

Effect of hydrogenation on dynamic mechanical relaxation 1. Atactic polystyrene

Hisayuki Nakatani^{a,*}, Koh-hei Nitta^a and Kazuo Soga^b

^aCenter for New Materials, Japan Advanced Institute of Science and Technology,
1-1 Asahidai, Tatsunokuchi, Ishikawa 923-12, Japan

^bSchool of Materials Science, Japan Advanced Institute of Science and Technology,
1-1 Asahidai, Tatsunokuchi, Ishikawa 923-12, Japan
(Received 5 June 1997; accepted 4 August 1997)

Dynamic mechanical behavior of a series of partially hydrogenated polystyrenes with various degrees of hydrogenation has been investigated. The primary relaxation process ascribed to glass transition shifts to higher temperatures and broadens with increasing degree of hydrogenation. There exist two secondary dispersions in a temperature range from 110 to 250 K. The frequency dependence of these relaxation processes and the molecular dynamics simulation suggest that the secondary relaxations are associated with the chair–chair flipping and oscillatory rotation of the cyclohexyl group. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: dynamic mechanical properties; hydrogenation; polystyrene)

INTRODUCTION

The hydrogenation technique has played an important role in the preparation of model polymers with controlled microstructure and molecular architectures^{1–4}. The hydrogenated polymers have the potential to be instrumental in investigating microstructure–properties relationships. In the circumstances, a number of investigators have prepared several types of polyolefins using hydrogenation techniques. Much attention has been focused on the hydrogenation of atactic polystyrene as a glassy polyolefin compound^{3–7}.

As compared with polystyrene, hydrogenated polystyrene, i.e., poly(vinyl cyclohexane), manifests a higher glass transition temperature^{4,6} and a lower density⁷ owing to the mobility and the bulkiness of the cyclohexyl substituent. The aim of the present work was to study the effects of hydrogenation on the glass transition process and the local molecular motion of the substituents. For this purpose, we prepared a series of hydrogenated atactic polystyrenes with various degrees of hydrogenation and examined the dynamic mechanical properties and morphology of these polymers. In addition, the molecular motion of cyclohexyl group was investigated by means of molecular dynamics simulations under a force field using a model with 50 monomer units.

EXPERIMENTAL

Materials

Atactic polystyrene (DIC2500) was commercially obtained from Dainippon Inc. Chemical Industry. The atactic polystyrene was purified by xylene–methanol precipitation prior to use. The silica-supported Ni catalysts (Ni(10wt%)SiO₂) were prepared by an incipient wetness technique using aqueous solutions of Ni(NO₃)₂·6H₂O (Nacalai Tesque Co.) and dried at 573 K for 2 h. Prior to

the hydrogenation reaction, the Ni/SiO₂ catalyst was reduced at 573 K for 2 h. Methylcyclohexane (Nacalai Tesque Co.) was distilled over calcium hydride before use.

The hydrogenation reaction of the atactic polystyrene (aPS) was conducted at 12 MPa using the Ni/SiO₂ catalyst in a 3.2% methylcyclohexane solution. The degree of hydrogenation was controlled by changing the reaction time and temperature. Details of the hydrogenation procedure are given in *Table 1*. The nomenclature used in this paper is as follows: e.g., HaPS56 is a hydrogenated atactic polystyrene with a degree of hydrogenation of 56 wt%. The resulting materials were dissolved in xylene to make a 1% solution and successively filtered to remove the catalysts. The filtrates were reprecipitated in a 15-fold excess of methanol, to which was added a small quantity of antioxidant, and the powder samples thus obtained were dried in a vacuum oven at 393 K for 40 h. The powder samples were pressed at 463 K under 10 MPa for 8 min and immediately quenched in an ice-water bath.

Sample characterization

The molecular weight and molecular mass distribution of hydrogenated atactic polystyrenes (HaPS) were determined via a high temperature gel permeation chromatography instrument (Senshu Scientific SSC-7100) using *o*-dichlorobenzene as the solvent at 403 K (see *Table 1*).

Differential scanning calorimetry (d.s.c.) measurements were conducted using a Mettler DSC 820. The samples of ca. 10 mg weight were sealed in aluminum pans. The glass transition temperature T_g of the samples were measured at a heating rate of 20 K/min.

