

Glass Transition of Thermotropic Polymers Based upon Vanillic Acid, *p*-Hydroxybenzoic Acid, and Poly(ethylene terephthalate)

XIN-GUI LI,^{1,*} MEI-RONG HUANG,¹ GUI-HE GUAN,² and TONG SUN²

¹Center of Membrane Separation Engineering, Tianjin Institute of Textile Science and Technology, Tianjin 300160, and ²Department of Polymer Materials, China Textile University, Shanghai 200051, People's Republic of China

SYNOPSIS

Differential scanning calorimetry (DSC) and dynamic mechanical and thermomechanical analyses are used to study the glass transition temperature (T_g) of the thermotropic liquid crystalline polyesters prepared by molten polycondensation of 4-acetoxyvanillic acid (V), 4-acetoxybenzoic acid (B), and poly(ethylene terephthalate) (E). The polyesters exhibit two glass transition ranges at 66–83 as well as 136–140°C, which are attributed to E segmental motion in the E-rich/B-rich phases of the polyesters, as well as to the local mobility of the B component in the B-rich phase. The lower T_g of the polyesters increases with an increase in the B and V unit contents or with increasing heating rate in the DSC measurements, but the higher T_g decreases slightly. The experimental T_g values are compared with the T_g values predicted from three equations on the basis of the sequence distribution and the monomer reactivity ratio of the polyesters. Uematsu's, Johnston's, and Couchman's equations all give a better fit with the experimental results. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

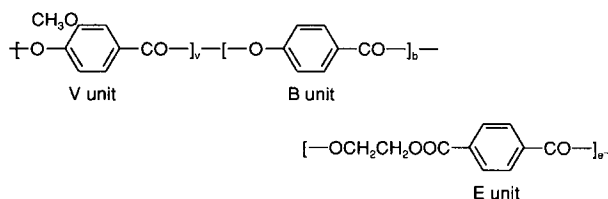
In the last two decades, there has been considerable interest in polymers exhibiting thermotropic liquid crystalline order.^{1–4} The interest in the polymers based on *p*-hydroxybenzoic acid/poly(ethylene terephthalate) (designated as BE polymer) stems from the formation of a thermally stable nematic liquid crystalline melt and their ease of processing and superior mechanical properties.^{1,2} The synthesis,¹ molecular structure,^{2,3} thermal behavior,⁵ rheological property,⁶ and nematic melt spinning⁷ of the BE polymers have been investigated by a number of workers. More recently, we have studied new polymers, which are a series of modified BE polyesters incorporating vanillic acid residue as a chain unit (designated as VBE polyesters).^{8–12} It has been shown that some of the VBE polyesters exhibit easier preparation and better mechanical

properties than the corresponding BE polyesters.⁸ The structure of the VBE polyesters has been characterized by high-resolution NMR,⁹ gel permeation chromatography,⁹ X-ray diffraction,¹⁰ and scanning electron microscope¹¹ measurements. The liquid crystalline texture of the VBE polyester melts has been observed by a polarizing microscope.¹² The present work is aimed at the glass transition of three series of the VBE polyesters by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermal mechanical analysis (TMA). For comparison, the glass transition temperature T_g of a series of BE polyesters is also characterized in this paper. Additionally, a few studies have been done on the variation of the T_g with the BE binary copolyester composition,¹³ however, there are few reports concerning the dependence of the T_g on the VBE ternary copolyester composition and sequence distribution. This paper is concerned with the relationship between the T_g and the terpolyester composition/sequence distribution/monomer reactivity ratio with the purpose of predicting the T_g values in the terpolyesters as a function of composition and diad sequence distribution.

* To whom correspondence should be addressed.

