of an amide linkage and a tetrahydropyran ring along the chains. Possible molecular arrangements providing all hydrogen bonds are ideally regularly formed between polymer chains are illustrated in Figure 7. In the presence of water hydrogen bond interactions must exist between the water molecules and the amide groups. The ring ether oxygens may also interact with the water molecules.

Poly(BOL) film has been found to exhibit some extent of permeability and permselectivity for alkali metal ions in water. Further work is in progress on the properties of poly(BOL) and will be published in the near future.

Acknowledgment. Thanks are given to Mr. M. Ito for his help in the experimental work.

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Preparation and Characterization of Head-to-Head Polymers. 5. Head-to-Head Polystyrene[1]

H. Inoue, M. Helbig, and O. Vogl*

Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003. *Received April 21, 1977*

ABSTRACT: Head-to-head (H-H) polystyrene was obtained by radical 1,4-polymerization of 2,3-diphenylbutadiene followed by selective hydrogenation with potassium and ethanol. The chemical, physical, and thermal properties of H-H polystyrene were studied and compared with those of both atactic and isotactic head-to-tail (H-T) polystyrene. The T_g of the H-H polymer was found to be nearly the same as the T_g of the atactic H-T polymer. The degradation behavior of H-H and H-T polystyrene was also very similar indicating that both types of linkages are of comparable stability.

In our earlier work we discussed the synthesis and characterization of head-to-head (H-H) poly(methyl cinnamate),[2a,4] H-H poly(methyl acrylate),[2b,4] and H-H poly(methyl crotonate).[3,4] It was found that the H-H polymers behaved differently from the head-to-tail (H-T) polymers. The glass transition temperatures of the H-H polymers as determined by differential scanning calorimetry or thermomechanical studies were 30 to 50 °C higher than those of the corresponding H-T polymers.

On the other hand, it was found to our surprise that H-H poly(methyl acrylate) showed the same thermal degradation spectrum as did the H-T polymer. Also the degradation behavior and the maximum rate degradation temperatures of both polymers were essentially identical. This result was not surprising if one considered Grassie's[5] earlier work on the thermal degradation of polystyrene where he suggested that the breakage of the H-T linkage in polystyrene does not require more energy than that of the H-H linkage. However, Grassie compared the degradation behavior of polystyrene with that of styrene–stilbene copolymers of low stilbene content. Therefore it was of interest to synthesize and investigate pure H-H polystyrene and compare its properties to those of the normal H-T polystyrene.

Several unsuccessful attempts have been made to prepare pure H-H polystyrene. Richards[6-9] used a step growth polymerization with the styrene dimer dianion as the starting material and obtained polymers of relatively low molecular weight and with a structure that did not contain entirely H-H linkages. Thus the more or less direct preparation did not seem to be feasible at this time.

An indirect preparation of H-H polystyrene was reported in a preprint by Asami[10] who studied the hydrogenation of poly(1,2-diphenylbutadiene) and poly(2,3-diphenylbutadiene). A complete paper has not appeared which would allow the verification of the data. Also, a polymer claimed to be H-H polystyrene of high molecular weight prepared by reduction of poly(2,3-diphenylbutadiene) with sodium and aniline has been investigated by light scattering, dilatometry, and stress relaxation methods.[11]

It was the purpose of our work to prepare pure H-H polystyrene by hydrogenation of 1,4-poly(2,3-diphenylbutadiene) and compare its chemical, physical, and thermal properties with those of atactic and isotactic H-T polystyrene.

Experimental Section

Materials. The following materials were obtained from Eastman Kodak Co.: benzene, tetrahydrofuran, ethanol, *n*-heptane, azobis(isobutyronitrile) (AIBN), and *p*-toluene sulfonhydrazide.

Benzene was dried over calcium chloride and distilled from sodium metal prior to its use.

Tetrahydrofuran (THF) was distilled over $LiAlH_4$ and stored over sodium metal.

Ethanol was dried with magnesium ethoxide and distilled prior to its use.

Spectrograde *n*-heptane was dried over sodium metal and distilled.

AIBN was recrystallized from dry ethanol and dried at 0.1 mm overnight at room temperature (mp 102.5–104 °C).

p-Toluene sulfonhydrazide was used after recrystallization from dry ethanol (mp 106.5–108 °C).

Potassium was obtained from Pfaltz and Bauer Co. and used in a freshly cut state.

Triethylaluminum (Ethyl Corp.), triisobutylaluminum (Ethyl Corp.), and *n*-butyllithium (Ventron Alfa Products) were used without further purification and diluted with *n*-heptane.

$TiCl_4$ was obtained from Ventron Alfa Products, distilled, and diluted with *n*-heptane prior to its use.

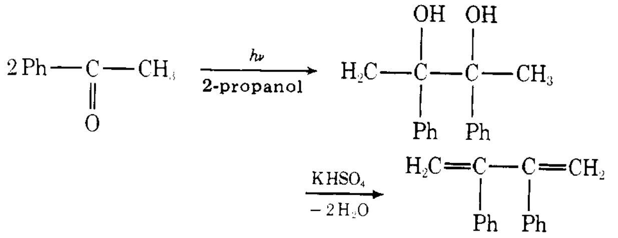
Sodium naphthalene was prepared according to a method described by Sorenson and Campbell.[12]

The palladium catalyst (10% on charcoal) was obtained from Pfaltz and Bauer Co.

Aniline was distilled under reduced pressure and stored over molecular sieves (4 Å) in a dry nitrogen atmosphere.

Preparation of 1,4-Diphenylbutadiene. 1,4-Diphenylbutadiene was prepared by reaction of triphenylcinnamylphosphonium chloride with benzaldehyde and lithium ethoxide in ethanol corresponding to a procedure described by McDonald and Campbell.[24] The colorless needles recrystallized from cyclohexane had a mp of 155–157 °C (lit.[24] 154–156 °C).

Preparation of 2,3-Diphenylbutadiene. 2,3-Diphenylbutadiene was obtained by the following sequence of reactions.



$$2\,\mathrm{Ph{-}\underset{\underset{O}{\|}}{C}{-}CH_3} \xrightarrow[\text{2-propanol}]{h\nu} \mathrm{H_2C{-}\overset{\overset{OH}{|}}{\underset{\underset{Ph}{|}}{C}}{-}\overset{\overset{OH}{|}}{\underset{\underset{Ph}{|}}{C}}{-}CH_3} \xrightarrow[-2\,\mathrm{H_2O}]{\mathrm{KHSO_4}} \mathrm{H_2C{=}\underset{\underset{Ph}{|}}{C}{-}\underset{\underset{Ph}{|}}{C}{=}CH_2} \quad (1)$$

The first step of the synthesis, the preparation of the 2,3-diphenyl-2,3-butanediol, was described previously.[13] We modified the reaction in the following way.

