Glass Temperature of Hydrogenated Polystyrene

Hans-Georg Elias[a]; Otto Etter[a]

[a] DEPARTMENT OF INDUSTRIAL AND ENGINEERING, CHEMISTRY SWISS FEDERAL INSTITUTE OF TECHNOLOGY, ZURICH, SWITZERLAND

PLEASE SCROLL DOWN FOR ARTICLE

Glass Temperature of Hydrogenated Polystyrene

HANS-GEORG ELIAS and OTTO ETTER

DEPARTMENT OF INDUSTRIAL AND ENGINEERING CHEMISTRY
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZURICH, SWITZERLAND

Summary

Atactic polystyrene was hydrogenated under different conditions. At incomplete hydrogenation, a mixture of polystyrene and poly(vinyl cyclohexane) results. The glass temperatures were studied under different conditions by differential thermal analysis and found to be 100°C for polystyrene and 80°C for poly(vinyl cyclohexane). The solubility of poly(vinyl cyclohexane) is reported for different solvents. The influence of DTA evaluation techniques was studied.

INTRODUCTION

The unperturbed dimensions of atactic poly(vinyl cyclohexane) are 7.5% higher, as expected if compared with polystyrene on a mass basis alone (*1*). This may be due to a stretching of the poly (vinyl cyclohexane) chain (PVCH) by the greater ring size of the cyclohexyl ring, or to a contraction of the polystyrene chain (PST) due to π-π interactions of the phenyl rings. Both effects will make the polymer chain stiffer.

To get some idea about the relative importance of these effects, measurements of glass transition temperatures may be helpful. The glass temperature is due to the set-in of cooperative motions of some 50 to 100 monomer units. A chain stiffening will increase the energy necessary for this process and thus increase the glass temperature. If there are π-π interactions, they will be expected not only between adjacent phenyl groups in the chain, but also between phenyl groups at different parts of the polymer chain and/or at different chains. These nonneighbor interactions will act as weak

cross-links. If the segmental length between cross-links is smaller than the cooperative length, the activation energy and the glass temperature will increase, owing to this fixation of chain elements. A $(T_g)_{PVCH} > (T_g)_{PST}$ will thus point on a dominant steric effect of the more bulky cyclohexyl group, a $(T_g)_{PVCH} < (T_g)_{PST}$ on a dominance of π-π interactions.

Comparison of the glass transition temperatures of polystyrene and poly(vinyl cyclohexane) is meaningful only if both polymers exhibit the same configuration. During hydrogenation a change in steric composition is not likely. We therefore hydrogenated a commercial, radical-initiated polystyrene and determined the glass transition temperatures of the polymers by differential thermal analysis.

EXPERIMENTAL

The polystyrene sample was a commercial suspension polymer (2) of the Badische Anilin and Soda Fabrik, Ludwigshafen (Polystyrol V), which was freed of residual monomer by after-treatment with water vapor in a vacuum. The partially reduced nickel carbonate was prepared according to (3), the Raney nickel according to (4).

All hydrogenations were carried out in decalene in autoclaves with a magnetic stirrer. Air was removed and the autoclaves were loaded with hydrogen of 75 (H1), 150 (H2), 180 (H3 and H4), and 160 atm (H5) and heated for $\frac{1}{2}$ hr to the temperatures and pressures given in Table 1. After the times given in column 9 of Table 1, the

TABLE 1

Hydrogenation of Polystyrene V

Expt.	Catalyst Type	Amount, g	Poly-styrene, g	Deca-lene, ml	Auto-clave, liters	Temp., °C	Pres-sure, atm	Time, hr.
H1	Red NiCO₃	30	7.5	250	0.5	200	140	4
H5	Raney-Ni	50ᵃ	6.0	200	0.25	200	210	48
H2	Raney-Ni	200ᵃ	30.0	1000	2	230	220	24
H3	Raney-Ni	200ᵃ	22.5ᵇ	750	2	250	250	24
H4	Raney-Ni	200ᵃ	30.0	1000	2	270	260	24

