadiene (HPB 5). For comparison, a ^{13}C NMR spectrum of isotactic poly(1-butene) (P1B 1), prepared in the polymerization of 1-butene with a Ziegler–Natta catalyst, is given in Figure 3. In the spectra of Figure 2 several weak peaks (5–12) are observed other than the four major peaks (1–4) of methyl, side-chain methylene, methine, and main-chain methylene carbons in the head-to-tail sequence of 1-butene units. The weak ^{13}C resonances of peaks 5–9 arise from carbon species in a sequence containing a single 1,4 unit isolated in a long sequence of head-to-tail 1,2 units:



The ^{13}C chemical shift assignments were made by using the Lindeman–Adams relationship.[16] The very weak resonances 10–12 may arise from a specific sequence structure of 1,2 units containing irregular head-to-head and tail-to-tail units.[17] The fraction of 1,2 units, x_{12}, was determined from the relative peak areas of resonances 4, 5, and 9. The results are given in Table II, together with the stereoregularities of regular head-to-tail 1,2 units.

The stereoregularities of hydrogenated 1,2-polybutadienes and isotactic poly(1-butene) were estimated from the areas of steric pentad peaks in the side-chain

Table II
Molecular Weight and Microstructure of Hydrogenated 1,2-Polybutadiene and Isotactic Poly(1-butene) Samples

	molecular weight		units	stereoregularity							
sample	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	x_{12}	mmmm	mmmr	rmmr mmrr	mmrm rmrr	mrmr	rrrr	mrrr	mrrm
HPB-5	86 000	1.2	0.96	0.07	0.14	0.20	0.27	0.13	(0.05)[a]	0.09	0.05
HPB-6	138 000	1.8	0.99	0.00	0.00	0.00	0.02	0.00	0.96	0.02	0.00
HPB-7	96 000	1.7	0.99	0.00	0.00	0.00	0.03	0.00	0.95	0.02	0.00
HPB-8	86 000	2.0	0.99	0.00	0.00	0.00	0.02	0.00	0.96	0.02	0.00
HPB-9	71 000	1.8	0.99	0.00	0.00	0.00	0.02	0.00	0.95	0.02	0.01
HPB-10	70 000	1.9	0.99	0.00	0.00	0.00	0.03	0.00	0.95	0.02	0.00
P1B-1	64 000	4.6	1.00	0.75	0.08	0.06	0.04	0.02	0.02	0.02	0.01
P1B-2	62 000	4.6	1.00	0.75	0.07	0.07	0.03	0.01	0.04	0.02	0.01

[a] The peak of the rrrr pentad at 26.7 ppm may overlap with the peak of methylene carbon 8 in the 1,4 unit (see Figure 2).

Table III
Calorimetric Characterization of Hydrogenated 1,2-Polybutadiene and Isotactic Poly(1-butene) Samples

			as hydrogenated		after quench	
sample	predominant microstructure	$\bar{M}_n$	T_m, °C	ΔH_m, cal/g	T_g,[a] °C	T_g,[b] °C
HPB-5	atactic	86 000			-28.8	-25.8
HPB-6	syndiotactic	138 000	n.d.	n.d.	-22.3	-20.1
HPB-7	syndiotactic	96 000	48	4	-23.5	-20.9
HPB-8	syndiotactic	86 000	45	3	-24.9	-22.2
HPB-9	syndiotactic	71 000	n.d.	n.d.	-25.3	-22.9
HPB-10	syndiotactic	70 000	n.d.	n.d.	-24.6	-22.6
P1B-1	isotactic	64 000	84	7	-33.6	-29.8
P1B-2	isotactic	62 000	90	8	-34.7	-30.1

[a] T_g onset measured at 20 °C/min after quenching (320 °C/min) from 187 °C. [b] T_g midpoint value.