The degree of hydrogenation was determined by ¹H nuclear magnetic resonance (n.m.r.). The results are presented in *Table 1*. The 300 MHz ¹H n.m.r. spectra were recorded on a Varian Gemini 300 spectrometer at 298 K on 10% (w/v) solutions in CDCl₃. The existence of a cyclohexane ring was confirmed by ¹³C n.m.r. measurements.

* To whom correspondence should be addressed

Table 1 Characteristics of samples

Sample	Time ^a /h	Temp. ^b /K	Deg. of H ^c /wt%	$M_w \times 10^{-5d}$	M_w/M_n
aPS	—	—	—	2.1	2.4
HaPS8 ^e	40	458	8	1.2	2.2
HaPS27 ^e	24	463	27	2.0	2.8
HaPS56 ^e	78	458	56	1.8	2.4
HaPS62 ^e	48	463	62	1.5	2.2
HaPS95 ^f	48	463	95	1.6	2.5
HaPS100 ^g	78	463	> 98	1.8	3.2

^aReaction time

^bReaction temperature

^cDegree of hydrogenation. Calculated by ¹H-n.m.r.

^dMolecular weight of hydrogenated polystyrene

^eNi-cat*/g/polymer *g = 0.1

^fNi-cat*/g/polymer *g = 0.2

^gNi-cat*/g/polymer *g = 0.3

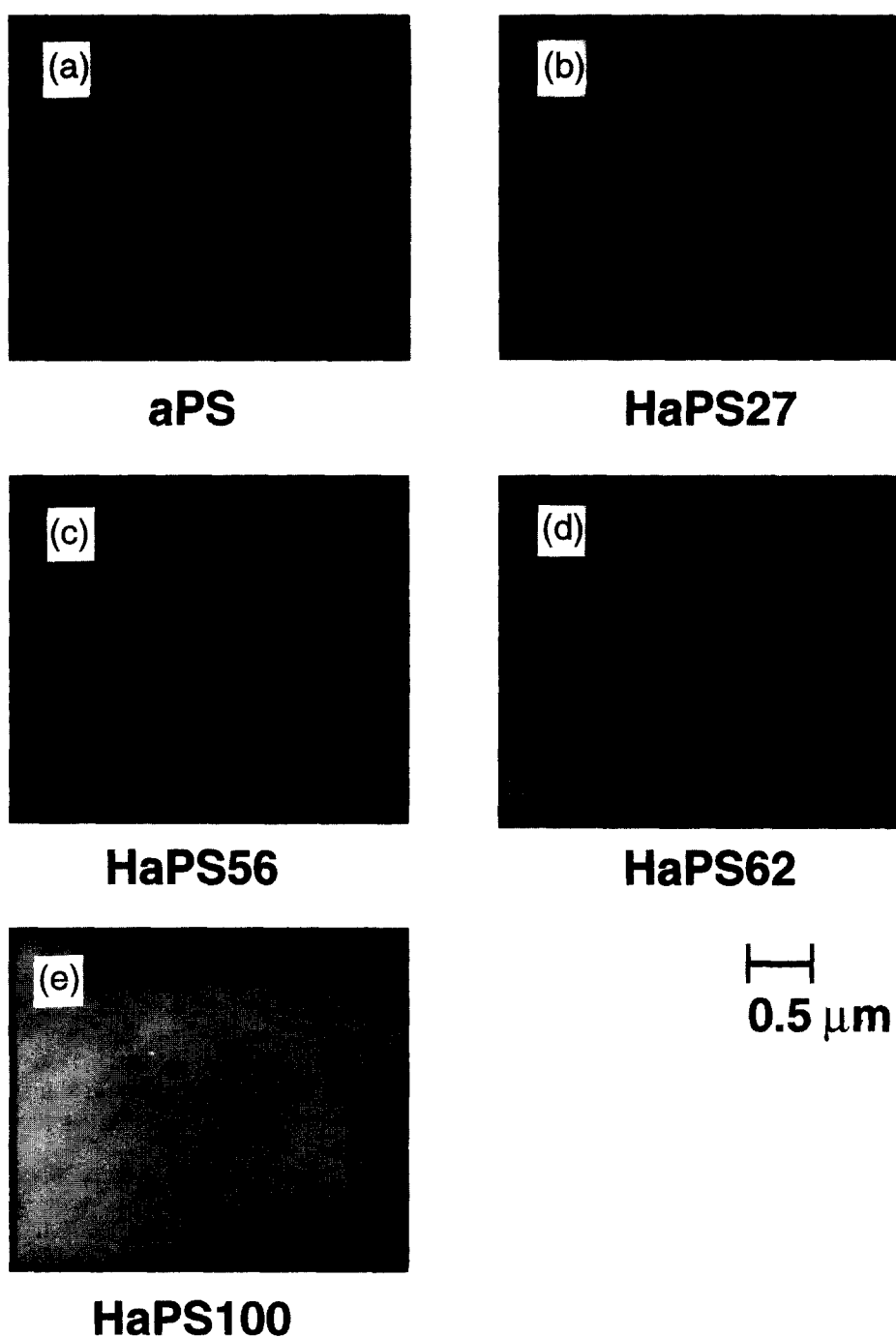


Figure 1 Transmission electron micrographs of atactic polystyrene and hydrogenated atactic polystyrene with various degrees of hydrogenation. The number behind HaPS denotes the percentage degree of hydrogenation

The morphology of HaPS films was examined with a Hitachi H-7100 transmission electron microscope (t.e.m.). The ultrathin films were sectioned into slices with an ultramicrotome at 133 K. Then, the ultrathin films were stained by ruthenium tetroxide for 12 h.

The small angle light scattering (s.a.l.s.) measurement was carried out with a commercial light-scattering photometer (IST Planning SALS-100S) using a He-Ne laser. The detector used was a photomultiplier that could rotate horizontally around a sample to scan scattering angles from 0 to 20°. The thickness of the samples used for the s.a.l.s. measurements was approx. 50 μm .

