Study on the Glass Transition Process of Polymer System Using Differential Scanning Calorimetry and Fourier Transform Infrared Spectroscopy

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The change in the infrared spectrum of polymer samples with temperature and their differential scanning calorimetry (DSC) experimental results are analyzed. According to the van’t Hoff equation at constant pressure, the changes in the absorbance ratio corresponding to high and low vibrational states are calculated, and the apparent enthalpy differences of the vibration energy states transformation of the characteristic group can be obtained. From the experimental results, we can find that characteristic vibration modes of a chemical group in a polymer are under the influence of the glass transition process of the polymer with a different extent. The characteristic vibration modes of the same chemical group behave differently due to the influence of the polymer system at which the chemical moiety is situated.

Keywords Polymer, glass transition process, polystyrene, polyvinyl methyl ether, FTIR micro-spectroscopy

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Introduction

Glass transition is a common nature of all materials. Any material in the liquid state can be passing through the glass transition process and be frozen into the glass state (amorphous) as long as it is under the appropriate cooling rate.1–4 Although the essence of the glass transition still can not be really understood so far, the glass transition process has been used for production and in life service by people with a long history. Generally a glass transition denotes a transition from the equilibrium liquid state to a non-equilibrium solid state in a multibody system.5,6 This kind of transition does not involve a change of a thermodynamic, but a dynamic sense, at least within the time scope of the experimental observation. An amorphous solid is in a static state in a dynamic sense, and can not relax within the time scale of an observation.5,41 The typical glass forming material is an ultra-cooled molecular liquid at under the crystal transition temperature. The density of the molecular liquid increases with the decrease of temperature. For the same reason it is also found that the glass transition exists in a series of particle systems with different sizes, from a micellar suspension to a cell biology system. The glass transition is a general phenomenon of a multibody system and is very important in condensed matter physics.

There are lots of theoretical models concerning glass transitions like as free volume theory, dynamic frustrated theory, mode-coupling theory, energy landscape mode and twinkle fraction theory etc.8–12,28 All of these theoretical models can help us to understand the nature of the glass transition, and each model has its reasonable parts. But, because most of these theories can only explain part of the glass transition behavior, a consensus still can not be obtained concerning the theory of glass transitions.4,8,13 Developed in the 1970s, Fourier transform infrared spectroscopy (FTIR) is a kind of interferometric infrared spectroscopy. As a kind of effective method for the identification and characterization of molecular structure, FTIR is a measurement with a high signal-to-noise ratio, high resolution, high scanning speed and wide measurable wavelength range. Since its development, FTIR has been widely used in chemical research, energy exploration, astronomical observations, weather analysis, environment monitoring, geological research, drug development, agricultural management, and other fields of analytical determination.29–33 The molecular orientation arrangement and aggregation inside the material will change with the corresponding change of the external conditions (load, temperature, pressure, etc.). The microscopic structure change and its energy contribution in the macro process can be obtained through calculations and analysis of the infrared spectra using the dynamic FTIR technique. There is much research on polymer systems using the FTIR technique; some of them are combined with other techniques, such as NMR, X-ray etc., which show that FTIR is a powerful tool for analyzing the microscopic structure and energy change in, but not limited to, the polymer system.34–44 Yabe and coauthors studied the temperature effect on the molecular structure of spider’s capture thread by using microscopic FT-IR spectroscopy. By measuring the FT-IR spectral change from 40 to 220°C, they found that the molecular conformation of silk fiber protein of a capture thread is denatured at over 60°C, whereas the viscid droplets on a capture thread retain their structure.41 This work demonstrates the power of the microscopic FT-IR technique at the micro level. The glass transition process can commonly occur in a
polymer system along with the change of parameters, such as the temperature or pressure, which would be accompanied by a micro energy change and a conformation transformation.\textsuperscript{3,45-49}