ᵃ Amount of alloy before preparation of Raney nickel.
ᵇ Hydrogenation product of Expt. H2.

solution was filtered (H1) or centrifuged (others) and the removed catalyst washed several times with decalene. The collected decalene solutions were precipitated into acetone. The white precipitate was filtered off and dried in a vacuum. The degree of hydrogenation was measured via UV spectroscopy in a Beckman DK2A spectrophotometer. The absorption band at 262 nm was used to measure the degree of hydrogenation. The microanalysis of samples H3 and H4 (fully hydrogenated) corresponded to the UV data:

M (110.2 calc.)   calc.   C, 87.20%; H, 12.80%
                     found C, 87.44%; H, 12.46%

DTA diagrams were taken with the du Pont Model 900 apparatus, in air with 25-mg samples, starting at $-60°C$ and below.

RESULTS

Hydrogenation of Polystyrene

The hydrogenation of polystyrene has been studied by a number of authors (5–9). Staudinger et al. (5,6) obviously worked with low-molecular-weight polystyrenes, because their poly(vinyl cyclohexane) was soluble in ether (see below). The same hydrogenation method was used by Warner and Keel (7), who tried to separate poly(vinyl cyclohexane) and nonreacted polystyrene by solubility. This method will work only if the hydrogenation is a nonrandom process with respect to the styrene units, i.e., if the reaction product is a mixture of nonreacted polystyrene molecules and totally hydrogenated polystyrene molecules only. According to Stuadinger et al. (5,6), hydrogenation of low molecular weight polystyrene is accompanied by degradation. Hydrogenation of high molecular weight polystyrene at 150°C with a nickel catalyst also led to degradation (7). On the other hand, no degradation is claimed for hydrogenation of high molecular weight polystyrenes with nickel, cobalt, or platinum catalysts (9) at the same temperature. No methods for the preparation of the catalysts were given in that paper, however.

The hydrogenation of polystyrene according to Staudinger and Wiedersheim (6) with a partially reduced nickel carbonate as catalyst at 200°C resulted in a degree of hydrogenation of only 37.6% (Expt. H1, Table 2). More drastic conditions are therefore necessary for the hydrogenation of high molecular weight polystyrenes.

TABLE 2

Results of Hydrogenation Experiments

Expt.	Catalyst	Temp., °C	Polymer yield, %	Degree of hydrogenation, %	$[\eta]_{toluene}^{25°C}$, ml/g
Starting material					111.9
H1	Red. NiCO$_3$	200	97.2	37.6	—
H5	Raney-Ni	200	98.4	42.8	94.2
H2	Raney-Ni	230	99.1	75.8	49.6
H3	Raney-Ni	250	99.7	100 ⎫	23.5
H4	Raney-Ni	270	99.4	100 ⎭	

Using Raney nickel as a catalyst, and changing the temperature from 200 to 230°C and the reaction time from 4 to 24 hr, we arrived at a degree of hydrogenation of 75.8% (Expt. H2). However, the intrinsic viscosity $[\eta]$ dropped from 111.9 to 49.6 ml/g (toluene, 25°C). This decrease of $[\eta]$ is due to degradation, because toluene exhibits approximately the same solvent interactions with polystyrene and poly(vinyl cyclohexane) respectively (see below).

Using partially hydrogenated polymer of Expt. H2 as a starting material, a complete hydrogenation took place at 250°C (Expt. H3). A one-step hydrogenation at 270°C (Expt. H4) resulted equally in a complete hydrogenation. The combined product H3/4 showed a drastic degradation, as measured by intrinsic viscosity.

