

# Characterization of Styrene–Methyl Methacrylate–*n*-Butyl Acrylate Terpolymers.

## II. Effects of Sequence Distribution on Glass Transition Temperature

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### Synopsis

The effects of sequence distribution on the glass transition temperature ( $T_g$ ) of the title terpolymers prepared by radical polymerization were studied.  $T_g$  was examined by thermomechanical analysis. The average diad concentrations, as estimation of sequence distributions were calculated from monomer reactivity ratios. A modified Gibbs–Dimarzio equation for binary copolymers was extended to terpolymers to explain the relation between observed  $T_g$  and average diad concentrations. The observed  $T_g$  showed good agreement with the calculated values determined by the extended equation.

### INTRODUCTION

For the relation between sequence distribution and the glass transition temperature ( $T_g$ ) of a copolymer, the modified Gibbs–Dimarzio equation was proposed by Uematsu and Honda<sup>1</sup> for binary copolymers, in which the stiffness energy of heterogeneously bonded chains is considered. The estimation of  $T_g$  based on this equation is widely conducted using measurements, such as that of sequence distribution by NMR. However, there is no report on the relation between sequence distribution and  $T_g$  of a multicomponent copolymer containing three or more components. Acrylic resins for industrial paints are usually multicomponent copolymers composed of components such as acrylate, methacrylate, and styrene. For the estimation of  $T_g$  of these multicomponent copolymers, the effects of sequence distribution on  $T_g$  was examined using, as a model polymer, the terpolymer of styrene (St)–methyl methacrylate (MMA)–*n*-butyl acrylate (BA) obtained by radical polymerization.

In this paper, the sequence distribution dependence of  $T_g$  of St–MMA–BA terpolymers was examined as well as the application of the modified Gibbs–Dimarzio equation to terpolymers. For the sequence distribution of the terpolymers, it was confirmed in Part I of this study<sup>2</sup> that the average diad concentration related to MMA obtained by <sup>1</sup>H-NMR measurement agrees with the result calculated from the monomer reactivity ratios based on the copolymerization theory. Consequently, average diad concentrations from monomer reactivity ratios related to the diad on all monomer units were used in this study. Measurement of  $T_g$  was conducted by thermomechanical analysis (TMA).

TABLE I  
 Characteristics of Terpolymers

Terpolymers	Monomer composition (mol)			Molecular weights by GPC		$T_g$ (°C)
	St	MMA	BA	$\bar{M}_n$	$\bar{M}_w$	
R1	0.38	0.40	0.22	10,200	23,100	57
R2	0.42	0.44	0.14	9,000	29,700	74
R3	0.58	0.20	0.22	7,900	29,800	55
R4	0.19	0.60	0.21	12,000	34,800	56
R5	0.11	0.68	0.21	26,100	63,900	55
R6	0.67	0.11	0.22	7,700	29,100	50
R7	0.27	0.28	0.45	11,200	29,100	12
R8	0.15	0.15	0.70	12,600	41,500	-18

 TABLE II  
 Characteristics of Homopolymers

Homopolymers	Monomers	Molecular weights by GPC		$T_g$ (°C)
		$\bar{M}_n$	$\bar{M}_w$	
H1	St	7,600	22,000	81
H2	MMA	24,000	45,100	93
H3	BA	23,000	59,300	-52

## EXPERIMENTAL

### Polymer Synthesis

A four-necked flask having a volume of 0.5 L was equipped with stirrer, thermometer, and a tube for introducing nitrogen gas. Into this flask were charged 140 g of toluene, 60 g of *n*-butyl acetate, 2 g of azobisisobutyronitrile, and 200 g of a monomer mixture consisting of St, MMA, and BA in various ratios. The polymerization was conducted at 75°C until the conversion attained 98% or more. The monomer compositions are shown in Tables I–III.

### Measurement of $T_g$

A polymer solution was applied to an aluminium plate (0.2 mm in thickness) with a bar coater manufactured by Nishiyama Seisakusho Co., Ltd., which is a steel rod wound with a steel wire of specific diameter, at a thickness of about 20  $\mu\text{m}$  (dry), and dried in an oven at 170°C for 30 min. It was left at room temperature for 24 h, and cut into small 2-mm squares to be used as test pieces. The weight contents of residual solvents and monomers left after oven drying were less than 200 ppm as determined from gas chromatography (GC-7AG, Shimazu Seisakusho Co., Ltd.) of each sample dissolved in acetone.

