

Glass Transition Behaviors of Random and Block Copolymers and Polymer Blends of Styrene and Cyclododecyl Acrylate.

I. Glass Transition Temperatures

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ABSTRACT: Glass transition temperatures have been studied for the random and block copolymers of styrene and cyclododecyl acrylate.

The random copolymers showed a single glass transition temperature, which provided a concave glass transition temperature—composition curve. This concave relationship was fairly well represented by the modified Gibbs—Dimarzio equation of Uematsu and Honda, which includes the influence of the specific character of cyclododecyl acrylate as a monomeric unit.

Each of the block copolymers as well as the blends of their component homopolymers showed two separated glass transition temperatures corresponding to the respective ones of poly(cyclododecyl acrylate) and polystyrene; these were independent of the total composition, owing to the incompatibility of the components.

KEY WORDS Cyclododecyl Acrylate / Styrene / Random Copolymer / Block Copolymer / Polymer Blend / Glass Transition Temperature / DSC / Modified Gibbs—Dimarzio Equation / Stiffness Energy / Sequential Distribution /

There have been numerous studies on the glass transition temperatures for various copolymer systems.¹⁻³ The relationships between glass transition temperatures and compositions for random copolymers have been expressed by several theoretical and empirical equations, such as the Gordon—Taylor,⁴ the Fox,⁵ and the Gibbs—Dimarzio equations.⁶ However, these expressions do not take into account the influences of adjacent dissimilar monomeric units on the steric and energetic terms in the copolymer backbones.

Recently, some authors⁷⁻¹¹ have pointed out the deviations from these equations for various random copolymers. Uematsu and Honda^{8,9} proposed a modified Gibbs—Dimarzio equation containing a parameter of chain stiffness energy of a dissimilar monomeric unit-linkage in copolymers. On the other hand, Johnston¹⁰ modified the Fox relationship by considering sequential distributions in copolymers.

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In the preceding papers,^{12,13} we reported that the radical copolymerization of cyclododecyl acrylate with styrene or acrylonitrile produced random-type copolymers, in which the characteristic reactivity of cyclododecyl acrylate was attributed to the specific characteristics of its cyclododecyl group, a large molar volume and cohesive energy. This reactivity would result in the peculiar structures of the copolymers.

A block copolymer presents a contrast to a random copolymer in the sequential distributions. Graham, *et al.*,¹⁴ noted that isopropyl acrylate could give a AB-type block copolymer with living polystyrene anions initiated by *n*-butyllithium—tetrahydrofuran, but other acrylates such as ethyl and cyclohexyl acrylates had not polymerized well. In our laboratory, however, a AB-type block copolymer of cyclododecyl acrylate and styrene could be obtained according to the Graham's method.

In this paper, we report the glass transition temperatures of the prepared random and block copolymers of styrene and cyclododecyl acrylate,

as investigated by DSC. The relationship between glass transition temperatures and compositions of the random copolymers was treated with the empirical equations. The modified Gibbs—Dimarzio equation by Uematsu and Honda gave a satisfactory explanation for the experimental results. On the other hand, the block copolymers as well as their component polymer blends had two glass transition temperatures which were independent of composition.

EXPERIMENTAL

Preparation of Random Copolymers

We previously reported¹³ that the free radical copolymerization of styrene (St) and cyclododecyl acrylate (CDA) provided random copolymers: The monomer reactivity ratios, r_B and r_A , are 0.6 and 0.33 ($M_A=CDA$), respectively; their product is 0.20. In this study, poly(cyclododecyl acrylate) (PCDA) and three kinds of random St—CDA copolymers (A-1, A-2, and A-3) were prepared in the presence of α, α' -azobisisobutyronitrile (AIBN) in benzene at 60°C with the variation in molar ratios of monomers for the times giving 10–15% conversions. The obtained copolymers were precipitated twice with a benzene—methanol system and dried *in vacuo* at 50°C for several days.