To test the relative influence of catalyst and temperature, we repeated Expt. H1 with Raney nickel instead of reduced nickelcarbonate (Expt. H5). The degree of hydrogenation obtained in this experiment was practically identical with that of Expt. H1. The type of catalyst is therefore of minor importance as compared with temperature. The hydrogenation reaction is stopped at a certain point, probably because of inactivation of the catalyst by adsorbed polymer. This explanation is borne out by the observation that after an initial rapid hydrogen uptake, the pressure decreases only slowly from 190 to 185 atm between 4 and 48 hr.

The weight-average molecular weight of the initial polystyrene was $M_w = 353,000$, the molecular weight of the totally hydrogenated product $M_w = 61,900$ (1). The intrinsic viscosity in toluene at

25°C decreased from $[\eta] = 111.9$ (polystyrene) to 23.5 ml/g [poly (vinyl cyclohexane)]. As $M_{psty}/M_{pvch} = 5.70$ and $[\eta]_{psty}/[\eta]_{pvch} = 4.75$, intrinsic viscosities in toluene may be used directly for the determination of the degree of degradation.

To find the primary reason for the degradation reaction, viscosities of a 0.00201 ml/g solution of polystyrene were measured under different conditions. The starting solution possessed an outflow time of 193.2 sec at 25°C, which decreased to 172.4 sec after a 24-hr treatment at 270°C under nitrogen without catalyst. The same treatment with Raney nickel in the agitated autoclave caused a drop to 158.7 sec. Replacement of nitrogen by hydrogen, i.e., using the hydrogenation conditions of Expt. H4, led to an outflow time of 159 sec. The degradation is thus due to the thermal and mechanical degradation and not to the hydrogenation process itself.

Solution Properties of Poly(vinyl cyclohexane)

Atactic poly(vinyl cyclohexane) is soluble at room temperature in hydrocarbons such as n-hexane, n-heptane, cyclohexane, decalene, benzene, toluene, and xylene; in chlorinated hydrocarbons such as chlorobenzene, bromobenzene, chloroform, carbon tetrachloride, 1,2-cis-dichloro ethylene, and 1,2-$trans$-dichloro ethylene; and in tetrahydrofurane. It is insoluble in dioxane, diisopropyl ether, and diethyl ether; in alcohols such as methanol, ethanol, propanol, i-propanol, cyclohexanol, and benzylalcohol; in esters such as methylacetate, ethylacetate, and methylpropionate; and in ketones such as acetone, butanone, pentanone-2, heptanone-2, and 3-methylheptanone-2.

Glass Temperature·of Polystyrene

Glass temperatures of atactic polystyrenes were reported to be between 80 and 101°C: 80 to 82 (*10*), 80 to 100 (*11*), 82 to 100 (*8b*), 82 (*12*), 83 (*13*), 87 to 99 (*14*), 90 (*15*), 90 to 100 (*16*), 100 (*17,18*), and 101°C (*19*). A limiting value is approached with increasing molecular weight at 100°C (*20*). Removal of residual monomer shifts the glass temperature T_g from 82 to 100°C (*8b*). Isotactic polystyrenes exhibit glass temperatures between 80 and 100°C (*11*) or 90°C (*19*), respectively. No influence of crystallinity on T_g was detected (*19*).

As the literature gave no reliable basis for the comparison of glass temperatures of polystyrene and poly(vinyl cyclohexane), we repeated the determination of glass temperatures of atactic polystyrene. DTA data were analyzed in terms of onset and extrapolated
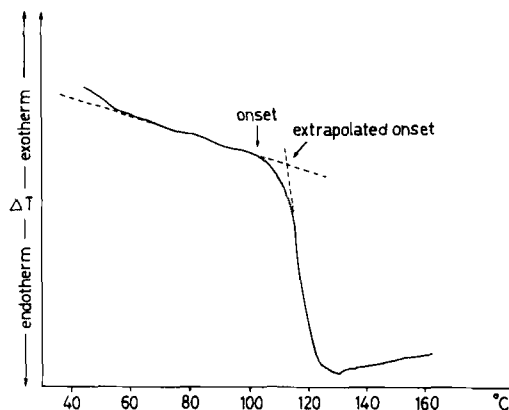

FIG. 1. DTA diagram of freeze-dried polystyrene (20 mg, air, starting temperature $-70°C$, heating velocity 20 deg/min, $\Delta T = 0.2°C/in.$).