A medium pressure mercury arc, thermometer, and condenser were attached to a 500 mL three-necked photoreaction flask. A mixture of 51 g (0.43 mol) of acetophenone, 400 mL of freshly distilled 2-propanol and one drop of acetic acid was placed in the flask. After irradiation with water cooling for 8 h the yellow-colored reaction solution was evaporated under reduced pressure and the oily residue was allowed to stand. The 2,3-diphenyl-2,3-butanediol crystallized slowly; it was isolated by filtration on a fritted glass funnel and washed with 200 mL of a mixture of acetone–petroleum ether (bp 40–60 °C) (1:4); the yield was 41 g (80%) of colorless needles, mp 123–124.5 °C, after two recrystallizations from acetone–petroleum ether.

The 2,3-diphenyl-2,3-butanediol was dehydrated following in general the procedure of Alder.[14] A 250 mL round-bottom flask equipped with a 20-cm Vigreux column, condenser, and receivers was filled with 43.7 g (0.18 mol) of 2,3-diphenyl-2,3-butanediol and 1.0 g of dried potassium hydrogen sulfate. The system was evacuated at ca. 1 mm and then gradually heated to 180 °C with magnetic stirring. At 70–80 °C water was distilled off and the desired product distilled between 125 and 140 °C. This fraction was collected and cooled. The solidified product was dissolved in 20 mL of methanol and stored below 0 °C. Crystals of 2,3-diphenylbutadiene were obtained which were filtered and dried at room temperature; the yield was 11.0 g (29%).

This product was purified by column chromatography using neutral alumina (CAMAG, Brockmann No. 1). The column dimensions were 2.0 cm × 27.0 cm. Solution and elution were carried out with a benzene–*n*-hexane (1:7) solvent system. The eluate was divided into ten fractions of 50 mL each; fractions 2–5 were combined and evaporated under vacuum, and the residue was recrystallized from methanol.

2,3-Diphenylbutadiene (8.4 g; 76% of the raw product) was recovered; the mp of the colorless needles was 49–50 °C. Its purity was checked by GC (column: Silicone SE-30, 5′ × 1/8″, 200 °C) and the level of impurity was found to be less than 0.01%.

1,4-Polymerization of 2,3-Diphenylbutadiene. 2,3-Diphenylbutadiene was polymerized in a sealed polymerization tube with AIBN. A typical polymerization is given in the following example: A 100-mL polymerization tube with three-way stopcock was filled with 17.1 g (83.0 mmol) of 2,3-diphenylbutadiene and 0.053 g (0.38 mmol) of AIBN. The tube was cooled in a dry ice–2-propanol bath and degassed at 0.1 mm. The degassing procedure was repeated four times, the last time after having melted the monomer in a warm-water bath (55 °C). The tube was then sealed while the lower part of it was placed in a dry ice–2-propanol bath.

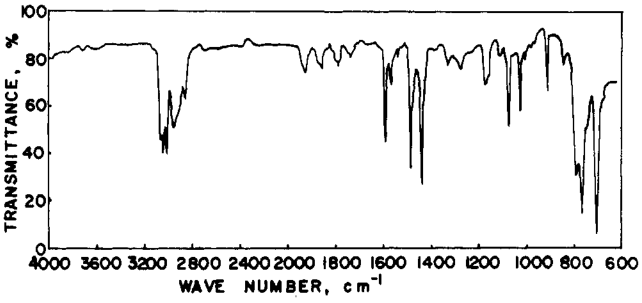


Figure 1. IR spectrum of poly(2,3-diphenylbutadiene) film.

The polymerization was carried out by placing the tube in a constant temperature bath at 60 °C. After the reaction was allowed to proceed for 48 h the tube was opened and the solid polymer was dissolved in 200 mL of benzene. The solution was added dropwise into 1 L of methanol to precipitate the polymer. The polymer was filtered and dried at 50 °C (0.1 mm) overnight. The yield was 16.5 g (96%). The infrared spectrum (film) is shown in Figure 1. The ^1H NMR spectrum (CCl_4, TMS standard) showed δ 6.85 (aromatic, 10 H) and 1.95 (methylene, 4 H). The ^{13}C NMR spectrum (30% (w/v) in chlorobenzene) showed absorptions as listed in Table IV. The UV spectrum (THF) showed a maximum at 250 nm with ϵ_{max} 9.1×10^3 L/(cm mol). Anal. Calcd for $(C_{16}H_{14})_n$: C, 93.15; H, 6.85. Found: C, 93.17; H, 6.81.

Additional examples of polymerizations of 2,3-diphenylbutadiene in which monomer and initiator concentration as well as polymerization time were varied are shown in Table I.

Hydrogenation of Poly(2,3-diphenylbutadiene). A 500-mL three-necked flask equipped with a three-way stopcock, a gas inlet, and a reflux condenser (with calcium chloride tube) was dried by warming with a heat gun and cooling the system under dry nitrogen. Poly(2,3-diphenylbutadiene) (1.0 g; 4.9 mmol) was placed into the flask while the flow of dry nitrogen was continued; 100 mL of dry THF and 5.7 mL (98 mmol) of dry ethanol were added through the three-way stopcock by means of hypodermic syringes. Potassium metal (3.7 g; 0.095 g atom) was now added periodically while the reaction mixture was stirred magnetically and the whole apparatus was flushed with dry nitrogen. The solution soon became cloudy because potassium ethoxide formed which was insoluble in the reaction medium. After 25 h the reaction was stopped by adding 20 mL of ethanol to destroy excess potassium. The solution was now dropped into 500 mL of methanol to precipitate the polymer, which was filtered and dried. The polymer was dissolved in 100 mL of benzene; the solution was filtered and the polymer was reprecipitated from methanol, filtered, and dried at 55 °C (0.1 mm) for 24 h and 0.94 g (94%) of the polymer was recovered. The degree of hydrogenation was 93% as determined by UV spectroscopy.

Therefore, the hydrogenation procedure was repeated once or twice to obtain a completely hydrogenated product. The results of our hydrogenation experiments of poly(2,3-diphenylbutadiene) to H-H polystyrene are reported in Table VII. The infrared spectrum (film) showed absorptions at: 3060 (m) and 3025 (s) (aromatic C–H stretching), 2930 (s) and 2875 (m) (asymmetric and symmetric stretching of CH_2), 1930 (w), 1860 (w), 1790 (w), 1600 (s), 1580 (w), 1490 (s) and 1450 (s) (aromatic C–C stretch and methylene scissoring), 1360 (b, w), 1185 (w), 1160 (w), 1070 (m), 1040 (w), 960 (w), 920 (w), 770 (s), and 710 cm^{-1} (vs) (aromatic C–H bending). The ^1H NMR spectrum (CCl_4, TMS standard) showed δ 6.85 (aromatic, 5 H), 2.10 (methine, 1 H), and 0.95 (methylene, 2 H). The ^{13}C NMR spectrum (30% (w/v) in chlorobenzene) showed absorptions as listed in Table VIII. The UV spectrum (THF) showed a maximum at 260 nm with ϵ_{max} 4.2×10^2 L/(cm mol). Anal. Calcd for $(C_8H_8)_n$: C, 92.26; H, 7.76. Found: C, 92.16; H, 7.70.