Dynamic mechanical properties were investigated using a dynamic mechanical analyser (Rheology Co., Ltd. DVE V-4) on sample specimens of the following dimensions: length 15 mm, width 3 mm, and thickness approx. 300 μm . The temperature dependence of the dynamic tensile moduli,

storage tensile modulus E' and loss modulus E'' , were measured between 113 and 463 K at a constant frequency of 50 Hz and a heating rate of 2 K/min.

RESULTS AND DISCUSSION

Structure and morphology

Figure 1 shows the transmission electron micrographs in which dark regions correspond to the stained aPS phase, whereas bright regions correspond to the HaPS phase. As shown in Figure 1, the HaPS62 and the HaPS56 exhibit a phase-separated morphology in which aPS domains are dispersed within a HaPS matrix. In the case of HaPS27, phase inversion seems to occur. Other samples showed homogeneous morphology.

The molecular aggregation state of HaPS was examined using a small-angle light scattering (s.a.l.s.) technique. As shown in Figure 2, the Debye-Bueche model is found to be applicable only for partially hydrogenated samples such as HaPS27, HaPS56, and HaPS62, suggesting that these partially hydrogenated samples form heterogeneous morphology. The correlation lengths, corresponding to the average distance between neighboring domains or phases⁸, can be derived from the ratio of slope to intercept. The resulting correlation lengths are as follows: 0.95 μm in HaPS27, 0.79 μm in HaPS56, and 0.65 μm in HaPS62. These results are consistent with those of t.e.m. observations.