TABLE 3

Apparent Glass Temperatures of Polystyrene V as a Function of Sample Treatment and Heating Velocity v

| | $(T_g)^{app}$, °C | | | |
| | Original beads | | Freeze-dried material | |
v, deg/min	onset	Extrapolated onset	Onset	Extrapolated onset
3	100	101.5	101	102
5	100	102	100	103
7	99.5	102	—	—
10	100	104	100	105
	100	105		
15	100	105.5	100	?
20	99	105.5	100	112
	101	106.5		
	101	106		
25	100	106.5	—	—
30	100	107	?	114

onset (cf. Fig. 1) and are collected in Table 3. This analysis was carried out because there seems to be considerable uncertainty in the literature about the evaluation of glass temperatures from DTA diagrams [cf. (27)]. To remove the last traces of monomer and other volatile impurities, the sample was freeze-dried from benzene solution and again run with different heating velocities v. The data show that the glass temperatures via "onset" data are independent of heating velocity and sample treatment (Table 3 and Fig. 2). The glass temperatures via "extrapolated onset" data are apparent glass temperatures, are increasing with increasing heating velocity, and are higher with the freeze-dried sample. Extrapolation to zero heating velocity gave the same glass temperature as the onset data $(T_g = 100°C)$, however.
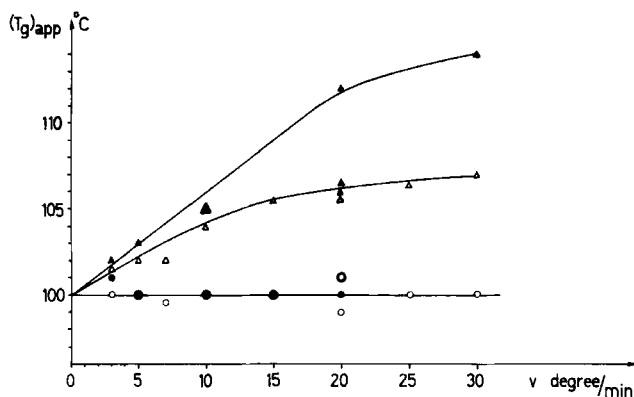

FIG. 2. Dependence of apparent glass temperatures $(T_g)_{app}$ of polystyrene from heating velocity v and sample preparation (O,△, beads; ●,▲, freeze-dried sample; O,●, onset; △,▲, extrapolated onset).

Glass Temperatures of Hydrogenated Polystyrenes

The glass temperature of poly(vinyl cyclohexane) was reported to be 90°C (15) (atactic) and 0°C (21) (isotactic). Very different melting points were given for isotactic poly(vinyl cyclohexane): 230 (15,16), 240 (22), 300 (23), 305 (24), 320 to 325 (21), 360 to 370 (25) [dehalogenation and hydrogenation of isotactic poly(halogen styrenes)], 372 (15), 370 to 375 (25), and 383°C (26). Decomposition of isotactic poly(vinyl cyclohexane) was reported to occur above 260°C (28) [but see (26)]. Differences may well be

TABLE 4

Glass Temperatures of Hydrogenated Polystyrenes as a Function of the Degree of Hydrogenation and Heating Velocity in DTA Experiments

