Multiple Molecular Relaxations of Hot-Drawn and Quenched Polymers above Their Glass Transition Temperatures*

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Synopsis

Thermal shrinkage of highly hot-drawn and quenched poly(methyl methacrylate) and polycarbonate of bisphenol A were measured. PMMA shows three-step thermal shrinkage under suitable experimental conditions above its glass transition temperature (T_g). Polycarbonate exhibits four kinds of molecular relaxation associated with shrinkage around and above its T_g. The effect of hot-drawing and quenching conditions on shrinking behavior is discussed. Almost all of the molecular relaxations are observed above T_g. The molecular origins of the relaxations are discussed in relation with the so-called T_{11} transitions of polymers.

INTRODUCTION

Thermal shrinkage of drawn polymers is an important problem in connection with the dimensional stability of cold-worked or molded plastics or with the thermal instability of highly drawn and heat-set fibers. This is just a manifestation of molecular motions in solid polymers; therefore, measurements of thermal shrinkage of drawn polymers can be used to study molecular motions of polymers in solid. Many investigators have dealt with isothermal shrinkage of drawn polymers,[1-3] but only one report except ours treated it thermoanalytically. Tobias and Taylor[4] have reported thermomechanical analysis of hot-drawn poly(vinyl chloride), but qualitatively. We have presented a new technique detecting molecular motions in solid polymers using thermal contraction under uniform rate of heating.[5,6]

One of the two objects of the present article is to show multiple molecular relaxations of highly hot-drawn and quenched poly(methyl methacrylate) and polycarbonate of bisphenol A. Almost all the molecular relaxations associated with shrinkage are above their glass transition temperatures. The other object is to relate them to Boyer's T_{11} polymer transitions.

EXPERIMENTAL

The PMMA sample used was suspension-polymerized Delpet, supplied by the Asahi Denka Co. Ltd. Viscosity measurements of benzene solutions gave a viscosity-average molecular weight of 8.97×10^4. Glass transition temperature of the PMMA was 106°C, determined by TMA at a heating rate of 5°C/min. Tacticity of the polymer has not yet been confirmed, but the polymer was as-

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KATO AND YANAGIHARA

sumed to be rather atactic judging from the glass transition temperature and the polymerization method employed. Films were made by extrusion at 240°C through a die or by casting from benzene solution. Panlite polycarbonate was obtained in the form of thin film (Teijin Kasei Co. Ltd.); it contained no additives detectable by IR spectroscopy. X-ray diffraction measurement of the as-received film revealed that the polymer was completely amorphous.

The weight-average molecular weight of the polycarbonate was 4.6×10^4, estimated from viscosity measurements in tetrahydrofuran solutions. Glass transition temperature of the polycarbonate of bisphenol A was 148.5°C, measured by DSC at a heating rate of 5°C/min. Sample films were hot drawn with a tensile machine at a certain elevated temperature at a strain rate of 0.02/min. The drawn samples were then quenched with cold air from a blower or with water of a certain temperature. Quenching speed was about 200°C/min for air quenching and about 20°C/sec for water quenching.

Thermal shrinkage of hot-drawn and quenched samples was measured with a thermomechanical analyzer designed and constructed in our laboratory. The instrument was equipped with a programmed temperature controller so that the sample temperature could be varied linearly with time at several rates of heating. The samples for TMA measurements were 10 mm long, 5 mm wide, and about 100 μm thick or less. As the samples were very thin, it was not necessary to consider the time lag of sample temperature to the recorded temperature, which was detected with an Alumel–Chromel thermocouple situated just next to the sample. A very small external stress of 1×10^5 Pa was usually applied during tempering to keep the sample tight. A signal differentiator for the output of a linear variable differential transformer (LVDT) was also supplied. Therefore, the sample temperature, the thermal shrinkage, and the rate of shrinkage were recorded simultaneously on the same chart with a multichannel recorder.