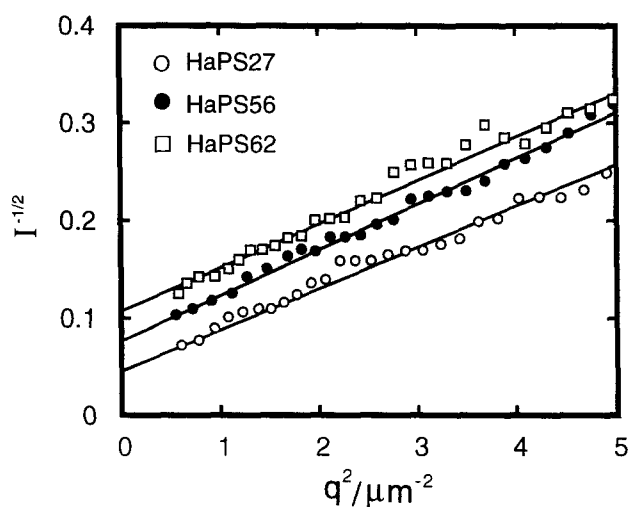


Figure 2 Debye-Bueche plots of partially hydrogenated polystyrene films

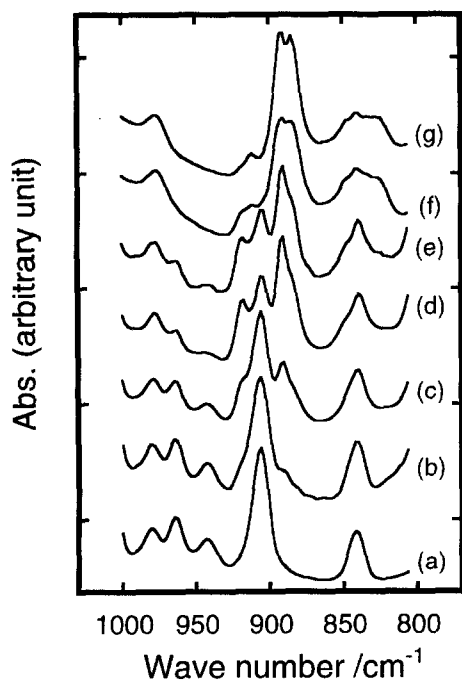


Figure 3 Infrared spectra in the 800–1000 cm^{-1} region of hydrogenated atactic polystyrene (HaPS). (a) aPS; (b) HaPS8; (c) HaPS27; (d) HaPS56; (e) HaPS62; (f) HaPS95; (g) HaPS100

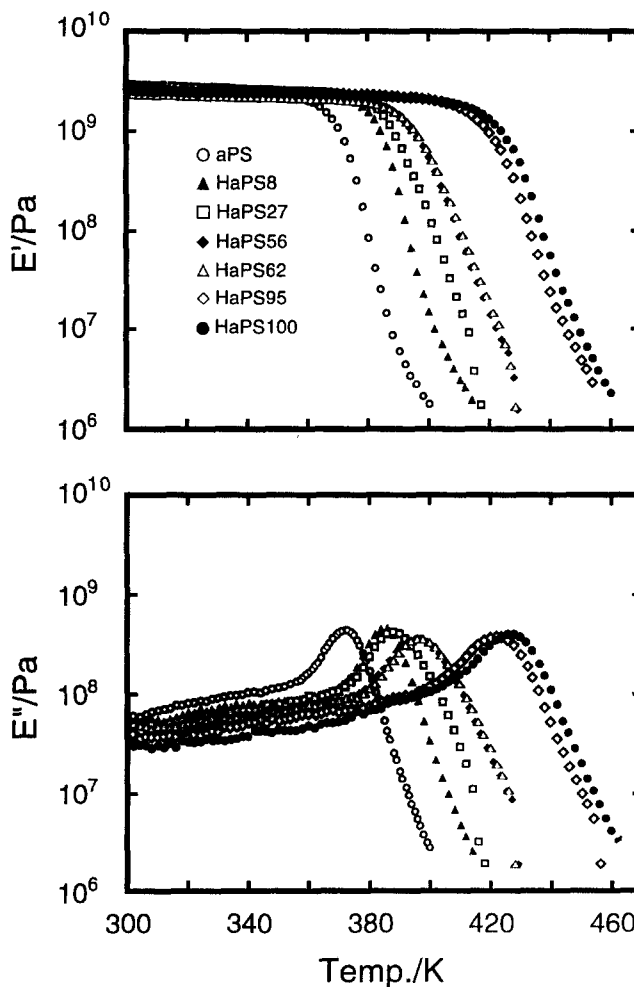


Figure 4 Temperature dependence of mechanical storage modulus (E') and loss modulus (E'') in the region of primary dispersion for all the films

Fourier transformation infrared (FTi.r.) spectra were examined at a resolution of 2 cm^{-1} with a JASCO FT-IR 500 spectrometer. Figure 3 confirms that the intensity of the 890 cm^{-1} band assigned to the cyclohexyl ring⁶ increases with increasing degree of hydrogenation. It should be noted here that the 918 cm^{-1} band, which is assigned to the aromatic ring CH out-of-plane deformation, distinctly presents for the partially hydrogenated samples such as HaPS27, HaPS56, and HaPS62. This indicates that the steric environment of polystyrene sequence^{9,10} in these partially hydrogenated samples is different from that of other samples owing to their phase-separated or heterogeneous morphology.

