

# Glass Transition Behavior of Emulsion-Polymerized Polymer Films Containing a Surface-Active Agent

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## Synopsis

The glass transition behavior of emulsion-polymerized poly(methyl methacrylate) and polystyrene films containing sodium laurylsulfate as emulsifier was studied by measurements of dynamic mechanical properties and thermal depolarization current. The film specimens of the emulsion-polymerized polymers were prepared by casting from their benzene solutions. The glass transition temperatures of the emulsion-polymerized films are higher than those of the bulk-polymerized films. The higher glass transition temperature of the emulsion-polymerized films is attributed to the colloidal properties of sodium laurylsulfate in the process of the film formation. The restriction of the molecular chains in the emulsion-polymerized films is attributed to the interaction between the hydrophobic groups of sodium laurylsulfate and the polymer molecules.

## INTRODUCTION

Stable polymer dispersions are readily obtained by emulsion polymerization with a surface-active agent as emulsifier. A powder is obtained from dispersions with a disperse phase in a glassy state such as poly(methyl methacrylate) (PMMA) and polystyrene (PS) on drying. Transparent films are obtained by casting from solutions of PMMA and PS powders dissolved in an organic solvent such as benzene, dioxane, and dimethylformamide, although the powders contain a surface-active agent with a hydrophilic group incompatible with the polymer molecules. The transparency of the films suggests that a microheterogeneous structure is formed in the films. Kreibich<sup>1</sup> and Kanetsuna and co-workers<sup>2,3</sup> proposed that the glass transition behavior of amorphous linear polymers such as PMMA and polystyrene is associated with the microheterogeneous structure in their glassy state from DSC studies of the annealing effect on glass transition behavior.

It is interesting, therefore, to investigate the glass transition behavior of emulsion-polymerized polymer films such as PMMA and polystyrene containing an emulsifier. In this paper the glass transition behavior of emulsion-polymerized PMMA and polystyrene films containing a surface-active agent is investigated by measurements of dynamic mechanical properties and thermal depolarization current and is compared with that of the bulk-polymerized polymer films to clarify the effect of microheterogeneous structure on the glass transition behavior of the emulsion-polymerized polymer films containing a surface-active agent.

## EXPERIMENTAL

### Materials

Emulsion polymerization of methyl methacrylate and styrene monomers was carried out in a nitrogen atmosphere at 70°C using 100 parts monomer, 400 parts water, 0.5 part sodium laurylsulfate (SLS), 0.3 part potassium persulfate, and 0.1 part sodium hydrogen sulfite. The yield of the emulsion-polymerized products was 96% for PMMA and 98% for PS. The film specimens of the emulsion-polymerized polymers were prepared in the following manner. The powders of PMMA and PS containing SLS were obtained by evaporating water from the dispersions. The powders were dissolved in benzene. Film specimens were obtained by casting from the benzene solutions. The PMMA and PS film specimens are called M-1 and S-1, respectively. The weight fraction of SLS is  $5.2 \times 10^{-3}$  in M-1 and  $5.1 \times 10^{-3}$  in S-1.

The emulsion-polymerized polymer specimens M-1 and S-1 were purified by dissolving them in dioxane, which is miscible with water, and reprecipitating with water. The process was repeated three times. Subsequently, the precipitates which were dried at 130°C in vacuo were dissolved in benzene. The film specimens were obtained by casting from the benzene solutions. The PMMA and PS film specimens are called M-2 and S-2, respectively.

Emulsifier-free emulsion polymerization of methyl methacrylate and styrene monomers was carried out under the same conditions as that of the emulsion polymerization using an emulsifier. The film specimens were prepared in the same manner as the specimens M-1 and S-1. The PMMA and PS film specimens are called M-3 and S-3, respectively.

Bulk polymerization of methyl methacrylate and styrene monomers was carried out by heating at 60°C for 24 hr and subsequently at 120°C for 16 hr between two glass plates using  $\alpha, \alpha'$ -azobisisobutyronitrile as a polymerization initiator, and films were obtained. The PMMA and PS film specimens are called M-4 and S-4.