Preparation of Atactic H-T Polystyrene. Atactic polystyrene was prepared by radical bulk polymerization of styrene in a vacuum sealed tube using AIBN as an initiator (Table II) methodically following the procedure of Overberger.[25] The infrared spectrum (film) showed absorptions at 2840 (m), 1930 (w), 1860 (w), 1790 (w), 1600

Table I
Polymerization of 2,3-Diphenylbutadiene

Monomer, g	Initiator Type	Initiator mg	Solvent Type	Solvent mL	Temp, °C	Time, h	Yield g	Yield %	η_{sp}/c,[a] dL/g	T_g, °C
5.0	AIBN	100	Benzene	10	60	86	3.0	60	0.094	110
5.0	AIBN	41			60	16	3.1	63	0.454	115
18.3	AIBN	100			60	39	17.4	95	1.080	117
17.1	AIBN	53			60	48	16.5	96	2.280	116
2.8	$(t\text{-Bu})_3Al$ $TiCl_4$	200 160	Benzene + *n*-heptane	10 3	50	111	~0			
3.0	$(i\text{-Bu})_3Al$ $TiCl_4$	390 330	Benzene + *n*-heptane	10 6	60	86	0.16	5		
3.0	BuLi	280	Benzene + *n*-heptane	20 10	25	111	0.31	10		
3.0	BuLi	70	THF	10	30	120	0.04	1.3		
3.0	Sodium naphthalene	150	THF	10	30	1.1	2.9	96	b	

[a] 0.2 g/dL in benzene at 30 °C. [b] This polymer cross-linked during polymerization.

Table II
Polymerization of Styrene with AIBN

Monomer, g	AIBN mg	AIBN mol %	Solvent Type	Solvent mL	Temp, °C	Time, h	Yield g	Yield %	η_{sp}/c,[a] dL/g	$\overline{M}_w$[b]	T_g, °C
9.0	50	0.4	Benzene	10	60	27	5.9	66	0.40	3.2×10^4	
58.6	200	0.3			60	27	56.0	96	1.67	2.9×10^5	98

[a] 0.2 g/dL in benzene at 30 °C. [b] $\overline{M}_w = 1.67 \times 10^5[\eta]^{1.37}$.[19]

Table III
Polymerization of Styrene with $Al(C_2H_5)_3/TiCl_4$[22]

									Toluene extract				Residue			
Monomer, g	$Al(C_2H_5)_3$, g	$TiCl_4$, g	Solvent Type	Solvent mL	Temp, °C	Time, h	Yield g	Yield %	%	η_{sp}/c,[a] dL/g	T_g, °C	Mp,[b] °C	%	η_{sp}/c,[a] dL/g	T_g, °C	Mp,[b] °C
27.1	0.72	0.33	*n*-Heptane	7	60	27	7.2	27	12	2.3	92	218	88	3.0		
45.1	1.80	0.95	*n*-Heptane	21	60	48	12.6	28	15	2.1			85	4.0	90	215

[a] 0.2 g/dL in tetralin at 30 °C. [b] Peak melting point by DSC.

(s), 1580 (w), 1490 (s), 1450 (s), 1370 (w, b), 1180 (w), 1160 (w), 1070 (m), 1030 (m), 910 (m), 760 (s), and 710 cm^{-1} (s).

Preparation of Isotactic H-T Polystyrene. Isotactic polystyrene was prepared by Ziegler-Natta polymerization of styrene in a vacuum-sealed tube in *n*-heptane as solvent (Table III) as described by Kern.[26] The obtained polymers were fractionated by extraction with toluene. The infrared spectrum (film) showed absorptions at 3040 (m), 3010 (s), 2900 (s), 2850 (m), 1600 (m), 1580 (w), 1490 (s), 1450 (s), 1030 (s), 1065 (w), 770 (s), and 710 cm^{-1} (s).

Measurements. A Perkin-Elmer 727 infrared spectrometer was used for measuring the IR spectra. The UV absorption spectra were measured in THF with a Beckman ACTA VI spectrometer.

The ^1H NMR studies were carried out with a Hitachi Perkin-Elmer R-24 spectrometer. ^{13}C NMR was observed by external locked field sweep in absorption mode with a Bruker B-22C high-resolution spectrometer at 22.63 MHz and complete proton decoupling. The measurements were carried out in chlorobenzene at 90 °C. Peak positions were determined with the quaternary carbon of chlorobenzene as reference and then expressed with reference to tetramethylsilane (TMS) after shifting by 134.3 ppm the distance between the resonances of TMS and the C_1 of chlorobenzene. The peak areas were estimated by cutting and weighing after having divided each peak by assumption of a Lorentz curve.

A Perkin-Elmer DSC-1B differential scanning calorimeter was used for the investigation of the thermal behavior of the polymers, including the determination of the glass transition temperature (T_g) and melting points (mp); the heating rate was in all cases 10 °C/min.

The thermal degradation of the polymers was carried out in a nitrogen atmosphere using a Perkin-Elmer TGS-1 thermobalance. Both TGA (thermogravimetric analysis) and DTG (differential thermogravimetric analysis) were done at a programmed temperature increase of 10 °C/min.

Results and Discussion

High molecular weight H-H polystyrene of high structural purity was prepared in a sequence of three reactions from 2,3-diphenylbutadiene which was first polymerized by a 1,4-polymerization followed by a chemical reduction of the double bond of poly(2,3-diphenylbutadiene).

2,3-Diphenylbutadiene was prepared in an overall yield of 25% from acetophenone which was first reduced to 2,3-diphenyl-2,3-butanediol which in turn was dehydrated under vacuum with $KHSO_4$. *trans,trans*-1,4-Diphenyl-1,3-butadiene was also prepared in reasonably good yields and high purity for polymerization attempts. The two compounds were purified and showed a level of impurities in the neighborhood of 0.01% by gas chromatography.

2,3-Diphenylbutadiene was polymerized with AIBN as the initiator. As can be seen in Table I, the yield of the polymer is nearly quantitative and the polymer has an inherent viscosity of as much as 2 dL/g. Polymerizations were carried out at 60 °C with relatively long reaction times to complete the reaction. At high initiator concentrations and in benzene solution, the inherent viscosity and consequently the molecular weight is low which is reflected also in the lower T_g of the polymer. As the initiator concentration is reduced and the polymerization is carried out in bulk the inherent viscosity and presumably the molecular weight increases and so does the T_g to a maximum value of 117 °C. The polymer obtained by this procedure is completely soluble in benzene.