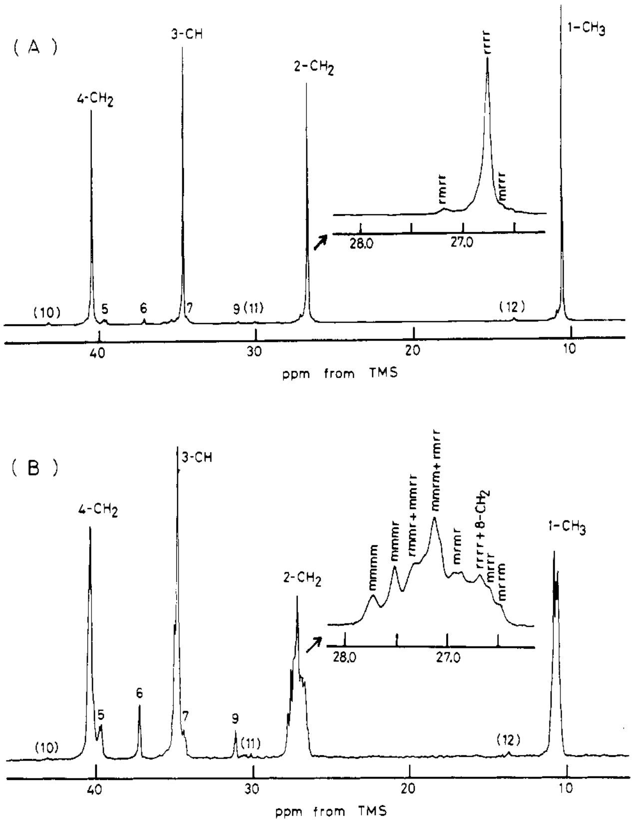


Figure 2. ^{13}C NMR spectra of syndiotactic HPB sample 7 (A) and atactic HPB sample 5 (B). Chemical shifts are in ppm downfield from Me_4Si.

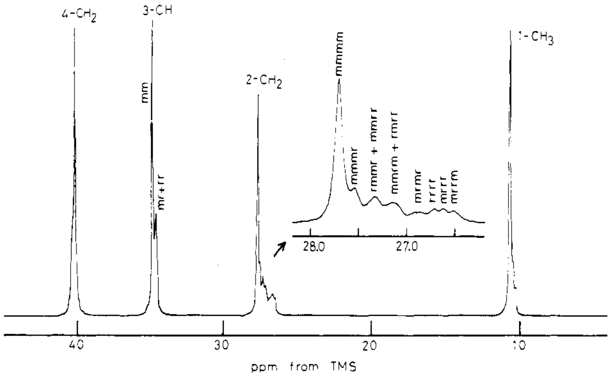


Figure 3. ^{13}C NMR spectrum of isotactic poly(1-butene) sample 1 obtained in the polymerization of 1-butene with a $Ti(OC_4H_9)_4/MgCl_2/Al(C_2H_5)_2Cl$ catalytic system. Chemical shifts are in ppm downfield from Me_4Si.

methylene carbon resonance 2, as expanded in Figures 2 and 3. The many different resonances in the expanded region reflect the sensitivity of the carbon nuclei to different stereosequences of pentad level as given in Figures 2 and 3. The assignments at pentad level have been made by Manzac et al.[17] and Asakura et al.[18] The spectra of hydrogenated 1,2-polybutadienes in Figure 2 confirm their assignments. The head-to-tail sequences of 1,2 units in the syndiotactic HPB are composed of a stereosequence involving the isolated meso unit, as represented by ---rrrrrrmrrrrrr---. This may be concluded from the result that the ratio of rmrr and mrrr fractions is 1:1 (see Table II). The steric pentad resonances of atactic HPB 5 containing relatively high content (4 mol %) of 1,4 units are not well resolved since the resonance of side-chain methylene carbon (2) directly bonded to an isolated 1,4 unit is not neglected and the resonance of methylene carbon 8 in the 1,4 unit is overlapped. Nevertheless, a qualitative analysis of the integrals of the steric pentads indicated that each pentad fraction follows the expected Bernoullian chain statistics, with $P_m = 0.52$, except for the resonance intensity of the rrrr pentad. It is most likely that the resonance of the rrrr pentad overlaps with the resonance of methylene carbon 8 in an isolated 1,4 unit.