RESULTS AND DISCUSSION

Figure 1 shows raw data of a PMMA sample, hot drawn for 300% at 95°C and air quenched with a blower immediately after drawing. The actual heating rate was 1.19°C/min. Curve (a) is the output of the Alumel–Chromel thermocouple,
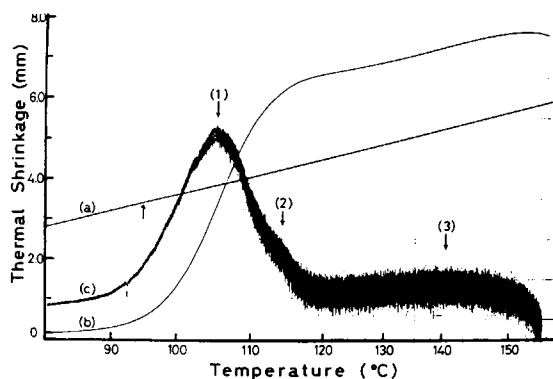

Fig. 1. Thermal shrinkage of a PMMA film, 300% hot drawn at 95°C and air quenched. Actual heating rate was 1.19°C/min: (a) sample temperature, (b) thermal shrinkage, (c) shrinking rate, (1) 107°C (T_g), (2) 116°C, (3) 142°C.

showing sample temperature, and the upward arrow on the curve corresponds to the drawing temperature. Curve (b) is the output of the LVDT that shows thermal shrinkage of the sample with temperature increase. This curve shows that almost all the frozen strain can be recovered with thermal treatment within experimental error. Curve (c) is a time derivative of the output of the LVDT and represents shrinking rate.

These data seem to show that the PMMA sample undergoes two-step thermal shrinkage, but there are two peaks and one shoulder on the derivative curve (c), corresponding to three molecular relaxations. The temperature of peak (1) is 107°C, and this is due to the molecular motions in the glass transition. The shoulder (2) is a small molecular relaxation and is located around 116°C. Peak (3) is a very broad one extending around 141°C, far above the T_g. The melting temperature of PMMA was reported higher than 200°C for the isotactic form, 160°C for the syndiotactic form, and 170°C for the "stereoblock" form. The melting temperature for PMMA which is of atactic nature has not been reported but may be estimated around 170°C, near that of the "stereoblock" form. Therefore, there was also a possibility that the highest-temperature peak might be due to the melting of crystallites in the sample. X-ray diffraction pattern of the solution-cast PMMA film shows only an amorphous halo which corresponds to the spacing around 6.55 Å, and this possibility was excluded.

Figure 2 shows thermal shrinkage of a PMMA sample, hot drawn and quenched under the same conditions as that in Figure 1, but the heating rate was almost eight times as high as that of the previous one. All peaks and a shoulder shift in the higher temperature direction with increase in heating rate, but the degree of shift is somewhat different. The second molecular relaxation finally forms a peak. The peak temperatures are 121, 149, and 166°C from low to high, respectively. Figure 3 shows the result when the drawing temperature is above the T_g. The PMMA film was hot drawn for 300% at 130°C and air quenched immediately after drawing. The actual heating rate was 4.27°C/min. Three molecular relaxations also appear clearly in this case. The peak temperatures are 118, 136, and 150°C from low to high, respectively.
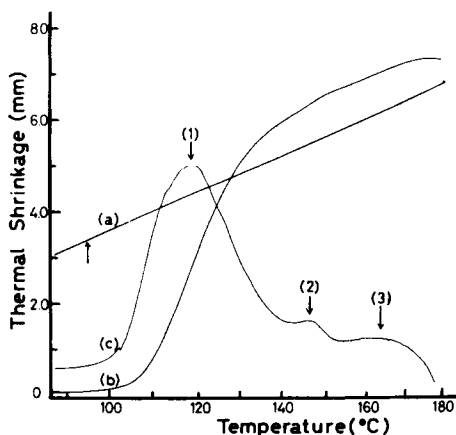