Other attempts have been made to prepare poly(2,3-diphenylbutadiene) with Ziegler-Natta type initiators, *n*-butyllithium, and sodium naphthalene as the initiators. With tri-*tert*-butylaluminum/$TiCl_4$ or triisobutylaluminum/$TiCl_4$ as the initiator in benzene/heptane mixtures at 50 °C and long reaction times, either no polymer or polymers in yields of less than 10% were obtained. Several attempts to use butyllithium as the initiator in benzene/heptane mixtures or in THF also gave polymers in less than 10% yields. 2,3-Diphenylbutadiene with sodium naphthalene as the initiator in THF gave, after a very short reaction time, an essentially quantitative yield of polymer. It turned out however that this polymer was completely insoluble and totally cross-linked. This seems to indicate that sodium naphthalene in 2,3-diphenylbutadiene not only induced 1,4 but also 1,2 polymerization leading to cross-linking through inclusion of the pendant double bond in a second polymer chain. As a consequence of the results of the experiments in Table I, the radical polymerization of 2,3-diphenylbutadiene with AIBN as the initiator was used for the preparation of poly(2,3-diphenylbutadiene) throughout this work.

For direct comparison of the H-H polystyrene with H-T polystyrene, atactic polystyrenes of two different molecular weights were also prepared in bulk or in benzene solution with AIBN as the initiator (Table II). For comparison, styrene was also polymerized with triethylaluminum/$TiCl_4$ as the initiator system as seen in Table III[25] to prepare isotactic polystyrene which was later used for comparative studies with atactic and H-H polystyrene (Table III).

Poly(2,3-diphenylbutadiene) obtained by radical polymerization with AIBN as the initiator was characterized by elemental analysis and infrared and NMR spectroscopy. The infrared spectrum which is shown in Figure 1 is in agreement with the proposed structure for the polymer. It did, however, not give sufficiently characteristic bands for a clear differentiation between 1,2 and 1,4 structure. However, it showed the absence of terminal olefinic methylene groups which would have been formed if 1,2 polymerization had occurred to a substantial amount. The absence of 1,2 structures detectable by infrared was indicated by comparison of the infrared spectra of poly(2,3-diphenylbutadiene) and monomeric α-methylstyrene. No absorbance at 1630 (vinylidene C–C stretch) and 1380 cm^{-1} could be observed in the spectrum of poly(2,3-diphenylbutadiene).

The ^1H NMR spectrum (Figure 2) indicated chemical shift peaks of the phenyl group at 6.87 and 6.52 ppm and of the methylene protons at 1.93 ppm but the spectrum also did not show a terminal methylene group which would have been expected at 5.25 and 4.94 ppm, which are the chemical shift values of the methylene protons of α-methylstyrene. Within the resolution of the ^1H NMR spectrum (which was done at room temperature on a 60-MHz instrument) no ethylene protons indicative of vinyl end groups could be detected.

The ^{13}C NMR spectrum (Figure 3) of poly(2,3-diphenylbutadiene) showed magnetic resonance peaks at 140.5 and 140.0 ppm which have been assigned to the C_1 of the phenyl group when attached respectively cis and trans to the olefinic carbons. The phenyl C_1 atom was assigned to the lowest field peak assuming that it has a similar chemical shift to the C_1 of chlorobenzene (134.3 ppm). The chemical shifts of the olefinic carbons are located at 138.4 ppm for the cis and 138.1 ppm for the trans carbon. The olefinic carbon assignment was based on the fact that the two peaks near 138 ppm disappeared after hydrogenation as can be seen in the spectrum in Figure 7. The methylene carbon atoms attached cis to an olefinic linkage absorb at 30.6 ppm and the methylene carbons attached trans absorb at 32.2 ppm. Furthermore, it should be noted that the phenyl C_1, the olefinic carbons, and the methylene carbon absorptions are split into two peaks each, as is indicated in Table IV. These splittings are attributed to the cis and trans configurations and the actual assignments are made according to a proposal of Duch and Grant[15] who proposed that the higher field chemical shift peaks originated from the trans configuration. Based on estimates of the areas under the individual peaks of the chemical shifts of the three carbon atoms which we have assigned to cis and trans configurations, the polymer consisted of approximately 57% *trans*-poly(2,3-diphenylbutadiene) and 43% of the cis isomeric structure. However, our assignments of ^{13}C resonances to cis and trans structures are somewhat uncertain because of unknown shielding effects. On the basis of these limited experiments we cannot, of course, make any suggestion as to the possible run numbers or distribution of the cis and trans structures in the polymer. It is, however, interesting that this structure contains the cis and trans configurations of the double bonds in essentially 1:1 proportion.

We have very carefully evaluated the ^{13}C spectrum for small amounts of resonance peaks which could be assigned to methylene carbons located between two phenyl-substituted carbons and would consequently represent indications for a 1,2 polymerization of the 2,3-diphenylbutadiene. Within the accuracy of our ^{13}C NMR measurements using 8500 scans, no indication for a 1,2 structure, namely the presence of a carbon resonance which could be assigned to a methylene group located between two phenyl-substituted carbons, could be found.

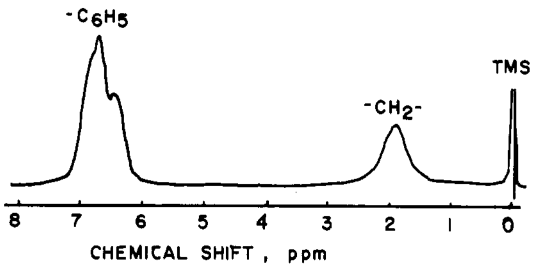


Figure 2. ^1H NMR spectrum of poly(2,3-diphenylbutadiene) 10% solution in CCl_4.

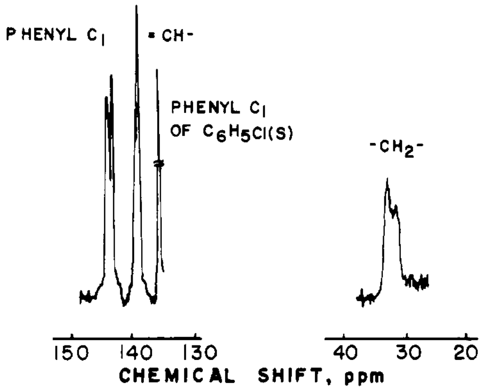


Figure 3. ^{13}C-NMR spectrum of poly(2,3-diphenylbutadiene) 30% solution in chlorobenzene at 90 °C; 8500 scans.

Table IV
Chemical Shifts and Peak Areas in ^{13}C-NMR Spectrum of Poly(2,3-diphenylbutadiene)

	Chemical Shift in ppm[a]		Peak area ratio in %	
Carbon	Cis	Trans	Cis	Trans
Phenyl C_1	140.5	140.0	47	53
	138.4	138.1	41	59
Methylene	30.6	32.2	42	58

[a] Relative to TMS.

