Thermal Analysis of Styrene–Alkyl Methacrylate Polymers. I. Glass Transition Temperatures

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Synopsis

The glass transition temperatures (T_g's) of several polystyrenes and styrene–alkyl methacrylate copolymers and terpolymers were measured using thermomechanical analysis (TMA) and differential scanning calorimetry (DSC). The polymers studied had number-average molecular weights from 3000 to 250,000 g/mole. The results indicate that the composition dependence of the T_g's for the copolymers and terpolymers can be satisfactorily described by a general Fox equation. In general, the measured T_g's of the copolymer and terpolymer samples depend more on the steric effects of the constituent pendent groups than on their molecular weights. The chain flexibility rather than the size of the pendent group is the determining factor in the glass transition properties of the styrene polymers.

INTRODUCTION

The use of a photoconductor overcoated with a thin layer of thermoplastic for holographic recordings was first reported by Urback and Meier.[1] An *in situ* reuseable thermoplastic optical memory employing a holographic mode has been demonstrated and discussed by several authors.[2,3] The application of styrene and alkyl derivatives of methacrylate copolymers and terpolymers as holographic recording materials has been explored by Anderson et al.,[4] Colburn and Tompkins,[5] and Lin et al.[6] This available information indicates that a detailed investigation of the T_g's of the polymeric styrenes is the prime prerequisite in the search for a styrene-type thermoplastic that can be effectively used as a holographic recording material. Another major requirement of a thermoplastic for holographic uses is thermal stability which is the topic of a subsequent article.[7]

When an amorphous polymer is cooled from a rubbery to a glassy state, it passes through a second-order transition known as T_g, which occurs because of the fact that the main-chain mobility and segmental jumping frequency are reduced to a point at which the backbone of the polymer becomes essentially frozen in place. Although a comprehensive study of the optimum T_g of a thermoplastic for holographic applications has not been pursued, it is expected that the T_g of the material must be high enough to prevent deformation during storage and, on the other hand, be low enough for recording a high-resolution hologram, which can be erased readily at some convenient operating temperature by a heat pulse without deteriorating the material. A T_g of 30–50°C is found to be practical for these applications.[6]

The styrene–alkyl methacrylate system was selected for the present investigation because styrene chains crosslink and methacrylate components undergo scission under the holographic operating conditions.[4] The alternative effects

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of crosslinking and scission provide an appropriate dynamic balance for stabilizing the thermoplastic during thousands of holographic record–erase cycles. Also, the results of internal plasticization of the polymer system using alkyl methacrylates is probably the most convenient method for adjusting the T_g of the system so that the material becomes applicable to holographic memory use. Preliminary studies by Colburn and Tompkins[5] and by Lin et al.[6] show that terpolymers of styrene–alkyl methacrylates are more favorable than the homopolymer or copolymers for holographic recording applications. Hence, it is particularly interesting to evaluate the steric effects of pendent groups of a copolymer or terpolymer on the glass transition properties of the polymer chains.

Several samples of atactic and isotactic polystyrenes, copolymers, and terpolymers of styrene with ethyl methacrylate (EMA), hexyl methacrylate (HMA), octyl methacrylate (OMA), decyl methacrylate (DMA), or octadecyl methacrylate (ODMA) with a number-average molecular weight ($\overline{M}_n$) of 3000–250,000 g/mole were selected for the investigation. The literature[8] density values and T_g's of some alkyl methacrylate homopolymers are summarized in Table I for reference. The trend of decrease in T_g with the size of the pendent groups is evident in Figure 1. This information is applied later in the data analysis. Polymer microstructure identification and composition determination were made by UV–IR spectroscopy methods, and molecular weight was determined by gel permeation chromatography (GPC). The T_g's were characterized by TMA and DSC techniques.