This can help us to understand the glass transition process deeply through studying the micro change process of each group in the polymer system. But within the traditional analysis methods of thermodynamic and dynamic commonly used in the study of glass transition process, most popular method can only obtain macroscopic change information in the glass transition process of a polymer system. The functional molecular group, whether participating in glass transition process or not, can seldom be specified at the micro level. The molecular orientation change of the arrangement and aggregation inside the material cannot be recognized very well either. By analyzing the change of the infrared spectra of the polymer system with the temperature, we can study the participation information of different molecular moieties in a homopolymer (polystyrene, PS110K) and miscible polymer blend (polystyrene/polyvinyl methyl ether, PS110K/PVME), and we can also study the glass transition behavior of the polymer system, which can deepen our understanding on the polymer glass transition process at the micro level.

**Experimental**

Polystyrene was purchased from Polymer Source (Canada) with a molecular weight of about 110 kg/mol, and used directly after being purchased. Polyvinyl methyl ether with the molecular weight of 67 kg/mol, purchased from TCI Company (Japan) in a 50% methanol solution, was used after removing methanol. PS110K/PVME of 3:1 mass ratio was dissolved in a toluene solution at a concentration of 1% (g/ml), and was under magnetic stirring at room temperature for 24 h until completely dissolved.

After being rotary evaporated to be less solvent the solution was put in a vacuum oven at a temperature of 40°C under a vacuum for one week and at 60°C again for more than 48 h until its mass no longer changed. A transparent blend film was made, which showed that the blend of PS110K and PVME had good compatibility, which could also be seen from the DSC results. The DSC thermograms were measured using a Mettler-Toledo DSC1 STAR\textregistered calorimeter. The temperature and heat flow were calibrated before the measurement. All samples were heated up to 50°C above its glass transition temperature at a rate of 10°C/min in a nitrogen atmosphere and was kept at that temperature to eliminate the thermal history. Then, the polymer sample was cooled to a temperature of about 50°C below its glass transition temperature at a cooling rate of 1°C/min, and was kept at this temperature for 10 min before being heated up to 50°C above its glass transition temperature again at a rate of 1°C/min. Polymer samples were infrared sampled under the wave number range from 750 to 4000 cm\textsuperscript{-1}. The sampled data were analyzed using Bio-Rad Win IR Pro 2.7 Ver. software. According to the infrared spectrum of the polymer system in the process of temperature changing, the characteristic vibration absorption frequency peak of each functional group in molecule had a certain degree of shift. This shift reflects the fact that mutual transformation between two different energy states of the vibration pattern of a certain functional group in the molecule: corresponding to the upper state A at a higher temperature and the low-energy state B at a lower temperature.

The van’t Hoff equation can be used to well describe the relationship between the concentration of the upper state A (C_A) and the low-energy state B (C_B):\textsuperscript{33}

$$\dfrac{C_A}{C_B} = \exp \left( -\dfrac{\Delta G}{RT} \right),$$

where $T$ is the absolute temperature, $R$ is the gas constant and $\Delta G$ is the difference value of the Gibbs free energy between the two different energy states of the vibration pattern of a certain functional group in the molecule. $\Delta G$ can be described using the following formula:

$$\Delta G = \Delta H - T\Delta S,$$

In the above formula, $\Delta H$ and $\Delta S$ are the enthalpy and entropy differences of the two different energy states of the vibration pattern, respectively. The relation between the absorption strength $A_a$(upper state)/$A_b$(lower energy state) and the concentration of upper energy state (C_A)/ lower energy state (C_B) are as follows:

$$A_a = a_AC_b, \quad A_b = a_BC_a.$$

Here $a$ is the molar light absorption coefficient of the polymer sample and $b$ is the length of the light absorption path of the polymer sample. Then the following equation can be obtained:

$$\dfrac{A_aa_A}{A_ba_b} = \exp \left[ -\dfrac{\Delta H}{RT} + \dfrac{\Delta S}{R} \right].$$

Take the logarithm on both sides:

$$\ln \left( \dfrac{A_a}{A_b} \right) = -\dfrac{\Delta H}{RT} + \dfrac{\Delta S}{R} \ln \dfrac{a_A}{a_B}.$$