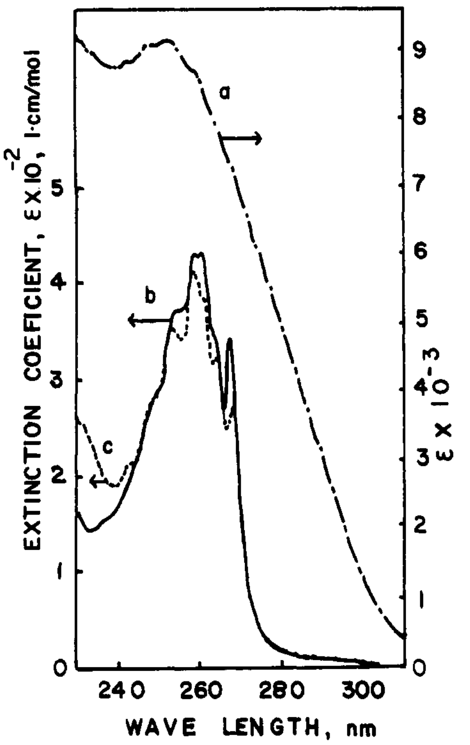
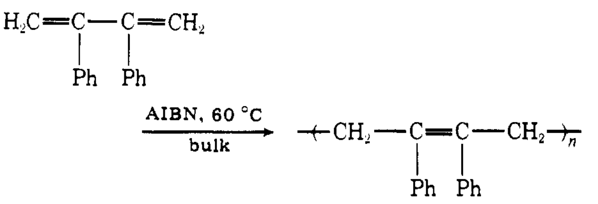


Figure 4. UV spectra of poly(2,3-diphenylbutadiene) and polystyrenes in THF: (a) poly(2,3-diphenylbutadiene); (b) atactic H-T polystyrene; (c) H-H polystyrene.

The ultraviolet spectrum of poly(2,3-diphenylbutadiene) is shown in Figure 4a and, as expected, is substantially different from that of polystyrenes. As will be seen later, this spectral difference is the most sensitive way of determining the poly(2,3-diphenylbutadiene) structure in H-H polystyrene.

According to all these spectral results, it can be concluded that the free-radical bulk polymerization of 2,3-diphenylbutadiene with AIBN as the initiator gave pure 1,4-poly(2,3-diphenylbutadiene) in high yield.



$$\mathrm{H_2C{=}\underset{Ph}{C}{-}\underset{Ph}{C}{=}CH_2} \xrightarrow[\text{bulk}]{\text{AIBN, 60 °C}} \left[\mathrm{CH_2{-}\underset{Ph}{C}{=}\underset{Ph}{C}{-}CH_2}\right]_n \qquad (2)$$

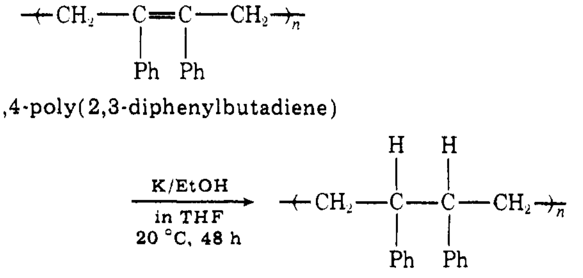
An alternate route for H-H polystyrenes would be to use 1,4-diphenylbutadiene as the starting material. This compound can exist in several stereoisomers, of which *trans,-trans*-1,4-diphenylbutadiene was the one actually prepared. Polymerization of this compound was expected to give poly(1,4-diphenylbutadiene) in which the phenyl groups would be attached to the already saturated carbon–carbon bond and the unsaturation would be between the two methine groups; it was expected that hydrogenation of this polymer would be easier. In spite of a number of attempts under a variety of conditions to polymerize 1,4-diphenylbutadiene to poly(1,4-diphenylbutadiene), however, all polymerization attempts were unsuccessful.

The final step for the preparation of H-H polystyrene was the hydrogenation of poly(2,3-diphenylbutadiene). Four different methods were used in our attempts to hydrogenate the 2,3 double bond of 1,4-poly(2,3-diphenylbutadiene). One hydrogenation method for polymers which has recently become popular was hydrogenation with diimide which is generated by thermal decomposition of *p*-toluene sulfonhydrazide in boiling aromatic hydrocarbons or ethers.[16,17] In our hands, under a variety of reaction conditions (temperature and time), this method produced very little hydrogenation of the 2,3 double bond of 1,4-poly(2,3-diphenylbutadiene); in addition, the hydrogenation products were impure and small amounts of sulfur-containing fragments were introduced into the polymer.

Catalytic hydrogenation with 10% palladium on charcoal was more effective (Table V) for the hydrogenation of 1,4-poly(2,3-diphenylbutadiene). Pd/C had to be used in relatively large quantities, almost equal to the polymer on a weight basis, and three hydrogenations were usually required to obtain 100% hydrogen uptake. The microanalysis obtained for the samples also suggested 100% hydrogenation. Further investigation of these samples by NMR spectroscopy and more characteristically and decisively by ultraviolet spectroscopy showed that 100% of the calculated amount of hydrogen might have been taken up by the polymer but the hydrogen uptake was not specific to the double bond. In addition to the hydrogenation of the 2,3 double bond in 1,4-poly(2,3-diphenylbutadiene), hydrogenation had also occurred on the phenyl rings of the polymer. In fact in this particular set of experiments, 16% of the double bond of the polybutadiene chain had not been hydrogenated. As a consequence, this method was abandoned because it did not selectively hydrogenate the 2,3 double bond; the catalytic hydrogenation was reserved for our later work on the synthesis of H-H poly(vinylcyclohexane).

Attention was now turned to the chemical reduction of poly(2,3-diphenylbutadiene), which was successfully carried out by a reduction of the polymer with potassium and ethanol in tetrahydrofuran. The use of potassium and ethanol enabled the preparation of pure polymer without the introduction of trace impurities. The reaction has to be carried out in a large volume of an inert solvent such as tetrahydrofuran in order for the reagents to react slowly and completely with the polymer without side reactions. During this process of hydrogenation a very small decrease in the inherent viscosity occurred. Hydrogenation of poly(2,3-diphenylbutadiene) of an inherent viscosity of 2.28 dL/g gave H-H polystyrene of an inherent viscosity of 1.64 dL/g. We have not attempted at this stage to study the relative solution properties of the two polymers to determine whether the decrease in inherent viscosity represented a decrease in molecular weight or simply a change in chain conformation.

In Table VI we have shown several typical experiments for the hydrogenation of poly(2,3-diphenylbutadiene) with potassium and ethanol in THF, including reaction conditions and yield of polymers. The reduction proceeds with high chemical purity of the final H-H polystyrene.



$$\left[\mathrm{CH_2{-}\underset{Ph}{C}{=}\underset{Ph}{C}{-}CH_2}\right]_n \xrightarrow[\substack{\text{in THF}\\ \text{20 °C, 48 h}}]{\text{K/EtOH}} \left[\mathrm{CH_2{-}\overset{H}{\underset{Ph}{C}}{-}\overset{H}{\underset{Ph}{C}}{-}CH_2}\right]_n \qquad (3)$$

1,4-poly(2,3-diphenylbutadiene)

H-H polystyrene

It was, however, not possible to obtain H-H polystyrene after only one reduction and the reduction procedure had to be repeated at least once or twice. The progress of the reduction could very easily be checked by ultraviolet spectroscopy because the extinction coefficient at 250 nm of poly(2,3-di-

Table V
Catalytic Hydrogenation of Poly(2,3-diphenylbutadiene) (Reaction Temperature = 100 °C; H_2 pressure = 1000 psi)

Polymer g	Pd–C in g	Solvent Type	Solvent mL	Time, h	Recovery, g	Deg of[a] hydrogenation, %
3.00	1.50	Ethyl acetate and 2-butanone	200 50	19	2.76	39
2.72	1.00	Ethyl acetate and benzene	150 50	15	2.26	86
1.00	0.50	Ethyl acetate and benzene	100 100	15	0.95	~100

[a] Calculated from elementary analyses. [b] Starting poly(2,3-diphenylbutadiene), η_{sp}/c = 1.08.