Thermal Properties. The melting temperature (T_m) and the enthalpy of fusion (ΔH_m) are given in Table I for almost monodisperse HPB samples 1–4 with ~10% 1,2 addition. Here, the value of T_m is quoted as the maximum temperature. In Table I, the "as hydrogenated" sample corresponds to an unannealed sample and the "after quench" sample was previously heated to 187 °C and cooled at 320 °C/min. The values of T_m and ΔH_m of the unannealed samples are almost independent of the chain length. However, the values for the quenched samples decrease clearly with increasing chain length. The marked drop in the T_m of high molecular weight HPB samples ($\bar{M}_n$ > 50 000) may be associated with a decrease in the crystallinity caused by a quenching treatment.

Table III lists the glass transition temperature (T_g), T_m, and ΔH_m of the atactic and syndiotactic HPB samples 5–10, together with the data of isotactic poly(1-butene) samples 1 and 2. The syndiotactic HPB samples 6–10 with nearly 100% 1,2 addition can be referred to syndiotactic poly(1-butene) samples. The T_g values of syndiotactic HPB samples increase with increasing chain length. On comparison of the T_g values at almost the same $\bar{M}_n$, a clear dependence upon the stereoregularity of poly(1-butene) is noted. The T_g value decreases in the series T_g(syndiotactic) > T_g(atactic) > T_g(isotactic). Similar dependence of T_g on the stereoregularity has been found for polypropylene[19] and poly(methyl methacrylate).[20] The difference in T_g between syndiotactic and isotactic poly(1-butene) is 9 ± 1 °C, which is much smaller than ~14 °C for polypropylene and ~81 °C for poly(methyl methacrylate). The result may correlate with the observation[15] that ^{13}C NMR spin–lattice relaxation times, T_1's, are longer for isotactic than for syndiotactic poly(1-butene) sequences. Taking these findings together, we can conclude that the isotactic sequences of 1-butene units possess a less restricted segmental mobility than do the syndiotactic sequences.

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A Calculation of Thermal Degradation Initiated by Random Scission. 1. Steady-State Radical Concentration

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ABSTRACT: Changes in molecular weight distribution and in sample volume were calculated for thermal degradation of a polymer. The thermal degradation scheme consists of random scission initiation, depropagation, and disproportionation termination reactions. A steady-state radical concentration was used in this study. The initial molecular weight distribution of the sample was expressed by a logarithmic normal distribution. Results were obtained in two ways: one was by approximate analytical solutions describing changes in molecular weight and in the sample volume, including effects of initial polydispersity of the sample; the other was by numerical calculation. Comparison among the analytical solutions obtained in this study, previously published solutions, and the numerically calculated results indicates that the solutions obtained in this study can apply to more general initial molecular weight distributions and agree better with the numerical results than previously published results. Effects of initial molecular weight, average zip length, initial polydispersity, and order of the termination reaction on changes in molecular weight, polydispersity, and the volume of the sample are discussed. A method to determine values of kinetic constants of random scission initiation and average zip length is described using experimental data in conjunction with the calculated results.

1. Introduction

The thermal degradation of polymers involves a large number of different lengths of polymer chains, both stable molecules and free radicals. Their interaction makes the degradation of polymers very complex. For this reason, many degradation studies have been oriented toward a global approach with the main emphasis on experimental studies. However, detailed understanding of the complex thermal degradation mechanism requires a close collaboration between theoretical and experimental approaches. The experimental approach has advanced significantly with improvements in modern instrumentation. On the other hand, it appears that advancement in the theoretical study of thermal degradation has not kept up even though more powerful computers have become available. The objectives of this study are to contribute to the understanding of thermal degradation by formulating and calculating a degradation model and to demonstrate the usefulness of theoretical results for understanding of the degradation mechanism.

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