Primary relaxation process

Figure 4 shows the temperature dependence of E' and E'' for the various hydrogenated polystyrene samples in the temperature range from 300 to 470 K. The sharp peak is the primary dispersion (designated as α dispersion) associated with the relaxation from glass-like to rubber-like

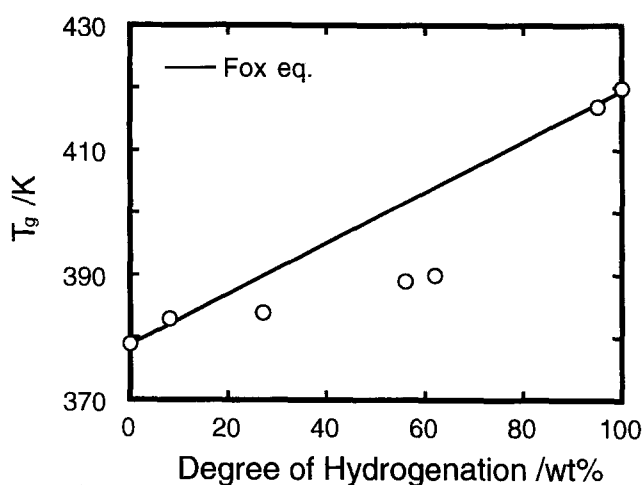


Figure 5 Glass transition temperature obtained from DSC measurements plotted against degree of hydrogenation. The solid line denotes the Fox relation¹¹

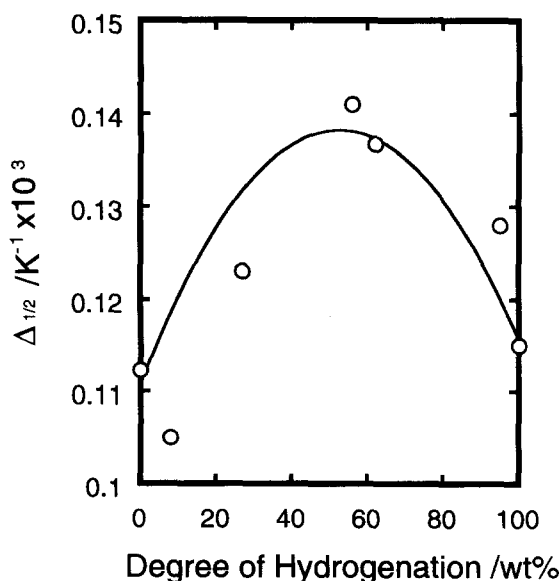


Figure 6 Half-width of E'' peak of the primary dispersion plotted against degree of hydrogenation

consistency; it shifts to higher temperatures with increasing degree of hydrogenation. The peak shift is attributed to the reduction in main chain co-operative movement resulting from more sterically hindered cyclohexyl group than in the case of aromatic group. In Figure 5, are plotted the glass relaxation temperatures T_g against the degree of hydrogenation, where the solid line represents the theoretical values calculated from the Fox equation¹¹, which is appropriate for random copolymers and/or miscible blends. The T_g s of partially hydrogenated samples are found to deviate from the Fox equation, suggesting overlapping of two α relaxation processes ascribed to the styrene-rich phase and to the cyclohexane-rich phase. Indeed, it is found that the glass transition peak broadens for the partially hydrogenated samples.

In order to characterize the overlapping behavior of the primary dispersion, we examined the half-width of the dispersion, which was determined by the width at half-maximum in the plot of E'' versus $1/T$. The resulting values of the half-width $\Delta_{1/2}$ are plotted in Figure 6. It has been found that partially hydrogenated polystyrene samples having multi-phase morphology show a higher value of $\Delta_{1/2}$ than pure polymers.