In Table I, the composition, density, and number-average molecular weight (M_n) for the random copolymers are presented. The composition was determined by carbon and hydrogen analyses, and the density was measured at 20°C by the flotation method with aqueous solutions of calcium chloride. The number-average molecular weight (M_n) was determined by GPC with a Waters Model R-4 as based on a calibration curve of monodisperse polystyrenes (Waters

Table I. Composition, density, and molecular weight of random copolymers of styrene (St) and cyclododecyl acrylate (CDA)

Sample	Mole fraction of CDA in copolymer	Density at 20°C	M_n	M_w/M_n
A-1	0.194	1.047	4.31×10^4	1.56
A-2	0.514	1.048	7.33×10^4	1.56
A-3	0.776	1.049	13.7×10^4	1.79
PCDA	1.000	1.050	18.4×10^4	1.94

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Preparation of Block Copolymers

According to the method by Graham, *et al.*,¹⁴ the block copolymers, Z-1 and Z-2, were produced by the addition of CDA to living polystyrene anions initiated with *n*-butyllithium—tetrahydrofuran in toluene as solvent under highly reduced pressure (10^{-4} mmHg) at room temperature. The obtained block copolymers were purified and dried by the same methods as used in the case of the random copolymers. Identity of these block copolymers was confirmed by TLC with silica gel and benzene as an eluting solvent (the details of the preparation will be published elsewhere).

The composition, density, and M_n of these block copolymers are listed in Table II. Table II also presents M_n of polystyrene (PSt) prepared under the same conditions as in the synthesis of the block copolymer without the addition of CDA, which would correspond to the PSt block component of the copolymer. These values were close to the M_n values expected from the molar ratios of St monomer and initiator.

The IR spectra of the block copolymers were in coincidence with those of the random copolymers.¹³ In addition, the densities of these co-

Table II. Composition, density, and molecular weight of block copolymers of styrene (St) and cyclododecyl acrylate (CDA)

Sample	Block copolymer				PSt ^b	
	Mole fraction of CDA in copolymer	Density at 20°C	M_n	M_w/M_n	M_n	M_w/M_n
Z-1	0.098 (0.199) ^a	1.048	13.1×10^4	1.37	9.02×10^4	1.35
Z-2	0.151 (0.290) ^a	1.049	1.28×10^4	1.59	0.66×10^4	1.07

^a Weight fraction of CDA in copolymer.

^b Prepared under the same conditions without the addition of CDA.

polymers in Tables I and II changed little with the variation in sequential structures but depended mainly on the compositions.

However, the block copolymers as well as the PSt-PCDA blends were molded into whitish, opaque films under reduced pressure at 160–195°C, in contrast to the colorless, transparent films of the random copolymers.

The polymer blends, Blend-1 (29.0-wt% PCDA–71.0-wt% PSt) and Blend-2 (50.0-wt% PCDA–50.0-wt% PSt), were respectively obtained by pouring the benzene solution of a mixture of PSt ($M_n=9.0 \times 10^4$) prepared with *n*-butyllithium and PCDA ($M_n=1.8 \times 10^5$) with AIBN into methanol.

DSC Measuring Procedures

Glass transition temperatures (T_g) were measured by DSC with a Perkin-Elmer Model DSC-1B at a scanning rate of 32°C/min under nitrogen streaming. For the measurements, a sample (6–8 mg) which had been heated up to 120–195°C was then quenched to 0°C in the apparatus. A thermogram was run, and T_g was determined as the temperature at which an endothermic peak started in the DSC thermogram.¹⁵

RESULTS AND DISCUSSION

Glass Transition Temperatures of Random St-CDA Copolymers

The DSC thermograms for PSt ($M_n=9.0 \times 10^4$), PCDA ($M_n=1.8 \times 10^5$), and random St-CDA copolymers, A-1, A-2, and A-3, are presented in Figure 1. Each of the random copolymers exhibited a single T_g as listed in Table III. Figure 2, shows a concave T_g vs. composition curve for the random copolymers.

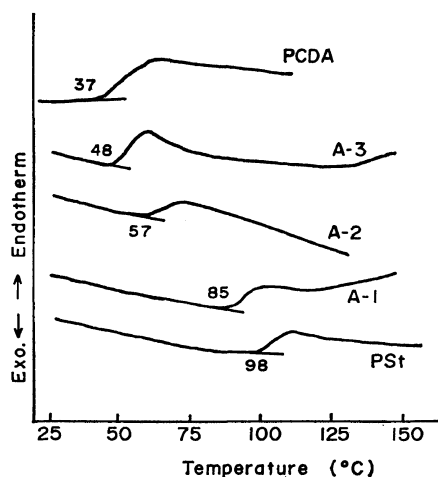


Figure 1. DSC thermograms of PCDA, PSt, and random St-CDA copolymers (A-1, A-2, and A-3).