All film specimens used in this study were treated at 120°C for three weeks in vacuo ( $\sim 10^{-3}$  mm Hg) in order to remove volatile materials from the specimens.

### Measurements

Intrinsic viscosity  $[\eta]$  was measured by an Ostwald viscometer using chloroform or toluene as solvent. Molecular weight  $M_w$  was calculated from Flory's equation<sup>4</sup> using the  $[\eta]$  data.

Dynamic mechanical properties were measured by a dynamic viscoelastic spectrometer Vibron DDV-II (Toyo Baldwin Co.). The heating rate was 1°C/min.

Thermal depolarization current (TDC) measurement was performed in the following manner. A sample was polarized with an electric field  $E_p$  at a temperature  $T_p$  for 20 min and subsequently cooled rapidly to room temperature before the field was removed. After short-circuiting the electrodes, the sample was heated at a constant rate  $\beta$ , 0.033°K/sec, and the depolarization current was measured using a Keithley Model 410A electrometer.

## RESULTS AND DISCUSSION

Figure 1 shows the dynamic mechanical properties of PMMA film specimens M-1 and M-4. The peaks corresponding to the glass transition of M-1 and M-4 are observed in the loss modulus curves. The glass transition temperature  $T_g$  of M-1 is higher than that of M-4. In the case of polystyrene specimens S-1 and S-4, the  $T_g$  of S-1 is higher than that of S-4, as shown in Figure 2. The molecular weight of M-4 and S-4 is  $3.3 \times 10^5$  and  $8.1 \times 10^5$ , respectively. It has been known<sup>5</sup> that the  $T_g$  of an amorphous linear polymer does not depend on the molecular weight of more than about  $10^5$ . The higher  $T_g$  of M-1 and S-1 is considered, therefore, to be characteristic of emulsion-polymerized PMMA and PS films containing SLS. The purified specimen M-2, which is considered to contain little SLS and polymerization initiators, shows the same  $T_g$  as that of the bulk-polymerized specimen M-4. On the other hand, M-3, which does not contain SLS, shows the same  $T_g$  as M-4. In the case of the PS specimens, similar results are obtained. The higher  $T_g$  of the emulsion-polymerized specimens M-1 and S-1 is therefore considered to be associated with SLS.

Figures 3 and 4 show the variation in the primary  $\tan \delta$  peaks of M-1 and M-4

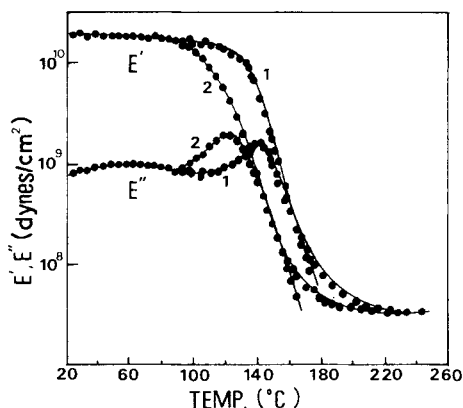


Fig. 1. Dynamic mechanical properties of emulsion- and bulk-polymerized PMMA specimens. Frequency of measurement is 11 Hz: (1) M-1; (2) M-4.

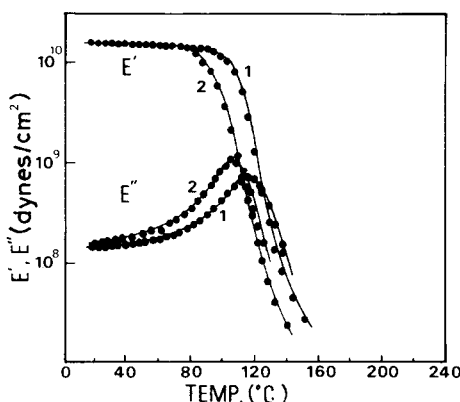


Fig. 2. Dynamic mechanical properties of emulsion- and bulk-polymerized polystyrene specimens. Frequency of measurement is 11 Hz: (1) S-1; (2) S-4.