Secondary relaxation process

It has been found that the hydrogenated samples showed two relaxation dispersions designated as β and γ between 110 and 250 K (see Figure 7). With increasing degree of hydrogenation, both β and γ peaks undergo gradual

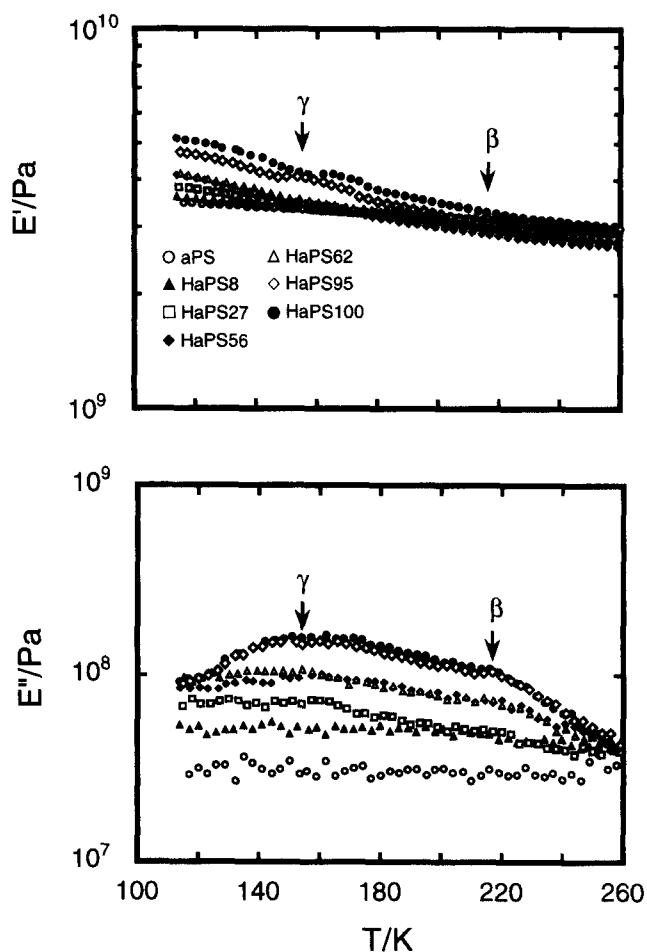


Figure 7 Temperature dependence of mechanical storage modulus (E') and loss modulus (E'') in the region of secondary dispersion for all films

increases, but the loci of both peaks are not changed. The dispersions are scarcely evident for aPS. These results demonstrate that both low-temperature relaxation processes are associated with specific internal or local molecular motions of cyclohexane group. For the purpose of obtaining the activation energies of both β and γ relaxations, the viscoelastic curves are superposed into relative master curves by means of horizontal shifts along the logarithm axis of angular frequency. The measuring frequency ranged from 0.1 to 200 Hz. The master curve for the β process was constructed by shifting the curves at temperatures between 203 and 253 K and the reference temperature was taken to be 223 K (Figure 8). In addition, the master curve for the γ process was constructed by shifting the curves at temperatures between 113 and 188 K and the reference temperature was taken to be 166 K (Figure 9). The semi-logarithmic plot of the shift factor a_T thus obtained against $1/T$ yields the apparent activation energy ΔH , giving 49 kJ/mol for the β process and 36 kJ/mol for the γ process. The ΔH value as well as the temperature location of the β process is identical to those of chair-chair flipping of cyclohexane ring in poly(cyclohexyl methacrylate) identified by Heijboer¹².

For cyclohexyl groups attached to a polymer chain, a very specific internal molecular motion can be postulated to account for the γ loss peak. In the present work, the