The amount of polymer sample is very small relative to the heating stage. Therefore, it is reasonable to think the enthalpy and entropy change between the different energy states of the vibrational mode of the sample molecules, can be neglected within a small temperature interval. Also, the molar light absorption coefficients of two different energy states have a similar relationship with temperature, so that the enthalpy change between two different energy states of the vibrational mode of polymer sample can be written as

$$\Delta H = R \frac{\partial \ln (A_A/A_B)}{\partial (1/T)}. $$
Results and Discussion

DSC thermograms measured for PS110K/PVME, pure PS110K, and pure PVME samples in the second heating process are reproduced in Fig. 1. It can be seen that the PS110K and PVME in toluene solvent form a miscible polymer blend with glass transition temperature between the glass transition temperatures of monomer. Due to the effect of self-concentration and the concentration fluctuation with the internal density inhomogeneity the PS110K/PVME blend has a broad glass transition temperature. The FTIR of PS110K (800 – 1000 cm–1) and PS110K/PVME (800 – 1000 cm–1) are shown in Figs. 2 and 3, respectively. It can be seen in Figs. 2 and 3 that the positions and shapes of the studied spectral bands change as a function of the temperature. For simplicity, the other FTIR bands of the polymer system are shown in Supporting Information (SI).

$$A_L/A_H$$ ($$A_L$$ stands for the light absorption strength and $$L/H$$ stands for light absorption frequency peak value of lower/higher energy state of a polymer sample) of the characteristic vibration modes in different polymer system analyzed in this work are listed in Table 1.

Table 1 L/H of the characteristic vibration modes in different polymer system analyzed in this work (Car stands for C in benzene ring)

| L/cm\(^{-1}\) | H/cm\(^{-1}\) | Vibration mode | Polymer system |
|-------------|-------------|----------------|---------------|
| 842.8       | 839.0       | Main chain C-C | PS110K        |
| 2850.9      | 2850.1      | Main chain C-C | PS110K        |
| 907.6       | 904.9       | Car-H out of benzene ring | PS110K |
| 943.6       | 941.3       | Car-H out of benzene ring | PS110K |
| 1804.8      | 1798.3      | Car-H out-of-plane bending | PS110K |
| 1944.8      | 1939.1      | Car-H out-of-plane bending | PS50K |
| 3001.9      | 3000.1      | Car-H stretch | PS110K |
| 3083.2      | 3079.0      | Car-H stretch | PS50K |
| 907.9       | 905.6       | Car-H out of benzene ring | PS110K/PVME |
| 946.4       | 944.0       | Car-H out of benzene ring | PS110K/PVME |
| 2851.0      | 2849.7      | Main chain C-C | PS110K/PVME |

It can be seen from Figs. 4 and 5 that at a temperature of 105°C the values of ln($$A_{839.0}/A_{839.0}$$) and ln($$A_{2850.1}/A_{2850.1}$$) both have an obvious turning point. The corresponding temperature (105°C) of the inflection point is very close to the glass transition temperature of PS110K, which indicates that the main chain C-C vibration of the homopolymer polystyrene is under the influence of the glass transition process. When the temperature is lower than the glass transition temperature of polystyrene, the main chain C-C vibration is weakened, subject to the constraint of the surrounding glassy environment, the electric dipole moment of C-C vibration is decreased and the frequency peak value of the vibration band changes. Reflecting on the infrared spectrum, there is a turning point near to the glass transition temperature of PS110K in its ln($$A_L/A_H$$) corresponding to the main chain C-C vibration band. This clearly shows that this vibration is affected by the system’s glass transition process.