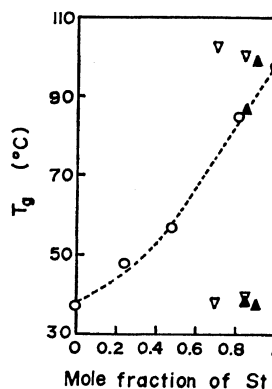


Figure 2. Relationship between glass transition temperatures (T_g) and compositions of St-CDA copolymers: (○) random copolymers; (▲) block copolymers; (▽) polymer blends.

Table III. Glass transition temperatures of random copolymers of styrene (St) and cyclododecyl acrylate (CDA)

Sample	Mole fraction of CDA in copolymer	T_g (obsd), °K (°C)	T_g (calcd), °K							
			Fox	Wood	Johnston	Modified Gibbs-Dimarzio eq by Uematsu and Honda				
						Case A	Case B	Case C	Case D	Case E
A-1	0.192 (0.355) ^a	358 (85)	348	354	356	352	359	352	356	357
A-2	0.514 (0.708) ^a	330 (57)	327	335	340	333	327	330	332	330
A-3	0.763 (0.880) ^a	321 (48)	317	322	325	325	314	323	320	320

^a Weight fraction of CDA in copolymer.

There have been some theoretical and empirical equations⁴⁻⁷ concerning the relationship between the glass transition temperatures and compositions of random copolymers. They can be expressed by the following Wood equation:⁷

$$W_A(T_g - T_{gA}) + KW_B(T_g - T_{gB}) = 0 \quad (1)$$

where T_g is the glass transition temperature of a copolymer containing the weight fractions, W_A and W_B , of two monomeric units, A and B, and T_{gA} and T_{gB} are the glass transition temperatures of the homopolymers, respectively. The Gordon—Taylor equation⁴ requires the constant, $K = \Delta\beta_B/\Delta\beta_A$, in eq 1 where $\Delta\beta_A$ or $\Delta\beta_B$ is the difference between the expansion coefficients of the rubbery and glassy states of homopolymer A or B. On the other hand, the Gibbs—Dimarzio equation⁵ defines $K = \alpha_B M_A / \alpha_A M_B$ in eq 1 where α_A or α_B is the number of rotatable bonds of a monomeric unit having the molecular weight, M_A or M_B . For the special case where $K = T_{gA}/T_{gB}$, eq 1 reduces to the Fox relationship.⁵

As easily confirmed, the Fox equation did not hold for the random St—CDA copolymers (see Table III). Equation 1 calls for linearity in a plot of T_g against $(T_{gB} - T_B)(W_B/W_A)$ with a slope of K , and further in a plot of T_g against $(T_g - T_{gA})(W_A/W_B)$ with a slope of $-1/K$.⁷ From Figure 3, since these plots for the random St—CDA copolymers deviated somewhat from the linear relations, the experimental coefficient (K_e) was approximately estimated to be 1.54. Actually,

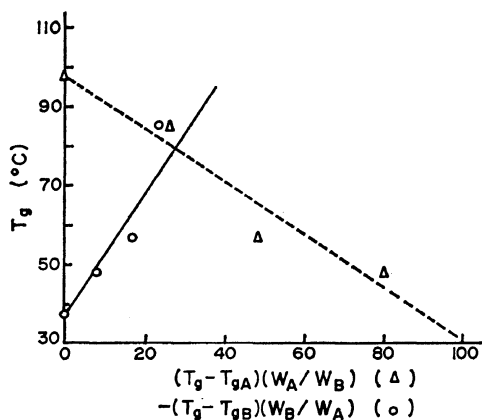


Figure 3. Plots of T_g vs. $(T_g - T_{gA})(W_A/W_B)$ and T_g vs. $-(T_g - T_{gB})(W_B/W_A)$ for random St—CDA copolymers.

the T_g 's calculated by assuming $K = K_e = 1.54$ in eq 1 did not agree with the observed T_g 's as given in Table III. Accordingly, neither eq 1 nor the Gordon—Taylor and the Gibbs—Dimarzio equations could satisfactorily express the concave relationship between T_g 's and compositions of the random St—CDA copolymers.