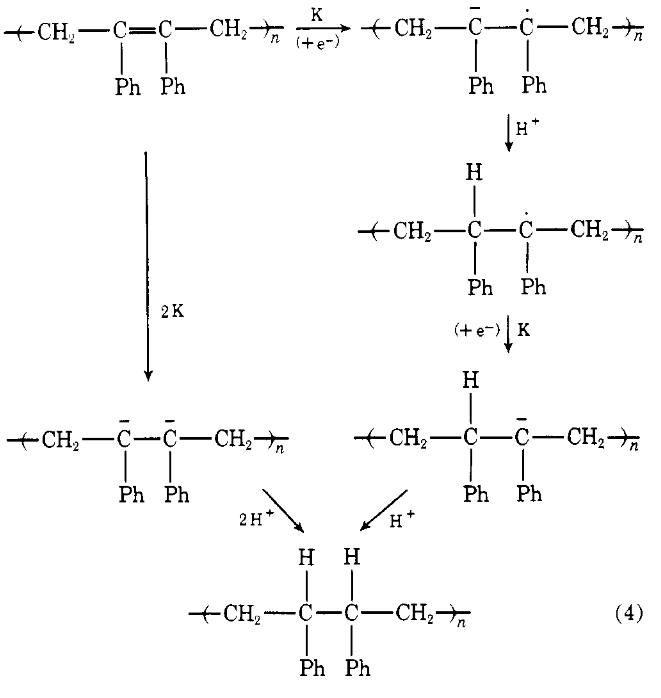
Table VI
Hydrogenation of Poly(2,3-diphenylbutadiene) with Potassium and Ethanol at 25 °C

Polymer[b] amount, g	Ethanol, mL	Potassium, g	THF, mL	Reaction time, h	Recovery, g	Deg of[a] hydrogenation, %	T_g, °C
6.40	14	10	600	45	6.05	93	96
5.90	14	10	600	48	5.90	97	97
5.70	14	9	600	48	5.10	100	97

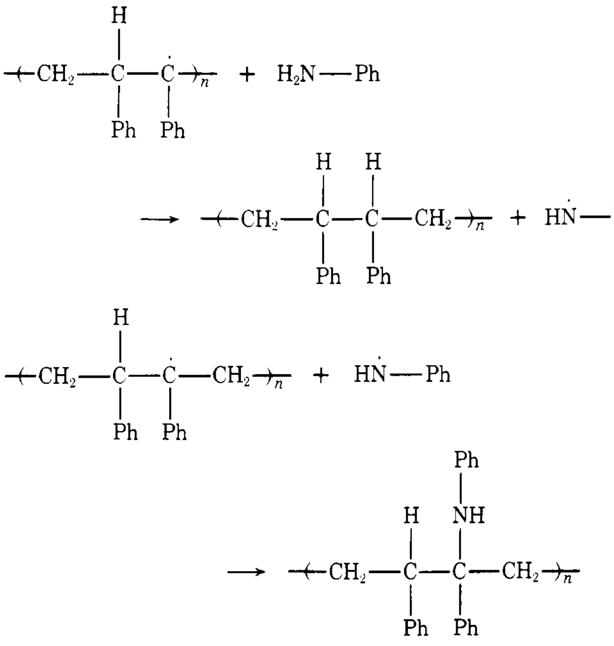
[a] Calculated from UV spectrum. [b] Poly(2,3-diphenylbutadiene), η_{sp}/c = 2.28 dL/g.

phenylbutadiene) is 9.1 × 10^3 L/(cm mol) and that of H-H polystyrene is 3.3 × 10^2 L/(cm mol), different by a factor of 30. (UV spectroscopy is therefore much more sensitive than NMR spectroscopy.) As can be seen in Figure 4, the absorption patterns of atactic H-T and H-H polystyrenes were slightly different but their absorption coefficients were nearly the same.

The mechanism of the reduction of poly(2,3-diphenylbutadiene) is probably similar to the mechanism which has been established for the chemical reduction of stilbenes to diphenylethanes.[18,19] Poly(2,3-diphenylbutadiene) has a substituted stilbene structure and consequently can form first an ion radical by the addition of an electron from potassium metal. By further potassium metal atom addition it can add another electron to form another anion on the carbon which is attached to the phenyl group and which is the locus of the radical function. This process can occur either in one step or in two separate steps with protonation of the initial anion. This sequence of reactions is described in eq 4.



Another route for the preparation of H-H polystyrene from poly(2,3-diphenylbutadiene) was hydrogenation with potassium and aniline (Table VII). Reaction times with this very active reducing agent were somewhat less than those in the reaction of poly(2,3-diphenylbutadiene) with potassium/ethanol. However, in spite of various modifications of the method, nitrogen was consistently found in the polymer to about 0.5% which indicated that one aniline group was introduced for every 10 to 20 double bonds reduced. The probable mechanism for the introduction of this aniline group is indicated in eq 5.



We believe that the relatively high concentration of reactants and the necessity of relatively high reaction temperatures were responsible for the incorporation of the aniline moiety into the polymer. Furthermore, the resonance stability of these aniline radicals would also favor radical recombination and introduction of aniline groups into the polymer.

Spectroscopic characterization of H-H polystyrene is described in the next few tables and figures. The infrared spectra

Table VII
Hydrogenation of Poly(2,3-diphenylbutadiene) with Potassium and Aniline at 25 °C

Polymer, g	Aniline, g	Potassium, g	THF, mL	Reflux time, h	Recovery, g	Deg of[a] hydrogenation, %
2.00	1.36	0.57	50	19	1.78	79
1.75	0.95	0.40	75	8	1.57	95
1.54	0.47	0.20	75	10	1.54	100

[a] Calculated from UV spectrum.

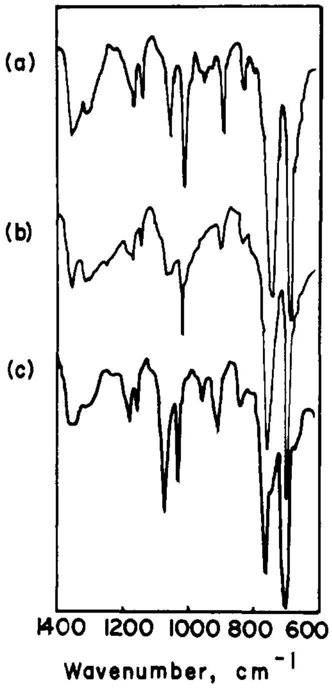


Figure 5. IR spectra of polystyrene films: (a) atactic H-T polystyrene; (b) isotactic H-T polystyrene; (c) H-H polystyrene.