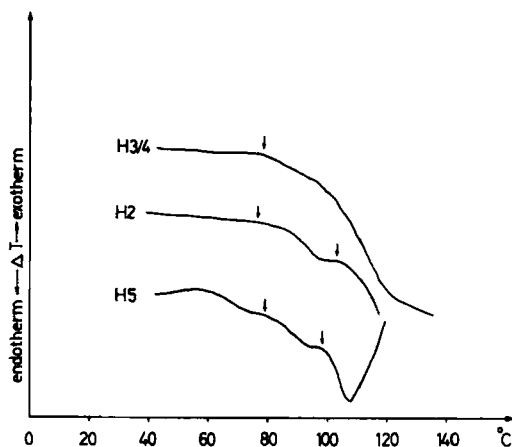| v, deg/min	H3/4(100%), $(T_g)_H$	Sample and degree of hydrogenation			
		H2(75.8%)		H5(42.8%)	
		$(T_g)_H$	$(T_g)_S$	$(T_g)_H$	$(T_g)_S$
10	80	76	100	74	95
		76	102		
		76	104		
15	—	74	105	75	95
20	80	76	100	78	100
		76	102	73	100
25	—	—	—	?	100
30	80	76	100	74	98
				79	98
	80	76 ± 1	102 ± 2	76 ± 2	98 ± 3

FIG. 3. DTA diagrams of hydrogenated polystyrenes. Heating velocity 20 deg/min (H2, H3/4) or 30 deg/min (H5). Glass temperatures are marked by arrows.

due to the different chemical constitutions of the samples, for example, cyclohexane rings incorporated in the chain (26).

Our own experiments were undertaken with polystyrenes of different degrees of hydrogenation using the onset data of DTA diagrams with different heating velocities (Table 4 and Fig. 3). The 100% hydrogenated sample H3/4 showed a glass temperature of 80°C. Two transition temperatures, $(T_g)_H$ and $(T_g)_S$, were present with the incompletely hydrogenated samples H2 and H5. The lower temperature, $(T_g)_H = 76°C$, was considered to be due to poly (vinyl cyclohexane) sequences, the higher one, $(T_g)_S$ (102, respectively, 98°C), to polystyrene sequences. This points either to a mixture of unreacted polystyrene molecules besides completely hydrogenated molecules or to a block character of the molecules. A mixture is more likely, as shown by the hydrogen uptake as a function of time.

CONCLUSIONS

During the hydrogenation process the active centers of the catalyst are clogged by the polymer, as could be shown by the time dependence of hydrogen uptake, as long as no higher temperatures are used. The resulting polymer is thus a mixture of completely hydrogenated and completely unreacted polystyrene. This view is confirmed by the existence of two glass temperatures in the incomplete hydrogenated samples, the values of which are independent of the degree of hydrogenation.

The glass temperature of the atactic poly(vinyl cyclohexane) is 20°C lower than that of atactic polystyrene. π-π interactions are thus more important than chain stiffening owing to the more bulky cyclohexane ring.

Acknowledgment

REFERENCES

1. H.-G. Elias and O. Etter, *J. Macromol. Chem.*, 1, 431 (1966).
2. H. Ohlinger, in *Polystyrol* (H. Kainer, ed.), Springer, Berlin, 1955, p. 8.