EXPERIMENTAL

All of the VBE terpolyesters and BE binary copolyesters in this study were synthesized by melt polycondensation reactions of 4-acetoxy-3-methoxybenzoic acid (V), 4-acetoxybenzoic acid (B), and poly(ethylene terephthalate) (E) ($\eta_{inh} = 0.6$ dL/g), as described in an earlier paper.⁸ Their nominal structure is shown:



The glass transition temperatures, T_g , were measured using a differential scanning calorimeter (DSC) (DuPont 9900) operating at six heating rates of 5, 10, 20, 30, 40, and 50°C/min in nitrogen at a flow rate of 50 mL/min. Polymer samples usually weighing 10–15 mg were used for DSC analysis. The T_g was determined from the intersection between the initial baseline and the sloping portion of the baseline due to the glass transition.

Dynamic mechanical analysis (DMA) was performed on as-drawn films of the polyesters at 11 Hz with a Toyo Baldwin Rheovibron DDV-II-EA apparatus in the temperature range from room temperature to 180°C at a heating rate of 2°C/min.

The changes in length (or thickness) parallel (or perpendicular) to the rod axis were measured on an as-drawn rod of the VBE polyester with a Perkin-Elmer 7 thermomechanical analyzer (TMA) with a scanning rate of 5°C/min under nitrogen while applying a load of ca. 200 mN. The penetration of a quartz rod with a flat tip under this small load gives an additional and independent information about transition temperature. Thermal linear expansion coefficient, α , was calculated by

$$\alpha = \Delta L/L \times \Delta T \quad (1)$$

where L is the sample height and ΔL is the dimension change of the sample in a certain temperature range ΔT .

RESULTS AND DISCUSSION

Glass Transition of BE Binary Copolyesters Observed with DSC

The glass transition data from this study and data from the literatures are collected in Figure 1.^{1,5,7,13–17}

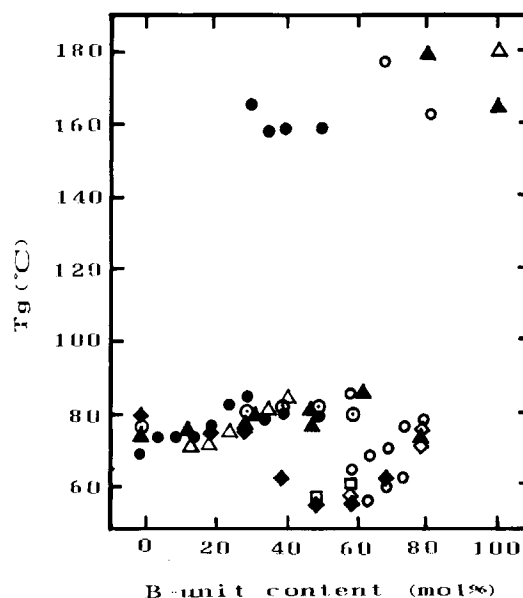


Figure 1 Glass transition temperatures of BE binary copolyesters as a function of the B-unit content by DSC measurements. (○) this study; (●) ref. 1; (⊙) ref. 14; (△) ref. 13; (▲) ref. 5; (◇) ref. 15; (◆) ref. 16; (□) ref. 17.

It is apparent that there are some differences between different sources,¹⁷ probably due to the differences in the procedures used to locate T_g , to the differences in the sequence distributions of the BE copolyesters, to the differences in the thermal histories of the samples, to the differences in the molecular weight and its distributions, and to the differences in the measuring conditions (including heating rate, sample size of the domains detected).

When the B-unit content is lower than 30 mol %, only one T_g is observed irrespective of the B-unit content. This single T_g seems to be practically independent of B-unit content up to 25 mol %. These data points give an average of 74°C for the T_g with a deviation of $\pm 4^\circ\text{C}$. However, in the copolyesters of B content ranging from 30 to 80 mol %, two distinct T_g s are observed, indicating that the copolyesters are phase separated into two phases, an E-rich phase (lower T_g 56–87°C) and a B-rich phase (higher T_g 158–180°C). As the B-unit content increases the two T_g s both remain invariant or increase slightly except for an abrupt decline in the lower T_g at the B-unit content of 60 mol %.