Two typical plots of ln($$A_L/A_H$$) value versus the temperature corresponding to C-H out of the benzene ring surface vibration patterns of PS110K are represented in Figs. 6 and 7, respectively. The same as main chain C-C vibration mentioned above, C-H out of the benzene ring surface vibration also has an obvious turning point at a temperature of about 105°C, which is near to the glass transition temperature of PS110K. This indicates that the C-H out of the benzene ring surface vibration mode of homopolymer polystyrene is also affected by its glass transition
process. All of the significant vibration modes corresponding to the different groups in homopolymer polystyrene PS110K were analyzed by us (some shown in SI). It can be concluded that basically all of the significant vibration modes in the PS110K that we analyzed were affected by its glass transition process, but within different degrees. This may be due to the strong π–π interaction between the benzene ring in the polystyrene, which makes the molecular vibrations to be easily restricted by the interaction.

When the temperature is higher than the glass transition temperature of polystyrene, the percolated network structure inside the polystyrene begins to collapse, and the constraint on each group becomes weak. Thus the characteristic vibration corresponding to each group will be under the influence of the glass transition process. We also conducted the same test and analysis on other homopolymer polystyrenes with different molecular weights by means of variable-temperature FTIR micro spectroscopy (shown in SI). The same results were obtained as the PS110K, which illustrates the universality of the above conclusion. This conclusion is consistent with results in the literature and can help to deepen our understanding of the polymer glass transition at the micro level. Figures 8 and 9 show two typical plots of the ln(A_L/\A_H) value of C–H out of the benzene ring surface vibration pattern of PS110K in a miscible polymer blend PS110K/PVME versus the temperature, respectively. It can be seen from the above two figures that in the miscible blend PS110K/PVME, due to the interaction between the polystyrene and polyvinyl methyl ether, the ln(A_L/\A_H) value of C–H out of benzene ring surface vibration has an obvious turning point near 50°C (about the PS110K/PVME blend glass transition temperature), instead of 105°C, at which the turning point occurs within the ln(A_L/\A_H) value of homopolymer polystyrene. While in the blend, there is no apparent slope change at 105°C within the curves of the ln(A_L/\A_H) value of these two vibration modes versus temperature. These results suggest that the effect of the interaction on the polystyrene C–H out of the benzene ring vibration by the polyvinyl methyl ether is very significant. This is consistent with the conclusion that the hydrogen bonding interaction between the hydrogen atoms of polystyrene’s benzene ring and oxygen atoms in the polyvinyl methyl ether is the main cause of
the miscibility in the PS110K/PVME blend. Above the blend PS110K/PVME glass transition temperature, the constraint on the characteristic vibration of C–H in polystyrene benzene ring is very weak, and so in the blend there is no apparent slope change at 105°C (polystyrene glass transition temperature) within its curve of ln(A_L/A_H) value versus temperature.

While the characteristic vibration modes corresponding to the PS110K main chain in the blend PS110K/PVME have different features. It can be seen from Fig. 10, except for an obvious slope change near 50°C (PS110K/PVME blend glass transition temperature) within the curve of ln(A_L/A_H) value versus temperature, there is another turning point near 105°C (PS110K glass transition temperature). This shows that the characteristic vibration modes corresponding to the main chain of the polystyrene in PS110K/PVME blend are under the influence of the blend PS110K/PVME glass transition and polystyrene, itself, glass transition (it is not shown in the DSC curve of the PS110K/PVME blend) simultaneously. When the temperature is above the glass transition temperature of PS110K/PVME blend, the percolated system network structure is collapsed, which leads to an abrupt slope change in the curve of almost all characteristic vibrational modes ln(A_L/A_H) value versus temperature. PS110K rigid clusters remain at this temperature and begin to melt gradually with the temperature increasing. At the polystyrene’s glass transition temperature, the constraint on the characteristic vibration corresponding to the main chain in PS110K is further decreased to be weak, and another obvious turning point occurs near to this temperature.

Conclusions

Through the analysis of the change of polymer samples’ infrared spectra with temperature and their DSC experimental results, we can find that the characteristic vibration modes are under the influence of their glass transition process to different extent. The characteristic vibration modes of the same chemical group behave differently due to the influence of the polymer system at which the chemical moiety is situated. This conclusion can help us to understand the polymer glass transition process at the micro level.

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Supporting Information

This material is available free of charge on the Web at http://www.jsac.or.jp/analsci/.

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