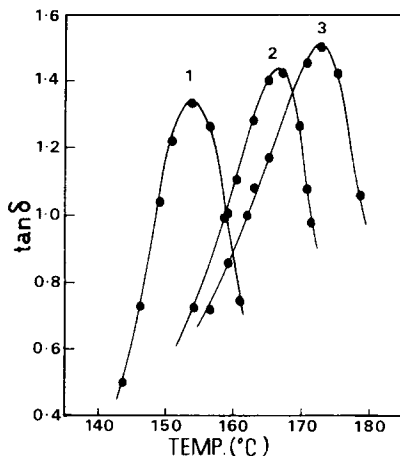


Fig. 3. Variation of primary  $\tan \delta$  peak with frequency of measurement for emulsion-polymerized specimen M-1: (1) 3.5 Hz; (2) 35 Hz; (3) 110 Hz.

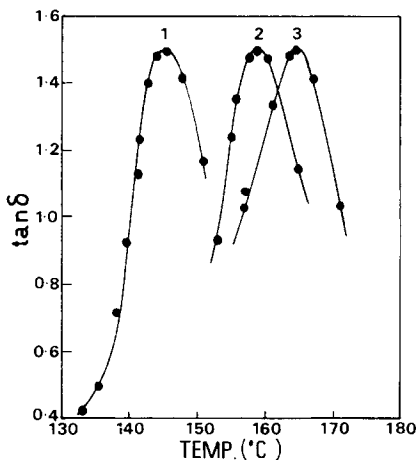


Fig. 4. Variation of primary  $\tan \delta$  peak with frequency of measurement for bulk polymerized specimen M-4: (1) 3.5 Hz, (2) 35 Hz, and (3) 110 Hz.

with the frequency of measurement, respectively. In the case of the emulsion-polymerized specimen M-1, the maximum of the primary  $\tan \delta$  peak increases with the frequency of measurement, while in the case of the bulk-polymerized specimen M-4, the maximum of the  $\tan \delta$  peak does not depend on the frequency of measurement. In the case of the PS specimens, the maximum of the primary  $\tan \delta$  peak is too large to be measured by the Vibron DDV-II. Fukasawa and Wada have shown that the maximum of the mechanical  $\tan \delta$  peak corresponding to the local mode relaxation in amine-cured epoxy resins increases with the frequency of measurement.<sup>6</sup> Previously, we found that in the series of cross-linked PMMA, the maximum of the primary mechanical  $\tan \delta$  peak increases with the frequency of measurement, while the maximum of the primary  $\tan \delta$  peak of PMMA which is uncrosslinked does not depend on the frequency of measurement.<sup>7</sup> The motion of the molecular chain segments at  $T_g$  in a cross-linked PMMA is considered to be partly oscillational. In the case of the emulsion-polymerized specimen M-1, it is considered, therefore, that restriction of

the molecular chains is developed during film formation and the molecular motion in the glass transition region partly becomes oscillational.

The TDC spectra of the PMMA and PS specimens are shown in Figures 5 and 6. The bulk-polymerized specimens M-4 and S-4 each show two pronounced peaks. The lower-temperature peaks of these specimens are known to be attributable to dipole orientation polarization associated with the glass transition of PMMA and PS, respectively.<sup>8,9</sup>

The higher-temperature peaks of M-4 and S-4 are not attributed to dipole orientation polarization, because the sign of the current of these peaks changes with small  $E_c$  ( $\sim 0.1 E_p$ ). It has been known that TDC arising from polarization due to trapped electrons injected from an electrode strongly depends on the collecting voltage  $E_c$  which is applied during TDC measurement, and the sign of the current changes with  $E_c$  fairly smaller than  $E_p$ .<sup>10,11</sup> The higher-temperature peaks of M-4 and S-4 are therefore considered to be attributable to the