EXPERIMENTAL

Polymer Samples

Sample designations of the polymers studied are summarized in Table II. The low molecular weight atactic polystyrene sample P10A was prepared by a method identical to that for copolymers and terpolymers as described later in this section. The medium molecular weight atactic and isotactic polystyrenes were purchased

TABLE I
Densities and Glass Transition Temperatures of Various Alkyl Methacrylate Polymers[7]

Polymer	Monomer designation	Pendent group	Density at 25°C, g/cm³	T_g, °C
Poly(methyl methacrylate)	MMA	—CH₃	1.170	105
Poly(ethyl methacrylate)	EMA	—CH₂CH₃	1.125	65
Poly(n-propyl methacrylate)	n-PMA	—(CH₂)₂CH₃	1.077	35
Poly(n-butyl methacrylate)	n-BMA	—(CH₂)₃CH₃	1.053	20
Poly(n-hexyl methacrylate)	n-HMA	—(CH₂)₅CH₃	1.008	−5
Poly(n-octyl methacrylate)	n-OMA	—(CH₂)₇CH₃	0.97	−20
Poly(n-decyl methacrylate)	n-DMA	—(CH₂)₉CH₃	0.95	−70[a] (−46)[b]
Poly(n-dodecyl methacrylate)	n-DDMA	—(CH₂)₁₁CH₃	0.929	−65
Poly(n-octadecyl methacrylate)	n-ODMA	—(CH₂)₁₇CH₃	0.92[c]	−100

[a] R. H. Wiley and G. M. Brauer, *J. Polym. Sci.*, 4, 351 (1949).

[b] Interpolated result from Figure 1.
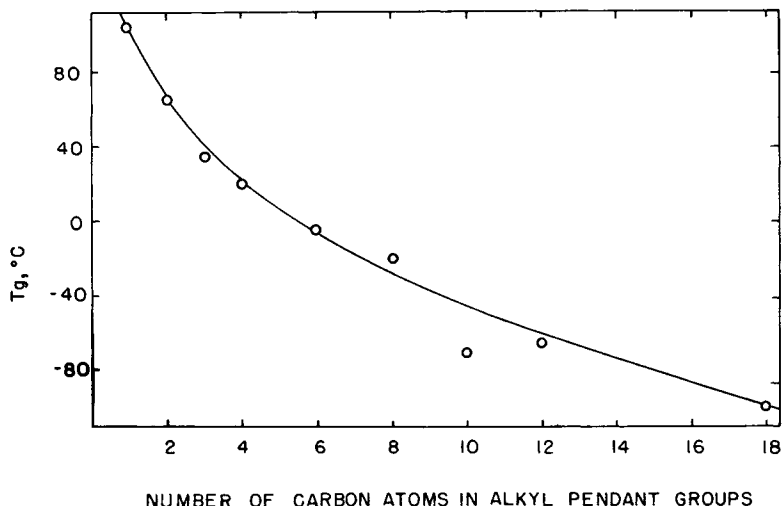
[c] Measurement of this work.

Fig. 1. Decrease in glass transition temperature of alkyl methacrylates as a function of number of carbon atoms in the alkyl pendent group.

from Polysciences, Inc. Prior to use, the atactic polystyrenes were purified by reprecipitation of the polymers from toluene solutions in methanol. In one case, the polymer sample was tested both as received (P10B) and as purified (P10C) for comparison. The isotactic polystyrene (P10E) was tested as received because of lack of an appropriate solvent for purification.

All copolymer and terpolymer samples were synthesized from the respective monomers as purchased from Polysciences, Inc., by a method similar to that reported by Anderson et al.[4] The polymerization reactions were carried out using 2,2-azobisisobutyronitrile as a free-radical initiator in toluene solutions at 68°C for 48 hr with constant stirring. The reactions were quenched by tert-butyl-catechol. The polymer products were recovered from the reaction solutions by adding the solution dropwise into a methanol bath where the polymers were collected as precipitates. The polymers then were dried in a vacuum oven at desirable temperatures. The terpolymer samples P33C and P33D were synthesized under identical conditions except that the polymerization reaction in P33D was quenched by tert-butycatechol but not in P33C.