Similar deviations from these equations have been demonstrated for various random copolymers.⁷⁻¹¹ These expressions do not take into account the influences of adjacent dissimilar monomeric units on steric and energetic terms in copolymer backbones. Therefore the deviation may be attributable to the different contributions of monomeric units in A—B bond to the glass transition temperatures of copolymers from those in A—A and B—B linkages.

Johnston¹⁰ proposed a modified Fox relationship for the alternating and random copolymers of α -methylstyrene and acrylonitrile, taking into account the probabilities, P_{AA} , P_{BB} , P_{AB} , and P_{BA} , of diads as follows:

$$(1/T_g) = (W_A P_{AA}/T_{gA}) + (W_B P_{BB}/T_{gB}) + (W_A P_{AB} + W_B P_{BA})/T_{gAB} \quad (2)$$

where T_{gA} , T_{gB} , and $T_{gAB} = T_{gBA}$ denote the glass transition temperatures of homopolymers A, B, and an imaginary alternating copolymer, respectively. These probabilities are calculated by computing the average run number (R) of Harwood and Ritchy¹⁶ as follows:

$$P_{AB} = R/200f_A, \quad P_{AA} = 1.0 - P_{AB} \quad (3)$$

where f_A and f_B are the mole fractions of A and B in copolymers. In his paper, no concrete estimation of T_{gAB} was presented. Here we assumed $T_{gAB} = (T_{gA} + T_{gB})/2$ for the random St—CDA copolymers; however, the calculated T_g 's were inconsistent with the observed ones (see Table III). This may indicate that the sequential distributions in these copolymers could not be a dominant factor for the deviation from the empirical equation. Since the inconsistency would be introduced by the faulty assumption of T_{gAB} , this further suggests that CDA and St monomeric units would give different contributions to T_{gAB} .

Uematsu and Honda^{8,9} presented a modified Gibbs—Dimarzio equation, estimating the different chain stiffness energy, ϵ_{AB} , for A—B bond

from ϵ_{AA} and ϵ_{BB} of the homopolymers as follows:

$$\epsilon = f_{AA}\epsilon_{AA} + f_{BB}\epsilon_{BB} + f_{AB}\epsilon_{AB} \quad (4)$$

$$(\epsilon_{AA}/kT_{gA}) = (\epsilon_{BB}/kT_{gB}) = (\epsilon_{AB}/kT_{gAB}) = (\epsilon/kT_g) \quad (5)$$

$$T_g = f_{AA}T_{gA} + f_{BB}T_{gB} + f_{AB}T_{gAB} \quad (6)$$

where f_{AA} , f_{BB} , and f_{AB} are the fractions of the rotational units with corresponding chain stiffness energies. They proposed four cases of A, B, C, and D according to the modes of triad linkages, in which the fractions can be calculated from the mole fractions and monomer reactivity ratios in copolymers.⁸

Here we tried to divide their case D into two cases D and E. In case D, a B monomeric unit producing a higher T_{gB} of homopolymer was assumed to have always ϵ_{BB} in any linkage-mode in a copolymer. This assumption was applied by Uematsu and Honda⁸ to various random copolymer systems, for example, methyl acrylate (A)—methyl methacrylate (B) and methyl acrylate (A)—St (B). In contrast to that in case D, each A unit forming a lower T_{gA} of homopolymer was supposed to have ϵ_{AA} in a copolymer in case E. This case was also suitable for the methyl acrylate (B)—vinylidene chloride (A) and vinyl chloride (B)—vinyl acetate (A) systems as reported by them.⁸