Fig. 2. Thermal shrinkage of PMMA film, 300% hot drawn at 95°C and air quenched. Actual heating rate was 8.93°C/min: (a) sample temperature, (b) thermal shrinkage, (c) shrinking rate, (1) 121°C (T_g), (2) 149°C, (3) 166°C.
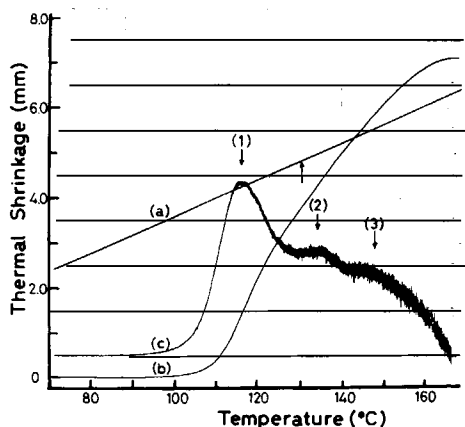
Fig. 3. Thermal shrinkage of a PMMA film, 300% hot drawn at 130°C and air quenched. Actual heating rate was 4.27°C/min: (a) sample temperature, (b) thermal shrinkage, (c) shrinking rate, (1) 118°C (T_g), (2) 136°C, (3) 150°C.

Ozawa[8] has shown that the heating rate dependence of peak temperatures of derivatives of thermoanalytical curves could be used to estimate the apparent activation energy associated with a molecular process, assuming that the rate of the process follows the usual Arrhenius-type reaction kinetics. As the heating rate increases, the peak temperatures of derivative curves shift to the higher temperature direction, and the reciprocal peak temperatures must be plotted linearly with logarithms of the heating rate. The apparent activation energy of the molecular process can be estimated from the slope of the straight line. Conversely, the lower the apparent activation energy is associated with the molecular process, the larger the shift with increased heating rate. Therefore, the apparent activation energy of the second molecular relaxation is the lowest of all, since the shift in temperature of the second peak is the largest.

At a given high temperature during straining under the influence of large external stress, movable molecular units having relatively small relaxation times under the drawing conditions are oriented. The samples are then quenched to a temperature at which the relaxation times are of the order of several hours or longer and the moving units remain frozen and oriented. On warming the samples, the relaxation times decrease and the molecular relaxations are observed as thermal shrinkage. The derivative of a shrinking curve is a quantity proportional to the relaxation strength per unit temperature difference, since the sample temperature is a linear function of time for uniform rates of heating.

Figure 4 shows thermal shrinkage of a polycarbonate film hot drawn for 90% at 140°C and air quenched. The actual heating rate was 4.33°C/min. There are one peak and three shoulders, representing four molecular relaxations on the derivative curve (c). We cannot decide yet which one of the two low-temperature ones corresponds to the molecular motions in the glass transition of this polymer.

Kochi and co-workers[9] have reported a molecular relaxation just below the glass transition for cold-drawn polycarbonate. Lunn and Yannas[10,11] found this by measuring the change in infrared dichroism, and ascribed it to limited backbone motion, less extensive than the glass transition molecular motions. If the molecular relaxation (1) on curve (c) is assumed to correspond to that reported
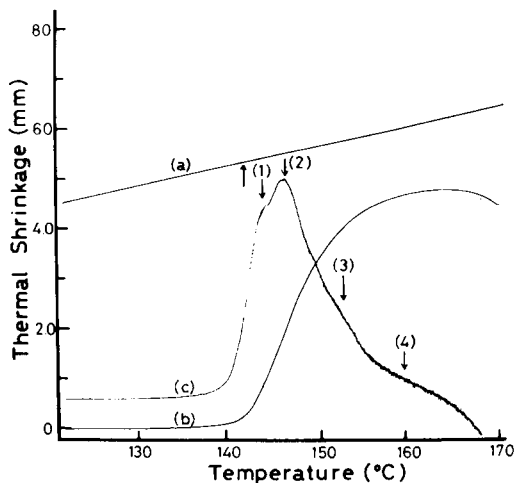
Fig. 4. Thermal shrinkage of polycarbonate film, 90% hot drawn at 140°C and air quenched. Actual heating rate was 4.33°C/min: (a) sample temperature, (b) thermal shrinkage, (c) shrinking rate, (1) 145°C, (2) 148°C, (3) 154°C, (4) 161°C.

by Kochi and others, the molecular relaxation (2) should be what is in the glass transition, and there are two other molecular relaxations above T_g for hot-drawn and quenched polycarbonate. The melting temperature of this polycarbonate has been reported by many investigators,[7] but reported values are scattered from 230 to 267°C. All these values are situated far above the temperature range covered by this work, and even the highest-temperature peak in Figure 4 is not due to the melting of crystallites in the sample.

