Glass transition of atactic polystyrene with less chain entanglements

Q. Dai [1], Y. Lu [1], G. Xue [1], Y. T. Liao [2]

[1] Morden Analytical Center, The State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, China
[2] Department of Textile Engineering, National Taipei Institute of Technology, Chung-Hsiao E. Road, Taipei, Taiwan

Summary
    Atactic polystyrene was dissolved and refluxed in benzene keeping the polymer concentration well below the critical concentration C^* value for chain overlap. After rapid freezing of the solution by injecting it directly into liquid nitrogen, the solvent was sublimated so that the expanded chain coils with few entanglements could be obtained. T_g for this material was found to be 11 K lower than the normal polystyrene even after annealing up to 470 K. Comparison of the infrared spectra shows some conformational differences between the freeze-dried and the normal PS. Upon shock-cooling and subsequent freeze-drying, all vibrational bands appear much sharper, indicating an increase in structure regularity.

Introduction
    It has been assumed that rapid freezing of a polymer solution well below the critical overlap concentration C^*, followed by sublimation of the frozen solvent, leads to a collapse of the individual molecular chains into spherical globules with no significant chain entanglement. [1] It has also been expected that the glass transition of polymer microparticles which contain only one or a few macromolecule chains to be different from the normal polystyrene. However, annealing these particles at or above their glass transition (T_g) could shift T_g to that similar to the ordinary PS. De Gennes has pointed out that in single chain systems, the requirement of adequate space filling necessarily implies that the polymer chains adopt a highly compact conformation [2]. On the other hand, polymer chains can expand in a very dilute solution. We injected a very dilute solution of polystyrene directly into liquid nitrogen so that the solution was frozen in a fraction of second. The expanded polymer coils would be frozen before shrinkage and are expected to maintain their expanded shape in

the solid state since the freezing speed is extremely fast. After subliming the solvent, PS powder with expanded coils could be obtained. The question then arises as to whether PS glass composed of such expanded coils differ in any way from ordinary PS glasses that are composed of a large amount of interpenetrating and entangled random coils. The purpose of this communication is to report some experimental differences in thermal and spectroscopic properties of these different types of PS and to propose an explanation for these differences in terms of chain entanglement and comformational relaxation.

Experimental Section

Monodisperse PS with molecular weight of 3.1×10^5 and dispersity of 1.04 was dissolved in purified cyclohexane or benzene to make 0.04% solution and refluxed for 6 hr. After rapid freezing the solution by injecting it directly into liquid nitrogen, the frozen solvent was then sublimed in vacuum. The remaining polystyrene powder, designated as the freezing-dried PS, was then kept under vacuum for one week at room temperature to evaporate the solvent residual. This is an important procedure since the remaining solvent inside the polymer powder might act as a plasticizer and thus lower down the observed glass transition temperature[3]. The dried PS was examined by the use of a FT-IR spectrometer (Nicolet FT-TR 170 SX). Differential scanning calorimetry was run on a Perkin-Elmer Model DSC-2C system. The heating rate was 10 °C min^{-1} while a nitrogen gas purge was used.

Result and Discussions

An interesting difference between the shock-cooled and subsequent freeze-dried PS from its very dilute solution in benzene and the normal PS with random coils could be observed in the DSC results as shown in Figure 1. For the treated PS, the DSC measuring procedure was as follows: the sample was first scanned from 290 to 430 K as shown in curve A, then followed by air cooling to 290 K. The second scan from 290 to 430 K made curve B. The sample was then cooled to 290 K and to start the third scan to 470 K (curve C). And the fourth scan was performed to make curve D. The ordinary PS was scanned in the same rate to make curve E. The "ordinary" PS means a sample identical to the treated ones in every respect but the shock-cooling and subsequent freeze-drying. All DSC results were summarized in Table 1.

Table 1. The glass transition temperature of freeze-dried PS from 0.04% benzene solution after annealing at 430 K

PS samples freeze-dried from	Glass transition temperature
Second scan (curve B)	92 °C
Third scan (curve C)	92 °C
Fourth scan (curve D)	102 °C
Ordinary PS	103 °C

ENDO

(A)

(B)

(C)

(D)

(E)