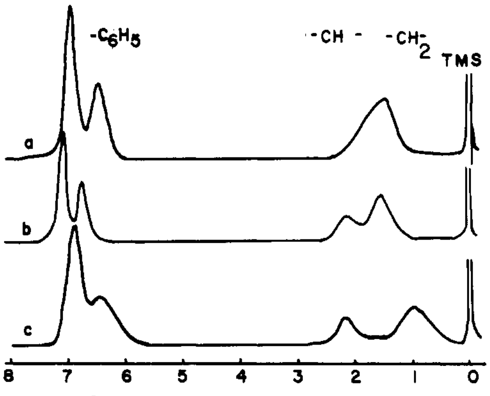


Figure 6. ^{1}H NMR spectra of polystyrenes (37 °C, 60 MHz, 10% solutions in $CDCl_3$ or CCl_4): (a) atactic H-T polystyrene, in CCl_4; (b) isotactic H-T polystyrene, in $CDCl_3$; (c) H-H polystyrene.

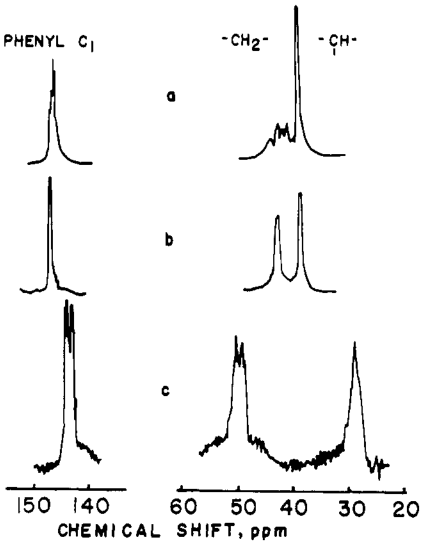


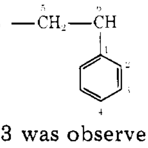
Figure 7. ^{13}C-NMR spectra of polystyrenes (chlorobenzene solution at 90 °C): (a) atactic H-T polystyrene, 40% solution, 2900 scans; (b) isotactic H-T polystyrene, 12% solution, 7250 scans; (c) H-H polystyrene, 30% solution, 8200 scans.

Table VIII
Chemical Shifts[a] in ^{13}C-NMR Spectra[b] of Atactic, Isotactic, and H-H Polystyrene

Carbon No.[c]	Atactic PS, ppm	Isotactic PS, ppm	H-H PS,[d] ppm
1	145.3	147.0	144.3
2	130.5	130.7	130.8
3	128.1	127.6	127.8
4	125.5	125.0	124.9
5	42.7	43.0	49.7
6	38.9	39.5	28.9

[a] Relative to TMS. [b] Samples are the same in Figure 7.

[c] Carbon numbers as follows



$—\overset{5}{C}H_2—\overset{6}{C}H—C_6H_5$

[d] Splitting of carbons 1 and 3 was observed. See Table IX.

of atactic, isotactic, and H-H polystyrenes are shown in Figure 5. It can be seen that the spectra of H-H and H-T polystyrene are essentially identical. We have one change in the peak at 1069 cm^{-1} as compared to the neighboring 1012-cm^{-1} peak.

It was known[20] that the single peak at 1069 cm^{-1} in the spectrum of atactic polystyrene splits to a double peak at 1062 and 1071 cm^{-1} in the case of crystalline isotactic polystyrene. In the case of our H-H polystyrene only one single peak at 1069 cm^{-1} can be observed which seems to indicate the absence of crystallinity. It is not surprising that the H-H polystyrene does not show any crystallinity by infrared. This IR result also confirms the results of the wide-angle x-ray diffraction measurements which were studied comparatively for all samples. (Only the isotactic polystyrene showed crystallinity.)

Tsuchida[21] had ascribed the infrared absorption at 961 cm^{-1} to T-T linkage. This linkage should, of course, have shown very significantly in our pure H-H polymer, which is also a T-T polymer. We have no specific indication for a T-T linkage and the 961-cm^{-1} band was not detected in our spectrum of H-H polystyrene.

^{1}H NMR spectra of atactic, isotactic, and H-H polystyrene obtained on a 60-MHz instrument at room temperature are shown in Figure 6. Higher resolution spectra are in the process

Table IX
Chemical Shifts and Peak Areas in the ^{13}C-NMR Spectrum of a Typical Sample of H-H Polystyrene

Type of carbon atoms	Chemical shift, ppm[a]		Peak area Ratio, %	
	Threo	Erythro	Threo	Erythro
Phenyl C_1	143.2	144.2/144.6	43	57
Methylene	49.4	50.8	43	57

[a] Relative to TMS.

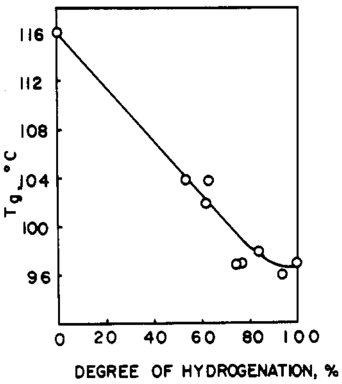


Figure 8. T_g's of partially hydrogenated poly(2,3-diphenylbutadiene).

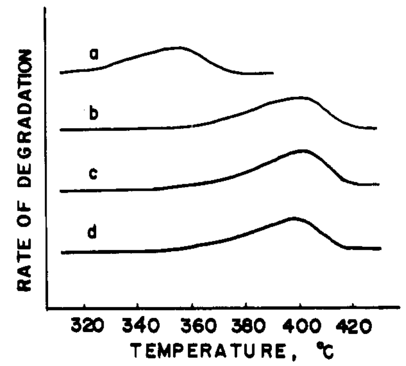


Figure 9. DTG of poly(2,3-diphenylbutadiene) and polystyrenes (heating rate 10 °C/min, under nitrogen): (a) poly(2,3-diphenylbutadiene); (b) atactic H-T polystyrene; (c) isotactic H-T polystyrene; (d) H-H polystyrene.

of being studied for a different objective. The degree of resolution obtained with this spectrometer did not allow any conclusions as far as the configurational structure of the polymers is concerned but it was sufficient to describe the differences in the chemical shifts of the various polystyrenes. The very good separation of the methine and methylene chemical shifts should be noted particularly.