A thermomechanical analysis apparatus (TMA standard) manufactured by Rigaku Denki Co., Ltd. was used. Measurements were conducted by a penetration mode; an attached differential system of high sensitivity was

TABLE III  
 Characteristics of Binary Copolymers

Binary copolymers	Monomer compositions (mol)			Molecular weights by GPC		$T_g$ ( $^{\circ}\text{C}$ )
	St	MMA	BA	$\bar{M}_n$	$\bar{M}_w$	
C1	0.74	0.26	—	10,300	31,800	76
C2	0.49	0.51	—	11,200	24,100	87
C3	0.24	0.76	—	13,400	33,700	83
C4	0.78	—	0.22	7,700	30,500	57
C5	0.55	—	0.45	9,100	28,600	3
C6	0.39	—	0.61	9,500	28,800	-15
C7	—	0.88	0.12	26,800	65,400	75
C8	—	0.79	0.21	27,100	64,900	56
C9	—	0.72	0.28	27,900	64,200	41
C10	—	0.58	0.42	30,400	69,700	25
C11	—	0.38	0.62	35,200	77,400	-24

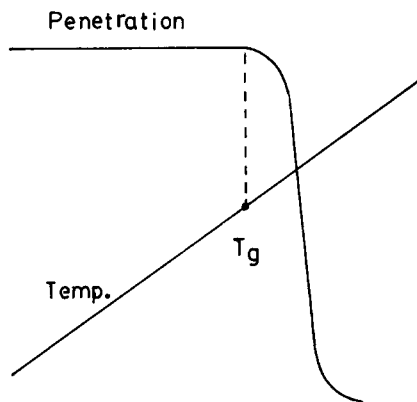


Fig. 1. Measurement of  $T_g$  by thermomechanical analysis (TMA): atmosphere, air; pin, quartz ( $R = 0.2$  mm); heating rate, 10 K/min; loading, 10 g; range,  $\pm 25$   $\mu\text{m}$ .

used.  $T_g$  was read from the chart as the temperature at which the penetration of the pin started. Measurements were conducted three times for each sample, and the average value was used. Variation in measured values was within  $3^{\circ}\text{C}$  for all samples. In Figure 1, an example of a TMA chart and the conditions for the measurements are shown.

### Measurement of Molecular Weight

Measurements were made by gel permeation chromatography (GPC). A 201G system manufactured by Waters Associates Inc. was used at  $25^{\circ}\text{C}$  using tetrahydrofuran as the solvent at a flow rate of 1.8 mL/min. Four  $\mu\text{Styragel}$  columns of  $10^5$ ,  $10^4$ ,  $10^3$ , and  $10^2$   $\text{\AA}$  were used in series. The molecular weight was obtained from a polystyrene calibration curve.

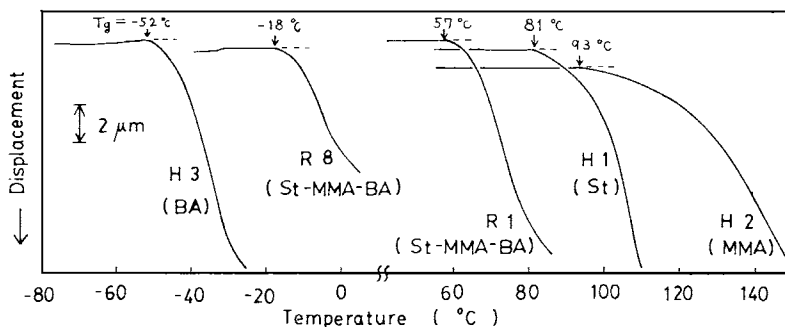


Fig. 2. Typical TMA outputs.

## RESULTS AND DISCUSSION

### Results of $T_g$ Measurement

For the  $T_g$  measurement of a polymer, there are both thermal energetic [such as differential scanning calorimeter (DSC)] and thermomechanical measurements (such as TMA). In this paper, we used TMA, effective for thin film and comparatively easy to use over a wide range of temperature. For a comparison of measured values using TMA and DSC, it had been reported by Lin and Wen<sup>3</sup> that  $T_g$  of a copolymer composed of St and methacrylate measured by both methods agree within 5°C.