Spectroscopy

A Varian Cary 14 UV–VIS spectrophotometer and a DigiLab Fourier transform infrared spectrophotometer were used to identify the chemical structure and constituent composition of the polymers. UV analysis was performed on 1% polymer solutions in chloroform. The absorption peaks at 220 and 269 nm were used as a quantitative identification of carbonyl groups and benzene rings in the polymer samples.

Samples for IR analysis were prepared by dissolving an appropriate amount of a polymer in chloroform and coating the solution on a NaCl substrate so that a polymer coating of less than 2.5×10^{-3} cm in thickness was established on the substrate. The IR absorptions at 1720 and 700 cm^{-1}, due to carbonyl groups and benzene rings, respectively, were employed for quantitative measurements of the mole fractions of styrene and methacrylates in the polymer chains.

TABLE II
Glass Transition Temperatures of Various Styrene Polymers as Determined by Thermomechanical Analysis and Differential Scanning Calorimetry in Air

Sample	Type	Monomer	Monomer feed, mole %	$\overline{M}_n$, g/mole	T_g, °C Measured	Eq. (4)	Eq. (5)
P10A	homopolymer (atactic)		—	3,300	66	—	—
P10B	homopolymer (atactic)		—	33,000	99	—	—
P10C	homopolymer (atactic)		—	33,000	99	—	—
P10D	homopolymer (atactic)		—	250,000	104	—	—
P10E	homopolymer (isotactic)		—	—	94	—	—
P21A	copolymer	ST/EMA	80/20	28,000	90	91	92
P22A	copolymer	ST/HMA	75/25	23,000	62	54	62
P22B	copolymer	ST/HMA	65/35	31,000	44	42	49
P22C	copolymer	ST/HMA	50/50	22,000	28	26	34
P23A	copolymer	ST/ODMA	90/10	23,000	32	12	41
P23B	copolymer	ST/ODMA	85/15	21,000	15	−11	21
P31A	terpolymer	ST/EMA/HMA	52/22/26	37,500	50	47	54
P32A	terpolymer	ST/HMA/ODMA	85/10/5	31,500	32	34	54
P33A	terpolymer	ST/OMA/DMA	85/7.5/7.5	26,500	58	51	62
P33B	terpolymer	ST/OMA/DMA	75/12.5/12.5	28,500	36	30	42
P33C	terpolymer	ST/OMA/DMA	85/9/6	5,800	39	40	47
P33D	terpolymer	ST/OMA/DMA	85/9/6	5,800	43	40	47

Gel Permeation Chromatography

All polymer samples were characterized in terms of their molecular weight distributions using GPC techniques. The analysis was performed on a Waters Associates Model ALC 202/401 liquid chromatograph coupled with a Model 6000 solvent delivery system. The instrument was equipped with four columns packed with an absorption medium known as μStyragel. The columns were connected in series with average packing pore sizes of 100, 500, 1000, and 10,000 Å. Calibration was performed using standard polystyrene samples as provided by the vendor of the chromatograph.

Polymer samples of 1% by weight in tetrahydrofuran (THF) were prepared for the analysis. A sample of 0.025 ml of a polymer solution was injected into the chromatograph for analysis using THF as a carrier solvent.

Thermomechanical Analysis

Usually, the glass transition temperature of an amorphous polymer can be detected readily by the TMA method, which measures the dimension change of a polymer under temperature-programmed heating or cooling conditions. A du Pont 942 thermomechanical analyzer was employed to monitor the displacement of a probe under an expansion mode on a sample which was heated at 10°C/min in air. The TMA sample was prepared by casting a polymer in an aluminum DSC sample cell. The T_g was determined as the temperature at which the TMA curve showed an abrupt change in slope. Typical TMA curves of several polystyrene homopolymer samples are shown in Figure 2 with the derived T_g values.