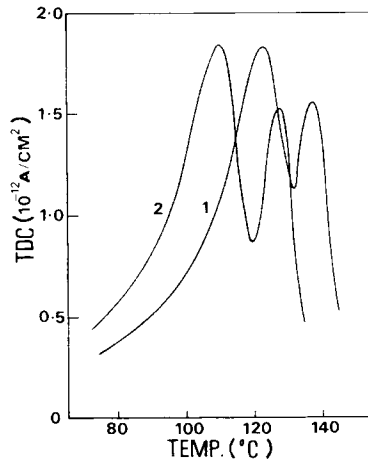


Fig. 5. TDC spectra of emulsion- and bulk-polymerized PMMA specimens: (1) M-1; (2) M-4.  $T_p = 125^\circ\text{C}$ ;  $E_p = 10 \text{ kV/cm}$ .

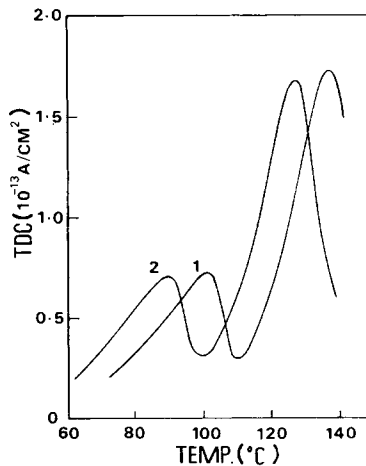


Fig. 6. TDC spectra of emulsion- and bulk-polymerized polystyrene specimens: (1) S-1; (2) S-4.  $T_p = 125^\circ\text{C}$ ;  $E_p = 10 \text{ kV/cm}$ .

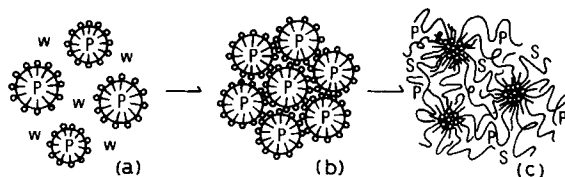


Fig. 7. Mechanism of the formation of microheterogeneous structure in emulsion-polymerized specimens M-1 and S-1: o, hydrophilic group of emulsifier; q, hydrophobic group of emulsifier; P, polymer; W, water; S, solvent.

polarization of injected electrons. The emulsion-polymerized specimens M-1 and S-1 also show two peaks, respectively. The temperatures of the lower-temperature peaks associated with the glass transition of M-1 and S-1 are higher than those of M-4 and S-4, respectively. The above results agree with those of the viscoelastic properties shown in Figures 1 and 2. The higher-temperature peaks of the emulsion-polymerized specimens M-1 and S-1 are observed at a higher temperature than those of the bulk-polymerized specimens M-4 and S-4, respectively. Boustead and Charlesby have shown that the depolarization of trapped electrons in polymers is promoted by the molecular motions.<sup>12</sup> It is considered, therefore, that the restriction of the molecular chains in the emulsion-polymerized specimens M-1 and S-1 still remains above  $T_g$ .

The restriction of the molecular chains in the emulsion-polymerized specimens M-1 and S-1 is supposedly associated with the colloidal properties of SLS in the process of film formation. We propose a mechanism of formation of a microheterogeneous structure in the emulsion-polymerized specimens M-1 and S-1 as shown in Figure 7. A stable polymer dispersion is obtained by interaction between the polymer and the hydrophobic group of SLS in the emulsion polymerization as shown in Figure 7(a). After removal of water the particles coagulate with each other as shown in Figure 7(b). When the polymer particles are dissolved in benzene, the clusters of the hydrophilic SLS group which is insoluble in benzene are probably surrounded by polymer molecules which interact with the hydrophobic SLS group. The clusters of SLS are therefore apparently soluble in benzene as shown in Figure 7(c). After removal of benzene, the clusters of the hydrophilic group of SLS probably disperse in the polymer matrix like small filler particles. The hydrophobic group which exists outside the clusters probably interacts with the polymer molecules to restrict the motion of the polymer molecules.

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