Figure 5 shows thermal shrinkage of a polycarbonate film hot drawn for 70% at 130°C and quenched with water to 50°C. The actual heating rate was 9.0°C/min. There are also four molecular relaxations shown on the derivative curve (c), but the temperature range and the relative strength are different from those in Figure 4, depending on the drawing, quenching, and heating conditions.
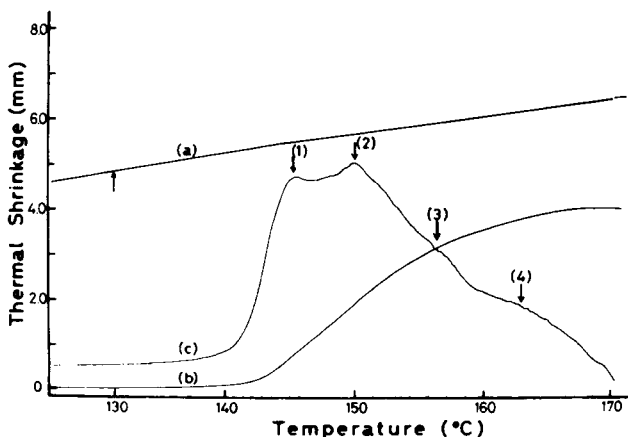

Fig. 5. Thermal shrinkage of polycarbonate film, 70% hot drawn at 130°C and water quenched to 50°C. Actual heating rate was 9.0°C/min: (a) sample temperature, (b) thermal shrinkage, (c) shrinking rate, (1) 147°C, (2) 151°C, (3) 157°C, (4) 164°C.

Drawing temperature, degree of drawing, heating rate, quenching conditions, and especially thermal treatment of restrained samples for a period of time at the high-temperature of drawing before quenching affect the shrinking behavior considerably. In some cases, the highest-temperature peak on a derivative curve becomes the most pronounced one.

Since the first report of Boyer[12] about so-called T_{11} transitions in atactic polystyrene, many reports dealing with this subject have been published, mainly by Gillham and co-workers.[13–16] But there still remains ambiguity even about the existence of a T_{11} transition as an essential property of amorphous polymers.[17,18]

There has been no report about transitions in polycarbonate above its T_g, but Furuta[19] has reported a high-temperature transition (150°C) in PMMA in his measurements of thermal diffusivity. Our experimental results of PMMA and polycarbonate give clear evidence that there are at least three molecular relaxations corresponding to superglass transitions above their glass transition temperatures. Recently, Cowie and McEven[20] have concluded in their extensive works that the superglass transition processes in amorphous polymers are not artefacts. Tobias and Taylor[4] reported that hot-drawn and air-quenched PVC also showed a molecular relaxation above its T_g. Therefore, it is natural to consider that the superglass transition processes should be rather general phenomena for amorphous polymers. Conversely, the superglass transitions should have kinetic character because they cannot be observed for samples well annealed under tension at elevated temperature without quenching. In cases of torsional braid analysis (TBA) and dynamic spring analysis (DSA), polymer molecules should have frozen strain energy which originates from solution casting or from differences in thermal expansion coefficients between the supporting material and the polymer measured.

Cold-drawn polycarbonate shows three molecular relaxations[6] associated with thermal shrinkage below its T_g, and these correspond well to the molecular motions in glass transition, β and γ relaxations from high to low named by Sacher. In his report,[21] Sacher stated that β and γ molecular relaxations could be detected only with a very sensitive method, and there is confusion about the existence of these in well-annealed polycarbonate. By analogy, it seems to us that these molecular relaxations above glass transition temperatures are inherent to the polymers and are repressed by intra- or intermolecular forces among the polymer molecules. In cases of cold-drawn or hot-drawn and quenched polymers, they can be released from repression and can appear with the aid of frozen strain energy. Therefore, one should be able to detect these molecular relaxations above T_g in the future, even for well-annealed polymers, if a very sensitive method will be applied.

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