^{13}C NMR spectra of H-H and H-T polystyrenes are shown in Figure 7. As can be seen, the ^{13}C NMR spectra showed complicated splitting. As a consequence the chemical shifts are listed in detail in Table VIII. The peak assignements for atactic and isotactic polystyrene are in good agreement with the results obtained by other authors.[22] It is expected that the phenyl C_1 and the methylene absorption in the ^{13}C NMR spectrum of H-H polystyrene should be significantly different from the phenyl C_1 and methylene resonances of the atactic and isotactic H-T polystyrene and are each split into peaks while the methine resonance is relatively unaffected. We assume that the splittings are caused by the erythro and threo configurations of the polymers. Table IX shows the estimated erythro/threo ratios for both phenyl C_1 and methylene carbon atoms which are in good agreement and also consistent with the ratio of cis and trans double bond character of poly(2,3-diphenylbutadiene) which was the original polymer. It indicated that the chemical reduction of the double bond of poly(2,3-diphenylbutadiene) had probably proceeded in a stereospecific manner by trans addition of the hydrogen to the double bond.

Table X
Thermal Degradation of Poly(2,3-diphenylbutadiene) and Polystyrenes (Sample Size = 2 mg; Heating Rate = 10 °C/min under Nitrogen)

	DTG		
Polymer	Initial degradation temp, °C	Max degradation temp, °C	TGA Half-volatilization temp, °C
Poly(2,3-diphenylbutadiene)	307	357	354
Atactic polystyrene	337	398	390
Isotactic polystyrene	357	403	390
H-H polystyrene	347	397	398

Of the physical characterizations which were carried out on this polymer, only the glass transition temperature (T_g) is discussed in this paper. Poly(2,3-diphenylbutadiene) shows a glass transition temperature of 116 °C, and the glass transition temperature of the resultant completely hydrogenated H-H polystyrene is 97 °C. Partially hydrogenated poly(2,3-diphenylbutadiene) samples have glass-transition temperatures between these two values. We appreciate here that the glass transitions of pure 1,4-*cis*-poly(2,3-diphenylbutadiene) and 1,4-*trans*-poly(2,3-diphenylbutadiene) should appropriately have been used for the comparison and for the plotting of the T_g dependence. Comparisons of the glass-transition temperature of the poly(2,3-diphenylbutadiene) and the various partially hydrogenated materials are shown in Figure 8. The scattering of the data at higher degrees of hydrogenation may indicate that it might have proceeded either in blocks or in random fashion or have selectively reduced one configuration of a double bond of the polymer over the other. Our (T_g) relation is based on hydrogenated samples of a degree of hydrogenation of more than 70%. There seems to be an indication that the hydrogenation has occurred relatively randomly.

For comparison, the T_g of H-T atactic polystyrene was 98 °C and the T_g of our isotactic polystyrene was found to be 92 °C, in very good agreement with known values. It is most interesting that H-H and isotactic H-T polystyrene and atactic H-T polystyrene (which consists of nearly 80% syndiotactic diads) have essentially the same glass-transition temperatures. This result is different from the results which were obtained by comparing the glass-transition temperatures of H-H polyacrylates and of H-H poly(vinyl chloride) with the corresponding H-T polymers where the glass-transition temperatures were approximately 30 °C higher for the H-H polymers. The consequences of these results will be discussed when the data for the glass-transition temperatures of more polyolefins are available.

The thermal degradation behavior of H-H and H-T polystyrenes was also investigated and is shown in Figure 9. It is shown, and this is also very characteristic and important, that the degradation temperatures obtained from DTG and also TGA (Table X) showed no significant difference between the H-H and the H-T polymers. As would be expected, poly(2,3-diphenylbutadiene) had a lower degradation temperature and overall lower thermal stability because of the possibility of forming allyl radicals by cleavage of the single bond of low dissociation energy between the two allylic methylene groups.

The results of the thermal stability of polystyrenes with a maximum degradation temperature of nearly 400 °C were consistent with statements in our recent papers that the H-H and H-T linkages are of comparative stability as long as the fourth substituent on the carbon atom is a hydrogen atom. If the group is different, then the thermal stability of the H-H linkage is lower. A more detailed study of the degradation behavior of H-H polystyrene and the determination of several mechanical properties will be the subject of a separate paper.

Acknowledgments. This work was supported by the Foster Grant Corporation. H.I. would like to thank the Osaka Research Institute for a year's leave of absence to study abroad. M.H. would like to thank the Friedrich Schiller University, Jena, GDR, for permission to work at the University of Massachusetts. This paper was written while O.V. was on sabbatical leave at the CNRS Centre de Recherches sur les Macromolécules, Strasbourg, France. We are also indebted to L. S. Corley for his efforts in the preparation of this manuscript.

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Polymerization of Cadmium Octadecylfumarate in Multilayers

D. Naegele,[1a] J. B. Lando,*[1b] and H. Ringsdorf[1a]

Institute of Organic Chemistry, Universitat Mainz,
Mainz, Federal Republic of Germany, and the Department of Macromolecular Science,
Case Western Reserve University, Cleveland, Ohio 44106. *Received May 20, 1977*

ABSTRACT: The UV-initiated polyreaction of Langmuir–Blodgett multilayers of cadmium octadecylfumarate was studied. For structural comparison the dimensions of the monoclinic unit cell of crystalline monomeric material were determined. The structure of the multilayers was characterized by x-ray and electron diffraction. Approximately the first ten layers showed hexagonal packing of the monomer molecules with the paraffin chains perpendicular on the support, whereas in thicker layers partial rearrangement occurred to the monoclinic modification. The monoclinic crystallites are arranged in three preferred directions, resulting from the original hexagonal symmetry. (Orientation of the monomer molecules was further characterized by infrared spectra.) Both modifications can be polymerized by UV light, the resulting polymer structure being the same in both cases. In the case of the monoclinic phase at approximately 40% conversion a phase transition monomer to polymer occurs. The kinetics of the reaction was followed by UV spectroscopy. By polymerization of alternating cadmium octadecylfumarate/cadmium stearate multilayers it could be shown that the reaction occurs independently from the nature of the neighboring layer in a separate plane.

In the last few years, first studies have been made of polyreactions in Langmuir–Blodgett multilayers (or "built-up monomolecular films").[2-5] The monomeric multilayers can be built up from monomolecular layers of the monomer on the gas/water interface by multiple deposition onto a solid support.[6,7] These multilayers can be polymerized to ultrathin polymer layers of controlled thickness. Their potential interest lies among other things in the increased mechanical stability in comparison to low molecular weight multilayers.

Concerning the building up of monomer multilayers, the question arises if the orientation of the molecules on the water surface is preserved during deposition or if new structures are formed. Second, it must be established if and how monomer orientation and layered structure change during the polyreaction.

Experimental Section

Materials. Commercial octadecylhydrogenfumarate was recrystallized several times from methanol, mp = 94 °C. The cadmium salt was prepared by shaking a solution of 6 g of octadecylhydrogenfumarate in 500 mL of chloroform with a solution of 9 g of cadmium acetate in 500 mL of water. The cadmium salt precipitates at the interface. After washing with water, methanol, and chloroform the raw product was recrystallized from a mixture of water/dioxane/chloroform. This mixture was also used for the preparation of a single crystal; the saturated solution (40 °C) was cooled at a rate of 0.5 °C/h.