Differential Scanning Calorimetry

The glass transition temperature can also be measured by DSC techniques which monitor the enthalpy change of a sample under a constant heating or cooling or isothermal operation. As a supplementary check, the T_g's of some
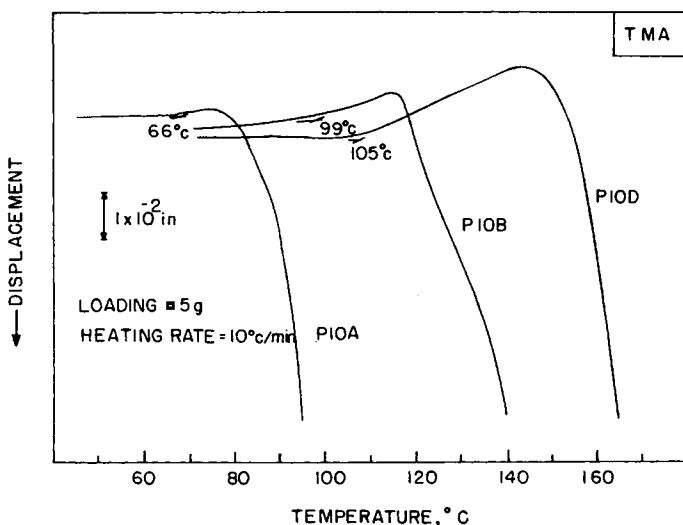

Fig. 2. Typical thermomechanical analysis curves of several polystyrene homopolymers.

polymers were also determined using a du Pont 990 DSC. Approximately 20 mg of a sample were packed into an aluminum sample cell which was sealed tightly with an aluminum lid. An empty sample cell with a lid was used as a reference of the measurement performed in air at a heating rate of 10°C/min. The T_g values of the DSC curve was identified as the temperature halfway between the onset of the two linear portions before and after the transition period,[9] as depicted in the typical DSC curves of the copolymer and terpolymers indicated in Figure 3. The agreement of the TMA and DSC techniques is generally better than 5°C.

GENERAL T_g EQUATIONS

For a polymer containing two or more constituent components, for example, copolymer or terpolymers, there exist certain parameters which satisfy the following general T_g relation:

$$\sum_{i=1}^{n} \gamma_i (T_g - T_{g_i}) = 0 \quad n = 2, 3, \text{etc.} \tag{1}$$

where γ_i denotes a constant characteristic of the ith component, which has a glass transition temperature T_{g_i}. Equation (1) is identical to that derived by Wood[10] for copolymers where $i = 2$. The constant γ_i can be readily related to the weight fraction, volume fraction, or mole fraction of the components present in the composite system. It must be noted that eq. (1) is valid only if the composite system forms a true polymer (e.g., a copolymer or terpolymer), not a polymer blend, eutectic, or interpenetrating network as described by Frisch et al.[11]

By simple rearrangement of eq. (1), one readily obtains

$$\frac{1}{T_g} = \frac{1}{\sum\limits_{i=1}^{n} \alpha_i w_i} \sum_{i=1}^{n} \frac{\alpha_i w_i}{T_{g_i}} \tag{2}$$
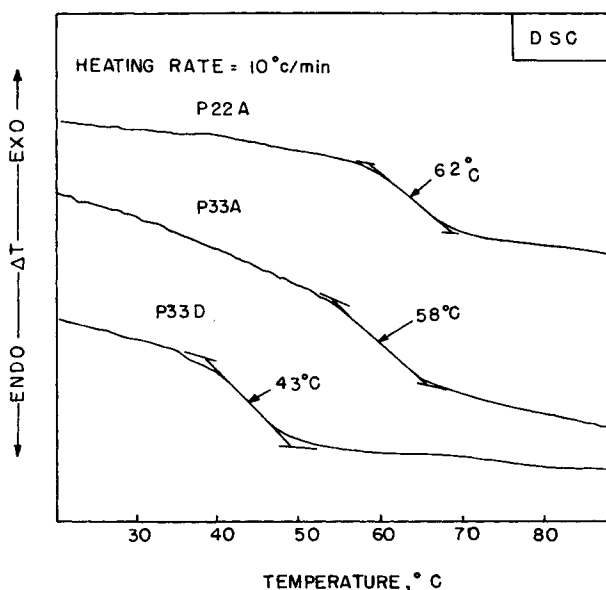