For the random St—CDA copolymers, the T_{gAB} 's, as determined as the slope of lines for the plots of $T_g(\text{obsd}) - (f_{AA}T_{gA} + f_{BB}T_{gB})$ against f_{AB} in Figure 4, were 333°K in case A, 314°K in case B, 261°K in case C, 285°K in case D, and 341°K in case E, respectively. The T_g 's calculated by using these T_{gAB} 's in eq 4 are listed in Table III. Among them, the calculated T_g 's in cases D and E fitted fairly well to the observed ones; however, in the other cases the values did not match well. These results would indicate that either assumption, from case D or E in the modified Gibbs—Dimarzio equation, could be applicable to the concave T_g vs. composition curve for the random St—CDA copolymers. At present we cannot directly determine whether the assumption in case D or in case E would be more suitable for this curve. If the completely alternating copolymer could be prepared, we could pick out the appropriate one by comparing the observed T_{gAB} of the alternat-

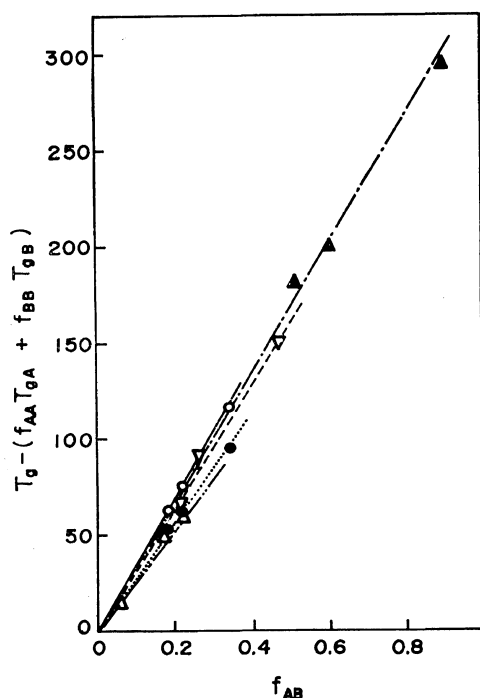


Figure 4. Plots of $T_g(\text{obsd}) - (f_{AA}T_{gA} + f_{BB}T_{gB})$ vs. f_{AB} for random St—CDA copolymers: (\blacktriangle) in case A; (∇) in case B; (\triangle) in case C; (\bullet) in case D; (\circ) in case E.

ing copolymer with the T_{gAB} 's calculated in these cases.

Recently Hirooka and Kato¹¹ reported that the relationships between the glass transition temperatures and compositions for various random copolymers were expressed as three forms, *i.e.*, concave, linear, and convex curves as represented by the modified Gibbs—Dimarzio equation by Uematsu and Honda. They further stated an empirical rule deduced from their experimental results that T_{gAB} of an alternating copolymer would be lower than that of the corresponding random copolymer with equimolar composition in the case of the concave curve. As presented in Figure 2, the random St—CDA copolymers showed a concave T_g —composition curve. According to their empirical rule, the imaginary T_{gAB} of alternating St—CDA copolymer may be expected to lie below this concave curve. The assumed $T_{gAB} = 285^\circ\text{K}$ (12°C) in case D would be more in keeping with this rule than $T_{gAB} = 341^\circ\text{K}$ (68°C) in case E.

As calculated by using ϵ_{BB} of St=1.43 (by Uematsu and Honda⁸) in eq 5, ϵ_{AA} of CDA was 1.19 kcal/mol and ϵ_{AB} was 1.10 kcal/mol in case D, respectively. In addition, the total chain stiffness energy (ϵ) of an imaginary random St—CDA copolymer having $f_A=f_B=0.5$ could be estimated to be 1.28 kcal/mol in eq 4. This total stiffness energy may be conveniently expressed as follows:

$$\epsilon = \epsilon_{AA}z_A + \epsilon_{BB}z_B \quad (7)$$

where z_A and z_B are the fractions of ϵ_{AA} and ϵ_{BB} in ϵ . In a St—CDA copolymer, St monomeric units can provide rigid skeletons, while CDA units can form flexible backbones in response to ϵ_{BB} and ϵ_{AA} . If the peculiar influences of side groups on the chain stiffness of copolymer backbones could be eliminated, then both z_A and z_B should be 0.5 for the equimolar random copolymer. Actually z_A for CDA units was 0.63, considerably larger than 0.37 of z_B for St units.