Measured values of  $T_g$  of terpolymer are shown in Table I. To determine the relation between composition or sequence distribution and  $T_g$ 's of various homopolymers and binary copolymers consisting of St, MMA, or BA obtained under the same polymerization conditions as those of terpolymers were measured by a similar method. The results are shown in Tables II and III. Figure 2 shows a typical TMA output for a sample. In Tables I–III, the measured molecular weight of each sample is given.

### Sequence Distribution Dependence of $T_g$

The modified Gibbs–Dimarzio equation for  $T_g$  of a binary copolymer can be represented by eq. (1) using the diad concentration ( $P_2\{M_iM_j\}$ ):

$$T_g = P_2\{M_1M_1\}T_{g_1} + P_2\{M_2M_2\}T_{g_2} + 2P_2\{M_1M_2\}T_{g_{12}} \quad (1)$$

where  $P_2\{M_1M_1\} + P_2\{M_2M_2\} + 2P_2\{M_1M_2\} = 1$ ,  $T_{g_1}$  and  $T_{g_2}$  are the  $T_g$ 's (K) of homopolymers 1 and 2, respectively, and  $T_{g_{12}}$  is the  $T_g$  (K) of the heterogeneously bonded chain.

Equation (2), which is an extension of eq. (1) for a terpolymer, was used to investigate the sequence distribution dependence of  $T_g$ . The measured value was compared to the value calculated from eq. (2).

$$T_g = \sum_{i=1}^3 \bar{P}_2\{M_iM_i\}T_{g_i} + \sum_{\substack{i,j=1 \\ i \neq j}}^3 \bar{P}_2\{M_iM_j\}T_{g_{ij}} \quad (2)$$

where  $\sum_{i,j=1}^3 \bar{P}_2\{M_iM_j\} = 1$  and  $\bar{P}_2\{M_iM_j\}$  is the average diad concentration.

TABLE IV  
 Monomer Reactivity Ratios  $r_{ij}$ <sup>5a</sup>

$r_{SM}$	0.50	$r_{SB}$	0.66	$r_{MB}$	1.74
$r_{MS}$	0.50	$r_{BS}$	0.19	$r_{BM}$	0.20

<sup>a</sup>S = St, M = MMA, B = BA.

### Average Diad Concentration of Terpolymer ( $\bar{P}_2\{M_iM_j\}$ )

Based on the copolymerization theory,<sup>4</sup> the values calculated from eqs. (3)–(6) using monomer reactivity ratios ( $r_{ij}$ ) were used for  $\bar{P}_2\{M_iM_j\}$  of the terpolymer. A detailed explanation for setting up these equations is omitted since it has already been described in Part I of this series.<sup>2</sup> The values of  $r_{ij}$  used for the calculation are shown in Table IV and the results for the  $\bar{P}_2\{M_iM_j\}$  calculation are given in Table V.

$$P_2\{M_iM_j\} = P_1\{M_i\}P_{ij} \quad (3)$$

$$P_{ij} = \frac{[M_j]/r_{ij}}{\sum_{h=1}^3 [M_h]/r_{ih}} \quad (4)$$

$$\frac{P_1\{M_1\}}{P_1\{M_2\}} = \frac{P_{21}P_{31} + P_{32}P_{21} + P_{23}P_{31}}{P_{31}P_{12} + P_{12}P_{32} + P_{13}P_{32}}$$

$$\frac{P_1\{M_2\}}{P_1\{M_3\}} = \frac{P_{31}P_{12} + P_{12}P_{32} + P_{13}P_{32}}{P_{12}P_{23} + P_{21}P_{13} + P_{13}P_{23}} \quad (5)$$

$$\bar{P}_2\{M_iM_j\} = \frac{1}{n} \sum_{n=1}^n P_2\{M_iM_j\}_n \quad (6)$$

where  $n$  is the conversion (%).