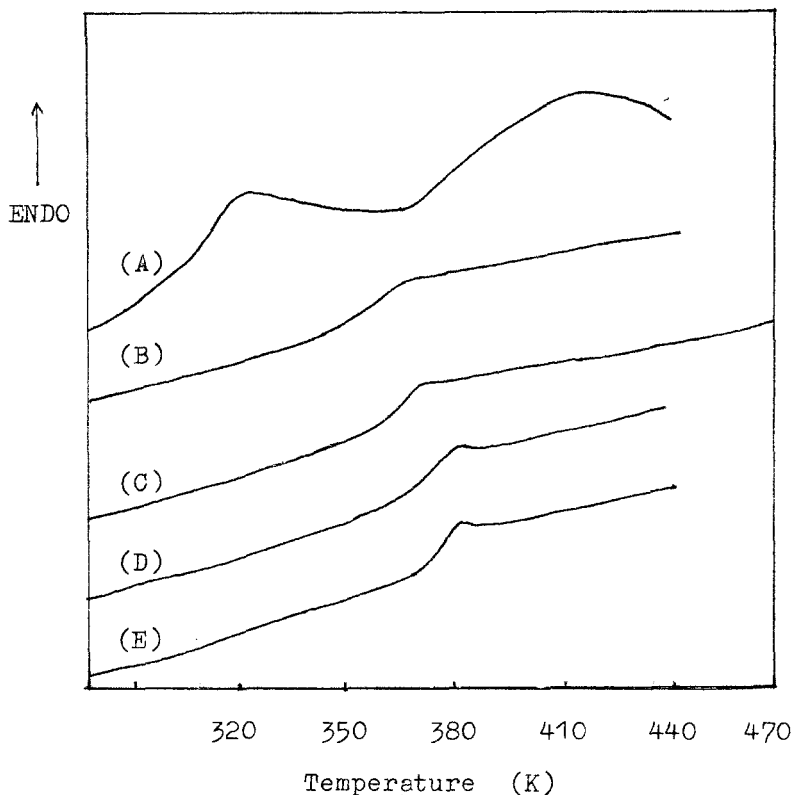320   350   380   410   440   470

Temperature   (K)

Figure 1. DSC curves of freeze-dried PS from 0.04% benzene
solution (A-D) and an ordinary PS (E)
(A) the first scan from 290 to 430 K;
(B) the second scan from 290 to 430 K;
(C) the third scan from 290 to 470 K;
(D) the fourth scan.

Figure 1 shows that the virgin expanded PS coils has a very
low apparent glass transition (T_g) temperature. Annealing the
sample at above T_g can shift T_g to higher   temperature. The
virgin material prepared by the present procedure is in a
non-equilibrium state, then on heating it is expected that
thermal changes will be seen in the DSC experiment as a sample
goes to its equilibrium condition. The apparent T_g in Figure

1(A) is not a glass transition process in the usual sense.
After two scans have been applied, the DSC behavior of the
treated PS composed of expanded coils became nearly constant,
indicating that the sample reached the equilibrium state. In the
second and third scans, T_g is 11 K lower than the normal PS,
even after heating the treated PS up to 430 K. However, the DSC
curve D scanned after heating the sample to 470 K became
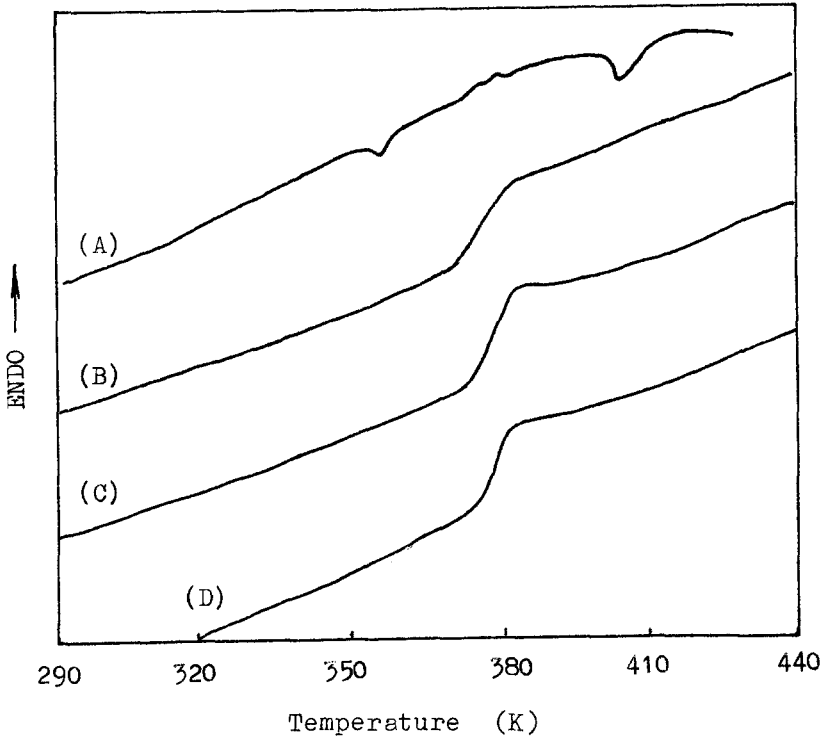similar to curve E which was recorded from an ordinary PS.

Figure 2. DSC curves of PS samples (A) the first scan of freeze-
dried PS from 1.0% solution; (B) the second scan; (C) the third
scan; (D) the scan for an ordinary PS.