As reported in our preceding paper,¹³ a CDA monomeric unit can be characterized by its large molar volume (245 cm³), of which cyclododecyl group shares 180 cm³ in comparison with 115 cm³ of a St unit. The great volume of cyclododecyl group may introduce more or less interchain and intramolecular spacing. This would make us suppose that the stiffness of copolymer backbones provided by St units could be considerably decreased by the internal plasticization effect of this side group of a CDA unit to yield the concave T_g —composition curve. As an example, we proved that a similar effect for a cyclododecyl group would lead to a lower T_g (81°C) of poly(cyclododecyl methacrylate) relative to 105°C of poly(methyl methacrylate).

Glass Transition Temperatures of Block St—CDA Copolymers and PSt—PCDA Blends

The glass transition behaviors of block copolymers and polymer blends are mainly influenced by the compatibility of their components.² For instance, a block copolymer composed of one homogeneous phase has a single glass transition temperature dependent on the whole composition as found in the block copolymer systems of methyl methacrylate—acrylonitrile by Beevers and White¹⁷ and styrene— α -methylstyrene by Baer.¹⁸ On the other hand, a copolymer with

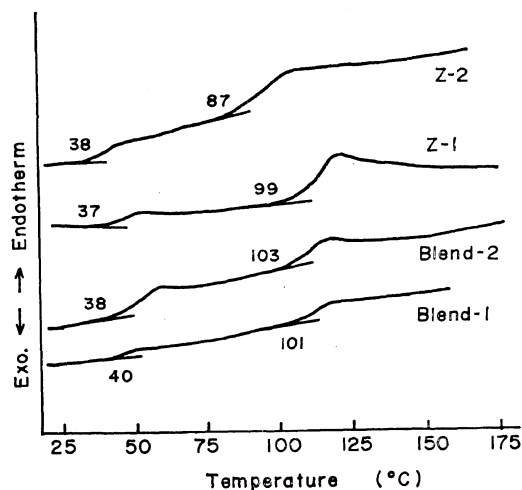


Figure 5. DSC thermograms of block St—CDA copolymers (Z-1 and Z-2) and PSt—PCDA blends (Blend-1 and Blend-2).

two heterogeneous phases shows the two glass transition temperatures corresponding to those of the homopolymers, as observed in the butadiene—acrylonitrile rubbers by Ambler.¹⁹

In the case of PSt and PCDA, their incompatibility could be noticed from the whitish, opaque films of PSt—PCDA blends. Figure 5 shows that the respective PSt—PCDA blends, Blend-1 (29.0-wt% PCDA) and Blend-2 (50.0-wt% PCDA), had double, separated endothermic peaks beginning at the same temperatures, 38–40°C and 101–103°C, corresponding to T_g 's of the components, 37°C of PCDA ($M_n=1.8 \times 10^5$) and 98°C of PSt ($M_n=9.0 \times 10^4$).

Similarly the block St—CDA copolymers, Z-1 and Z-2, were molded into the opaque films and had double endothermic peaks, as shown in Figure 5, for which the T_g 's of the PCDA blocks of both were the same, 37–38°C, while T_g of the PSt block of Z-2 was 87°C lower than 99°C of the PSt block of Z-1. The change in T_g 's of these PSt blocks should be mainly ascribed to the difference in their molecular weights, because T_g of the corresponding homopolymer ($M_n=6.6 \times 10^3$) to the PSt block of Z-2 was also 85°C lower than 98°C of the one ($M_n=9.0 \times 10^4$) to the PSt block of Z-1. Concerning the molecular weight dependence on the glass transition temperatures of polystyrenes, similar results have

been reported by Fox and Flory²⁰ and Hatakeyama and Kanetsuna²¹ that the glass transition temperatures of polystyrenes become considerably lower with a decrease in the molecular weights below 10^4 .

Consequently, the respective PCDA blocks and PSt ones of the block copolymers had T_g 's corresponding to those of the homopolymers like the components of the blends. These results would suggest that the components could behave independently in the separated phases owing to their lack of compatibility. As seen in the DSC thermogram for Z-2 in Figure 5, this block copolymer gave a peculiarly increasing slope in the middle of the both T_g 's which may be attributable to a slight interaction of the components. A further study on the glass transition behaviors in the dielectric properties of these copolymers will be reported later.

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