### Determination of $T_{gij}$ of Heterogeneously Bonded Chain ( $T_{gij}$ )

The determination of  $T_{gij}$  was carried out using eq. (1) for the binary copolymers (C1–C11). As the diad concentrations in eq. (1), those obtained by calculating with eqs. (3) and (6), and eqs. (7) and (8)<sup>4</sup> were used:

$$P_{ij} = \frac{[M_j]/r_{ij}}{\sum_{h=1}^2 [M_h]/r_{ih}} \quad (7)$$

$$\frac{P_1\{M_1\}}{P_1\{M_2\}} = \frac{P_{21}}{P_{12}} \quad (8)$$

The determination of  $T_{gij}$  was conducted so that the measured  $T_{gij}$  values of homopolymers and binary copolymers and calculated values of  $\bar{P}_2\{M_iM_j\}$  (shown in Table VI) would actually be used and in accordance with eq. (1). The slopes of linear lines obtained by plotting for each binary copolymer were

TABLE V  
Average Diad Concentrations  $\bar{P}_2\{M_iM_j\}$  (mol), Calculated for Terpolymers<sup>a</sup>

Terpolymers	$\bar{P}_2\{SS\}$	$\bar{P}_2\{MM\}$	$\bar{P}_2\{BB\}$	$\bar{P}_2\{SM\}$	$\bar{P}_2\{MS\}$	$\bar{P}_2\{SB\}$	$\bar{P}_2\{BS\}$	$\bar{P}_2\{MB\}$	$\bar{P}_2\{BM\}$
R1	0.085	0.126	0.020	0.190	0.220	0.116	0.085	0.063	0.095
R2	0.105	0.143	0.011	0.232	0.256	0.083	0.060	0.043	0.067
R3	0.259	0.022	0.016	0.139	0.158	0.183	0.164	0.020	0.039
R4	0.016	0.335	0.053	0.127	0.147	0.047	0.027	0.114	0.134
R5	0.005	0.449	0.054	0.080	0.092	0.025	0.013	0.135	0.147
R6	0.390	0.006	0.012	0.085	0.095	0.197	0.187	0.009	0.019
R7	0.036	0.063	0.193	0.080	0.113	0.154	0.121	0.104	0.136
R8	0.010	0.019	0.486	0.021	0.036	0.120	0.104	0.094	0.110

<sup>a</sup> Conversion of terpolymers,  $n = 100$  (%); S = St, M = MMA, B = BA.

TABLE VI  
Average Diad Concentrations,  $\bar{P}_2\{M_iM_j\}$  (mol), Calculated for Binary Copolymers

Binary copolymers	Monomers		$\bar{P}_2\{M_iM_j\}$		
	$M_1$	$M_2$	$\bar{P}_2\{M_1M_1\}$	$\bar{P}_2\{M_2M_2\}$	$2\bar{P}_2\{M_1M_2\}$
C1	St	MMA	0.517	0.029	0.454
C2	St	MMA	0.154	0.180	0.666
C3	St	MMA	0.026	0.542	0.432
C4	St	BA	0.569	0.010	0.421
C5	St	BA	0.209	0.106	0.685
C6	St	BA	0.084	0.304	0.612
C7	MMA	BA	0.775	0.011	0.214
C8	MMA	BA	0.624	0.058	0.318
C9	MMA	BA	0.517	0.075	0.408
C10	MMA	BA	0.334	0.174	0.492
C11	MMA	BA	0.143	0.383	0.474

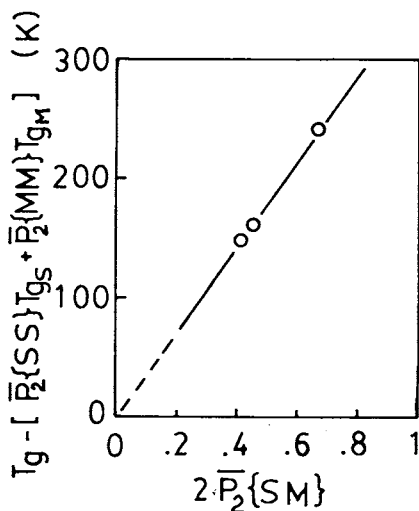


Fig. 3. Plots for determination of  $T_{gi}$ , obtained by eq. (1) for St-MMA copolymers.

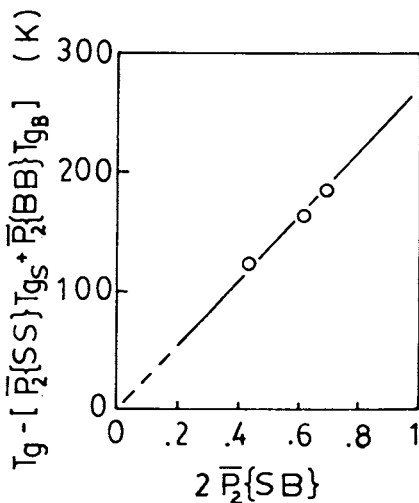


Fig. 4. Plots for determination of  $T_{gi}$ , obtained by eq. (1) for St-BA copolymers.