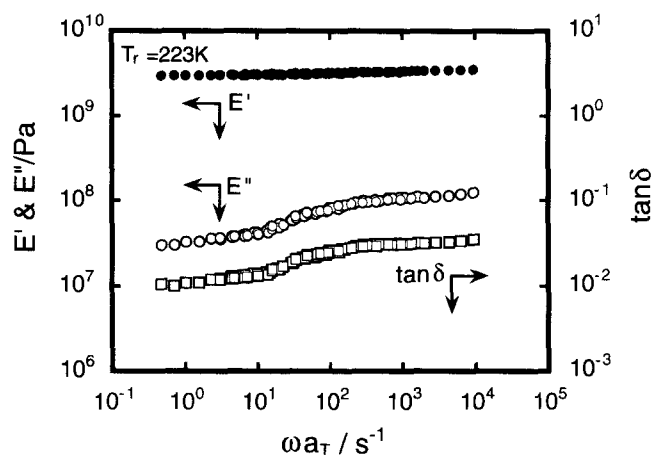


Figure 8 Logarithmic plots of the storage modulus (E'), loss modulus (E''), and $\tan \delta$ against frequency for HaPS100 film reduced to 223 K

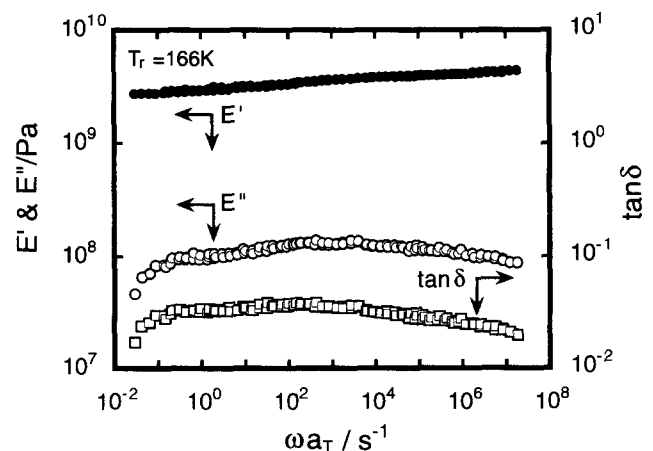


Figure 9 Logarithmic plots of the storage modulus (E'), loss modulus (E''), and $\tan \delta$ against frequency for HaPS100 film reduced to 166 K

molecular motion of cyclohexyl group was studied by means of molecular dynamic simulation using InsightII® (Biosym Tech. Ltd), the MSI computer program, in which the CFF91 force field is chosen. The stereoregularity of pre-hydrogenated polymer, aPS, was meso diad $[m] = 0.6$ determined by ¹³C-n.m.r.. Assuming that the stereoregularity was little changed by this hydrogenation reaction, the model polymer having meso diad $[m] = 0.6$ configuration was used in simulation. A rotational movement of a central cyclohexyl group in the model of 50 monomer units was examined via the following procedure: (1) the optimization of conformational energy employed a CFF91 force field; (2) the potential energy profile for rotation of a cyclohexyl group was generated by scanning the entire $-180-180^\circ$ conformation energy space for the torsion angle between main chain and cyclohexyl group in increments of 5° .

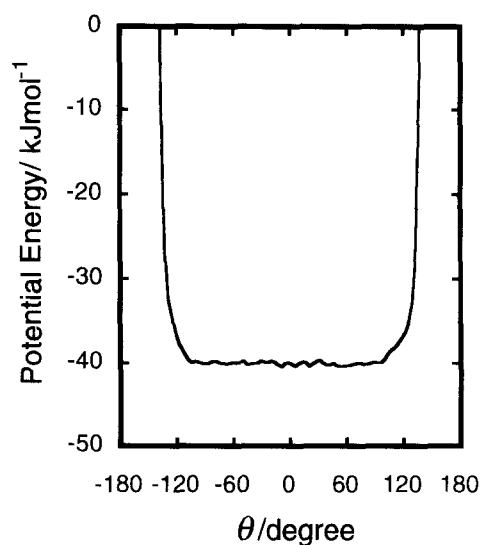


Figure 10 Potential energy profiles for torsion angles between the backbone chain and cyclohexyl side group