Figure 2 shows DSC curves of PS glasses prepared by
shock-cooling and freeze-drying its benzene solution with
concentration of 1.0%-wt. The thermal behavior for the virgin
PS powder indicates that it was also in a non-equilibrium state.
However, the DSC curves of this sample became similar to the

normal PS after two scans had been applied, as shown in Figure
2C. DSC results for PS freeze-dried from varing solutions were
listed in Table 2.

Table 2.The glass transition temperature of freeze-dried PS from
solutions with varying concentration

PS samples freeze-dried from	Glass transition temperature
0.04% benzene solution	92 ^{o}C
0.50% benzene solution	102 ^{o}C
1.00% benzene solution	102 ^{o}C
0.04% cyclohexane solution	98 ^{o}C
Ordinary PS	103 ^{o}C

Single molecules of PS were isolated by the preparation
conditions described by Richardson 30 years ago, and by Kumaki
recently.[4] More recently Qian has put forward the concept of
local nematic interactions between neighboring chain segments in
the condensed state as a kind of cohesional entanglements
usually considered[5]. These cohesional entanglements are
important to the physical properties of polymers around T_g and
in their glassy state. When these entanglements lock into place
the long range cooperative conformational changes of the chain
that are necessary for rubber elasticity and so prevent their
occurrence, the polymer exhibits glassy state properties. During
heat, the cohesional entanglements will gradually melt or
disentangle, thus unlocking the long range cooperative motions.
The polymer transforms into its rubbery state. We expected that
the less of cohesional and topological entanglements exist, the
lower glass transition temperature it exhibits. As polystyrene
is dissolved in benzene to make a very dilute solution, the
chains expanded. Recently Qian has put forward another concept
of a concentration boundary of the solution from very dilute to
semi-dilute[6]. At and beyond the critical concentration value,
designated as C_s, the effect of inter-chain interactions begin
to be felt by the chains in solution. The C_s value of
polystyrene with M_w of 3×10^5 was about 0.05% measured by the
excimer fluorescence,[6] which is well below the chain
overlapping concentration C*. Based on this concept we propose
that the coils of polystyrene in a very dilute solution
(concentration below C_s) are expanded with few entanglements. If
this solution was frozen fast enough to maintain the expanded
shape, polystyrene composed of coils with few entanglements
could be obtained in solid state. This expanded coils are
expected to exhibit T_g lower than normal PS. However, the
conformational relaxation time of PS at 470 K must be short, and
the fourth scan in Fig. 1 is similar to that of an ordinary PS.
If the concentration of the polymer solution is above C_s coils
shrink before freezing resulted in considerable number of chain
entanglements. Then the polymer might show lower transition
temperature in its initial DSC curve due to the effect of

thermal history, but the T_g after annealing would be in the same level as an ordinary PS. This is the case of glass transition of the PS prepared by shock-cooling and freeze-drying method from its 1.0%-wt solution. Table 2 illustrates an influence of solvents to T_g as well as concentration dependence. For PS, benzene is a better solvent than cyclohexane. In solution of benzene, PS chain is more expanded, and thus the PS powder prepared by freeze-drying method is expected to have less entanglements. As a result, the freeze-dried PS from benzene solution shows lower glass transition than that from cyclohexane.

The FT-IR spectra of the shock-cooled and freeze-dried PS and a normal PS were measured and their band widths are shown in Table 3.

Table 3. The bandwidths (wavenumber) of IR spectra for a PS freeze-dried from 0.04% benzene solution and an ordinary PS

Band position (wavenumber)	3025	2920	1601	1492	1451	753	697
Freeze-dried PS	14	38	13	11	12	30	19
Ordinary PS	17	44	16	14	20	37	30

IR bands for the freeze-dried PS seem sharper than those for the ordinary PS. For example, the width of the 1451 cm^{-1} band appears to be significantly narrower, from 20 cm^{-1} full width at half maximum (FWHM) in the normal PS to 12 cm^{-1} in the freeze-dried sample. Upon shock-cooling and subsequent freeze-drying, all vibrational bands appear sharper, indicating an increase in structural regularity.

References

1. Liu C, Morawetz H. (1988) Macromolecules, 21: 515.
2. de Gennes, P-G. (1979) "Scaling Concepts in Polymer Physics", Cornell University, Chap.2.
3. Xue G, Lu Y, Shi G, Dai Q. (1994) Polymer, 35(4): 892.
4. Kumaki J. (1990) J. Polym. Sci.: Part B: Polym. Phys. 28: 105.
5. Qian R. Abstracts of China-U.K. Bilaternal Conference on Polymer Science, Beijing, China, April 1992.
6. Qian R, Cao T, Chen S, Bai F. (1983) Chinese Science, 12: 1080.