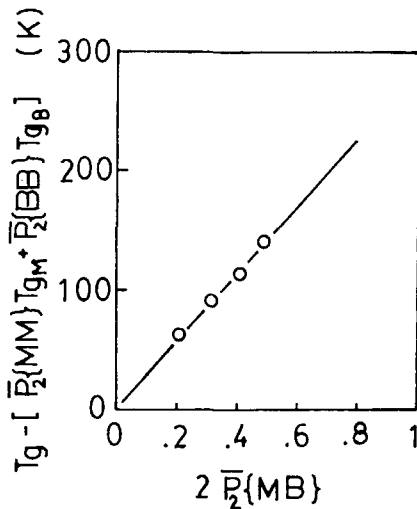


Fig. 5. Plots for determination of  $T_{gij}$ , obtained by eq. (1) for MMA-BA copolymers.

TABLE VII  
 $T_{gi}$  and  $T_{gij}$  (K) Obtained

Monomers			
$i$	$j$	$T_{gi}$	$T_{gij}$
St	—	354	—
MMA	—	366	—
BA	—	221	—
St	MMA	—	356
St	BA	—	271
MMA	BA	—	275

used, as shown in Figures 3-5. In these figures, the plots are on a line passing through the origin.  $T_g$  of the binary copolymer follows the modified Gibbs-Dimarzio equation. The  $T_g$  value of each bonded chain is shown in Table VII.

#### Application of the Extended Modified Gibbs-Dimarzio Equation

The results by which the  $T_g$ 's of terpolymers were calculated according to the extended modified Gibbs-Dimarzio equation [eq. (2)] are shown in Table VIII. For comparison, the values calculated from Fox's equation<sup>6</sup> [eq. (9)] using the  $T_g$  values of homopolymers are shown in Table VIII.

$$1/T_g = \sum_{i=1}^3 W_i/T_{gi} \quad (9)$$

where  $W_i$  is the weight fraction of component  $i$  and  $T_{gi}$  is the  $T_g$  (K) of homopolymer  $i$ .

As evident from Table VIII, in the case of terpolymers of nearly all compositions, the  $T_g$  values calculated from eq. (2) show considerably good agreement with measured values. This demonstrates that eq. (2) is reasonable. Thus, when  $T_g$  values of homopolymers of St, MMA, and BA and  $T_g$  values of



TABLE VIII  
 Observed vs. Calculated  $T_g$  Values of Terpolymers

Terpolymers	$T_g$ (°C) (obs)	$T_g$ (°C) calcd by eq. (2)	$T_g$ (°C) calcd by eq. (9)
R1	57	52	38
R2	74	62	52
R3	55	46	37
R4	56	53	40
R5	55	54	41
R6	50	46	34
R7	12	15	1
R8	-18	-18	-27

heterogeneously bonded chain ( $T_{gij}$ ) are given, the  $T_g$ 's of terpolymers consisting of these monomers can be estimated by eq. (2), using average diad concentrations. However, values calculated from eq. (9) are 10–20°C lower than the measured values for various samples, demonstrating poor applicability of this equation. Although  $T_g$  of a copolymer is treated with average polymer composition in Fox's equation, our results suggests that a more accurate estimation of  $T_g$  is possible by taking the sequence distribution dependence of  $T_g$  in a terpolymer into consideration.

### SUMMARY

Using St-MMA-BA terpolymers of various compositions, we investigated the sequence distribution dependence of  $T_g$ . The measured  $T_g$  values showed good agreement with those calculated from the modified Gibbs-Dimarzio equation for binary copolymers extended to terpolymers. This equation could also be used to estimate the  $T_g$  of the terpolymer. This equation may be used to compute  $T_g$  values of St-methacrylate-acrylate terpolymers having other alkyl side chains in the methacrylate or acrylate, because these polymers all have the same main chain, using the following:

$$T_g = \sum_{i=1}^3 \bar{P}_2\{M_i M_i\} T_{gi} + \sum_{\substack{i,j=1 \\ i \neq j}}^3 \bar{P}_2\{M_i M_j\} T_{gij}$$

where  $T_{gi}$  is the  $T_g$  (K) of homopolymer  $i$  and  $T_{gij}$  is the  $T_g$  (K) of heterogeneously bonded chain  $i-j$ .

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