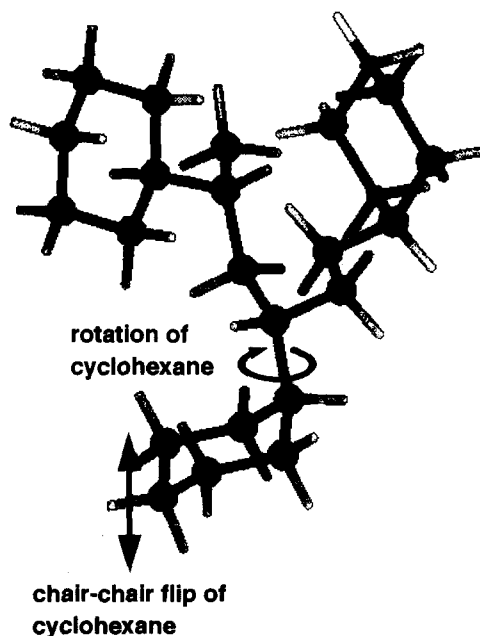


Figure 11 The schematic feature of the secondary relaxations of the β and γ process

Figure 10 shows the potential energy profiles for the rotation, i.e., torsion angles between the backbone chain and cyclohexyl side group. These results apparently indicate that there is sterical hindrance for rotational movement of the cyclohexyl group. Thus, the potential energy profile shows only one minimum of potential energy in a limited range of $\pm 120^\circ$, giving *ca.* 40 kJ/mol depth, which is comparable with the activation energy of the γ process. According to Shimizu *et al.*¹³, the oscillatory or vibrational relaxation process can be arisen from the heat-transfer mechanism between a vibrational degree of freedom and other ones working as a heat bath. Therefore, the oscillatory relaxation process is not required to overcome the potential barrier and may be associated with energy-absorbing transitions from a higher vibrational level. Consequently, the γ process can be associated with a molecular process responsible for the rotational oscillatory motion or oscillatory rotation of cyclohexyl groups around single bonds linking to the backbone chains, as speculated by Frosini *et al.*⁵.

The schematic feature of the secondary relaxations of the β and γ processes is illustrated in Figure 11.

CONCLUSIONS

In the present study, we have examined the effects of cyclohexyl content on the dynamic mechanical relaxation for hydrogenated polystyrene at various degrees of hydrogenation. It was found that the partially hydrogenated polymers form a phase-separated morphology which affects the shape and loci of the primary dispersion ascribed to the glass transition. Moreover, it was found that the

hydrogenated polystyrenes show the secondary relaxation ascribed to cyclohexyl side-group in the low temperature. The dispersion in the higher temperatures is associated with chair–chair flip motions of the cyclohexyl group, and the lower-temperature relaxation peak involves various specific vibrational modes including oscillatory rotation of the cyclohexyl group around a bond between the substituent and the backbone chain.

REFERENCES

1. Mays, J., Hadiichristidis, N. and Fetters, L. J., *Macromolecules*, 1984, **17**, 2723.
2. Bates, F. S., Rosedale, J. H., Bair, H. E. and Russell, T. P., *Macromolecules*, 1989, **22**, 2557.
3. Gehlsen, M. D. and Bates, F. S., *Macromolecules*, 1993, **26**, 4122.
4. Krishnamoorti, R., Graessley, W. W., Balsara, N. P. and Lohse, D. J., *Macromolecules*, 1994, **27**, 3073.
5. Frosini, V., Magagnini, P., Butta, E. and Baccaredda, M., *Kolloid-Z. Z. Polym.*, 1966, **213**, 115.
6. Abe, A. and Hama, T., *Polym. Lett.*, 1969, **7**, 427.
7. Gehlsen, M. D., Peter, A., Weimann, F. S., Bates, F. S., Harville, S., Mays, J. W. and Wignall, G. D., *J. Polym. Sci.*, 1995, **33**, 1527.
8. Khabatta, F. B., Warner, F., Russell, T. and Stein, R. S., *J. Polym. Sci. Polym. Phys. Ed.*, 1976, **14**, 1391.
9. Kobayashi, M., Nakaoki, T. and Ishihara, N., *Macromolecules*, 1989, **22**, 4377.
10. Auriemma, F., Petraccone, V., Poggetto, F. D., De Rosa, C., Guerra, G., Manfredi, C. and Corradini, P., *Macromolecules*, 1993, **26**, 3772.
11. Fox, T. G., *Bull. Am. Phys. Soc.*, 1956, **1**, 123.
12. Heijboer, J., *Kolloid Z.*, 1960, **171**, 7.
13. Shimizu, K., Kawamura, Y. and Wada, Y., *Rep. Prog. Polymer Phys. Japan*, 1972, **15**, 301.