3. C. Kelber, *Ber. Deut. Chem. Ges.*, **49**, 55 (1916); *Ber. Deut. Chem. Ges.*, **57**, 136 (1924).
4. H. Adkins, *J. Am. Chem. Soc.*, **70**, 695 (1948); H. R. Billica and H. Adkins, *Org. Syn.*, **29**, 24 (1949).
5. H. Staudinger, E. Geiger, and E. Huber, *Ber. Deut. Chem. Ges.*, **62**, 263 (1929).
6. H. Staudinger and V. Wiedersheim, *Ber. Deut. Chem. Ges.*, **62**, 2406 (1929).
7. A. J. Warner and D. K. Keel, U.S. Pat. 2,726,233 (1953), International Telephone & Telegraph Corp.; ref. in *Chem. Zbl.*, **1956**, 9312.
8. R. H. Boundy and R. F. Boyer (eds.), *Styrene, Its Polymers, Copolymers, and Derivatives*, Reinhold, New York, 1952 (a) p. 689, (b) p. 598.
9. A. Steinhofer, R. Polster, and H. Friedrich, Ger. Pat. 1,131,885 BASF (1962).
10. W. J. Roff, *Fibers, Plastics and Rubbers*, Academic Press, New York, 1956.
11. F. Danusso and G. Polizzotti, *Chim. Ind. (Milan)*, **44**, 241 (1962).
12. R. F. Boyer and R. S. Spencer, *J. Appl. Phys.*, **15**, 398 (1944).
13. J. J. Keavney and E. C. Eberlin, *J. Appl. Polymer Sci.*, **3**, 47 (1960).
14. K. H. Illers, *Ber. Bunsenges Physik. Chem.*, **70**, 353 (1966).
15. F. P. Reding, cited in R. F. Boyer, *Rubber Chem. Technol.*, **36**, 1303, 1311 (1963).
16. B. Ke (ed.), *Newer Techniques of Polymer Characterization*, Wiley (Inter-science), New York, 1964, p. 357.
17. L. E. Nielsen, *The Mechanical Properties of Polymers*, Reinhold, New York, 1962, Table 2.4.
18. Data quoted by F. Würstlin in *Die Physik der Hochpolymeren*, Vol. III (H. A. Stuart, ed.), Springer, Berlin, 1955, p. 671.
19. S. E. Petrie, in *Newer Techniques of Polymer Characterization* (B. Ke, ed.), Wiley (Interscience), New York, 1964, p. 396.
20. R. F. Boyer, *Polymer Preprints* **6**, 721 (1965).
21. E. A. Mushina, A. I. Perelman, A. V. Topchiev, and B. A. Krentsel, *J. Polymer Sci.*, **52**, 199 (1962).
22. N. G. Gaylord and H. F. Mark, *Linear and Stereoregular Addition Polymers*, Wiley (Interscience), New York, 1959, Table V-5, p. 484.
23. K. R. Dunham, J. Vandenberghe, J. W. H. Faber, and L. E. Contois, *J. Polymer Sci.*, **A1**, 751 (1963).
24. T. W. Campbell and A. C. Haren, Jr., *J. Appl. Polymer Sci.*, **1**, 73 (1959).
25. G. Natta and D. Sianesi, *Atti Accad. Naz. Lincei Rend. Classe Sci. Fis. Mat. Nat.*, **26**, 418 (1959).
26. A. D. Ketley and R. J. Ehrig, *J. Polymer Sci.*, **A2**, 4461 (1964).
27. H. Wilski, *Kolloid-Z.*, **210**, 37 (1966).
28. C. G. Overberger, A. E. Borchert, and A. Katchman, *J. Polymer Sci.*, **44**, 491 (1960).

Zusammenfassung

Ataktisches Polystyrol wurde unter verschiedenen Bedingungen hydriert. Bei unvollständiger Hydrierung ergibt sich ein Gemisch aus Polystyrol

und Polyvinylcyclohexan. Die Glasübergangstemperaturen wurden bei verschiedenen Bedingungen durch Differentiol thermoanalyse untersucht. Für Polystyrol ergab sich ein Wert von 100° und für Polyvinylcyclohexan 80°. Die Löslichkeit von Polyvinylcyclohexan in verschiedenen Lösungs-mitteln wurde bestimmt. Der Einfluss der DTA Methodik wurde unter-sucht.

Résumé

Le polystyrolène atactique a été hydrogené dans des conditions variées. L'hydrogénation incomplète produit un mélange de polystyrolène et de polyvinylcyclohexane. Les températures de transitions vitreuses ont été étudiées dans des conditions variées par la méthode d'analyse thermique différentielle et trouvées être 100°C pour le polystyrolène et 80°C pour le polyvinylcyclohexane. On donne la solubilité du polyvinylcyclohexane pour des solvants différents. L'influence des techniques d'évaluation par ATD a été étudiée.