Fig. 3. Typical differential scanning calorimetric analysis curves of several styrene–alkyl methacrylate copolymers and terpolymers.

or

$$T_g = \cfrac{1}{\sum\limits_{i=1}^{n} \beta_i v_i} \sum\limits_{i=1}^{n} \beta_i v_i T_{gi} \qquad (3)$$

where α_i and β_i are constants associated with the relative activities of the ith component whose weight fraction in the polymer is w_i and whose volume fraction is v_i. In these expressions, α_1 and β_1 are taken to be 1, and component 1 has the lowest glass transition temperature among all the polymer components in the copolymer of terpolymer. When $i = 2$, eq. (2) is identical to the Mendelkern, Martin, and Quinn expression.[12] If the constants α_i and β_i are taken to be 1, eqs. (2) and (3) can be simplified to

$$\frac{1}{T_g} = \sum\limits_{i=1}^{n} \frac{w_i}{T_{gi}} \qquad (4)$$

and

$$T_g = \sum\limits_{i=1}^{n} v_i T_{gi} \qquad (5)$$

Equation (4) is a general form of the Fox equation derived specifically for copolymer systems.[13] It is interesting to note that the assumption of $\alpha_2 = 1$ usually is satisfactory but that the assumption of $\beta_2 = 1$ generally is not fulfilled.[10] Therefore, it is expected that eq. (4) is a better approach than eq. (5) in predicting the composition dependence of the glass transition temperatures of copolymers or terpolymers. An expression in terms of mole fraction is similar to eq. (4) and is therefore not pursued.

RESULTS AND DISCUSSION

Results of the spectroscopic analyses show that the feed styrene and alkyl methacrylate monomer contents in the radical-initiated polymerizations generally agree reasonably well with those in the final copolymers or terpolymers as indicated in Table II. This result can be attributed to the similar relative reactivities of styrene and alkyl methacrylate radicals.[14] No significant difference in T_g's was detected between the as-received (P10B) and purified (P10C) polystyrene samples and between the unquenched (P33C) and quenched (P33D) terpolymers.

The measured results as given in the sixth column of Table II show that the T_g's depend more on the geometry of the constituent groups than on their molecular weights, with the exception of very low $\overline{M}_n$ (e.g., 3000–6000 g/mole). Comparing the homopolymers, the atactic polystyrene with a change in $\overline{M}_n$ of approximately eightfold, from 33,000 g/mole for P10B to 250,000 g/mole for P10D, shows an increase in T_g of only 5°C. Although the molecular weight for the isotactic polystyrene (P10E) was not measured because of the lack of an appropriate solvent, the steric restriction of the isotactic conformation appears to be responsible for a slightly lower T_g, as opposed to the higher T_g of the atactic polystyrene.
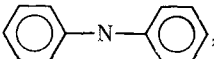
Among the styrene–alkyl methacrylate copolymers, which have practically the same $\overline{M}_n$ except for P33C and P33D, the size of the pendent groups appears

to be more effective than the amount of the groups present in lowering the T_g. This result is clearly shown by the trend of the rapid decrease in T_g with increase in size of the pendent groups from H for P10B, to EMA and HMA for P21A and P22A, and ODMA for P23A and P23B. The effects of pendent group contents are obviously less marked when comparing the measured T_g's of the copolymers.

Similar steric effects are also evident among the terpolymers. The polymer with small pendent groups, P31A, shows a high T_g, while the one with the largest pendent groups, P32A, gives the lowest T_g. Although the styrene content in P33A is over 30% more than that in P31A, the T_g of P33A is only 8°C higher than that of P31A. This is apparently a tradeoff of the higher steric effects of the pendent groups in P33A than in P31A. Such steric effects are consistently displayed in samples P33A, P33B, P33C, and P33D, whose constituent groups are identical but compositions vary. Sample P33B, with the highest contents of bulky pendent groups of OMA and DMA, shows the second-lowest T_g among the terpolymers tested.

It is interesting to compare the T_g's of P21A and P33A, which have similar $\overline{M}_n$ and styrene content. The T_g of P21A is 32°C higher than that of P33A, which has two bulky groups. The moderate steric effects from a small pendent group is seen between P22A and P31A. The effects of ODMA on the polymer chains in P23A appear to be similar to those of OMA/DMA on the polymer chains in P33C and P33D. Since P23A, P33C, and P33D all have similar styrene contents, the steric effects contributed by ODMA are the same as the combined results of OMA and DMA regardless of the individual compositions of the OMA and DMA groups and their molecular weights.

In general, the glass transition temperatures of linear polymers vary drastically with the polymer chain flexibility; that is, the more flexible the chain structure, the lower the T_g of the polymer. This situation is shown in the family of linear methacrylate polymers as indicated in the data of Table I and Figure 1. On the other hand, it has been found that the T_g's of linear polymers increase with the size of their pendent groups, as shown in the following series of polymers: Polyethylene, polypropylene, polystyrene, and poly(vinyl carbazole), whose side

groups are —H, —CH$_3$, —⟨O⟩, and ⟨O⟩—N—⟨O⟩, have T_g's of $-120°$, $-16°$, $83°$, and $208°$C, respectively.[15]

There seem to be some tradeoffs between chain flexibility and steric effects of the pendent groups on the polymer chains. In the present linear styrene–methacrylate system it is apparent that the increase in flexibility of the alkyl pendent groups is predominantly more important than the steric effects accompanying the increase in group size. The profound effects of tacticities on the bulk glass transition characteristics of polystyrenes[16] and poly(methyl methacrylate)[17] have not been considered in the present studies because details of the tacticities of the styrene polymers are not available.

The T_g's calculated from eqs. (4) and (5) are summarized in the last two columns of Table II. In this calculation, $T_g = 99°$C for polystyrene is used except for two low molecular weight terpolymers, P33C and P33D, in which cases $T_g = 77°$C is employed for polystyrene. This selection is considered to be more realistic because the copolymers and terpolymers studied are comparable to the

medium molecular weight atactic polystyrene. Other information required in the calculations is obtained from the data collected in Table I. The interpolated value of $-46°C$ as obtained from Figure 1, instead of the literature value,[8] is used for the T_g of poly(n-DMA) in the analysis. As expected, the agreement between the measured T_g's and those calculated from eq. (4) is better than those from eq. (5). However, in some cases the assumption of $\alpha_2 = \alpha_3 = 1$ as depicted earlier apparently is not applicable. In general, the T_g's of the styrene–alkyl methacrylate copolymers and terpolymers can be predicted reasonably accurately by the general Fox equation, eq. (4).

CONCLUSIONS

The simplified Fox equation has been reasonably successful in predicting the T_g's of copolymer and terpolymers of the styrene–alkyl methacrylate system based on the compositions of the individual components. The T_g of a polystyrene can be drastically lowered either by copolymerizing or terpolymerizing styrene with 10% to 30% of alkyl methacrylates. The chain flexibility, attributed to the effects of pendent groups, apparently is more important than the size of the groups in depressing the T_g of the final copolymers or terpolymers. Molecular weight seems to have no significant effect on the T_g. During the search of thermoplastic media for holographic recording applications, it is essential that an effective method be established for close control of the T_g's of the materials under investigation. Obviously, other thermodynamic properties such as viscosity and enthalpy of a material under glass transition conditions are important parameters which need to be clarified.

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