Glass Transition of VBE Terpolyesters Observed with DSC

As one introduces V as a comonomer with the BE polymer for the preparation of VBE terpolyesters, the glass transition temperature, T_g , increases slightly as compared to that of the BE polymer

shown in Figure 2. The T_g remains invariant at 65°C as V-unit content is varied from 0 to 3.5 mol %. But the T_g increases from 66 to 69°C as the amount of V unit is increased from 3.5 to 5 mol %. This may be attributed to the increased stiffness and aromaticity of the polymer chain on the introduction of the V unit. Furthermore, at a given E-unit content of ca. 35 mol %, the T_g of the VBE terpolyesters will increase obviously from 69 to 87°C with an increase in V content from 15 to 35 mol % (Fig. 3).

On the other hand, the DSC thermograms of the VBE terpolyesters with a given V content of 5 mol % and different B-unit contents indicate that their T_g s are increased (from 68, 74, 77, to 83°C at a heating rate of 20°C/min) with an increase in the B content from 60, 65, 70, to 75 mol %. This may be attributed to the enhanced stiffness of the terpolyester chains on the increase of B unit.

Dependence of Glass Transition Temperature for VBE Terpolyesters on Heating Rate in DSC Test

Figure 4 shows the relationships between heating rate and the T_g of five VBE terpolyesters by DSC measurements. The T_g increases with increasing heating rate. Kyotani et al. investigated other thermotropic polyesters and found a very similar dependence of T_g on heating rate.¹⁹ Probably, the reason for this increase in T_g is that the actual temperature within the samples is lower than the temperature around the samples in the DSC measurement at a larger heating rate. These results may be of importance in determining measuring condition and useful service temperature limit.

In Figure 4 two copolyesters with the V/B/E ratios of 0/60/40 and 0.5/60/39.5 exhibited two T_g s probably due to their distinct biphasic structure (also see Fig. 1). The lower T_g (57–70°C) may be due to the motion of the E segment in the E-rich phase

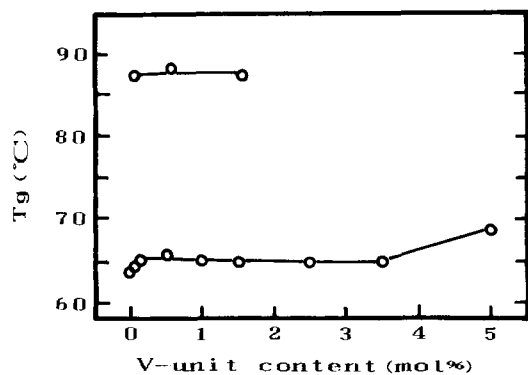


Figure 2 Glass transition temperature of VBE terpolyesters with a fixed B-unit content of 60 mol % as a function of V-unit content at a heating rate of 20°C/min.

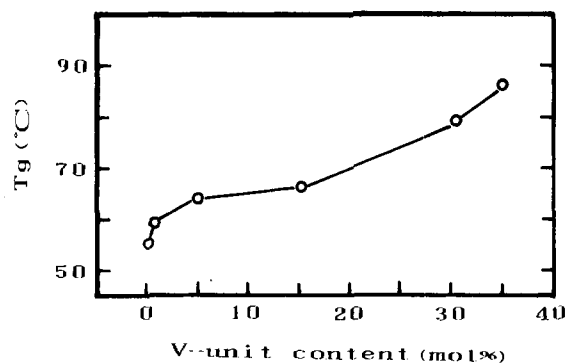


Figure 3 Glass transition temperature of VBE terpolyesters with a fixed E-unit content of 35 mol % as a function of V-unit content at a heating rate of 20°C/min.

and the higher T_g (85–94°C) might be related to the main chain motions of the E segment located within the E-rich phase in an environment similar to the poly(ethylene terephthalate).¹⁸ These results are somewhat similar to those from DMA studies reported by Benson et al.¹⁸ The other three copolyesters having V/B/E ratios of 5/60/35, 5/65/30, and 5/75/20 showed only one T_g , maybe owing to their obscure biphasic structure because the addition of more unit V might result in more random chain structure of the copolyesters.⁹

Glass Transition of VBE Terpolyesters Observed with DMA

The four relaxation processes or transitions from this study and the literature are collected in Figure 5 for the BE copolyesters. Obviously, the transition

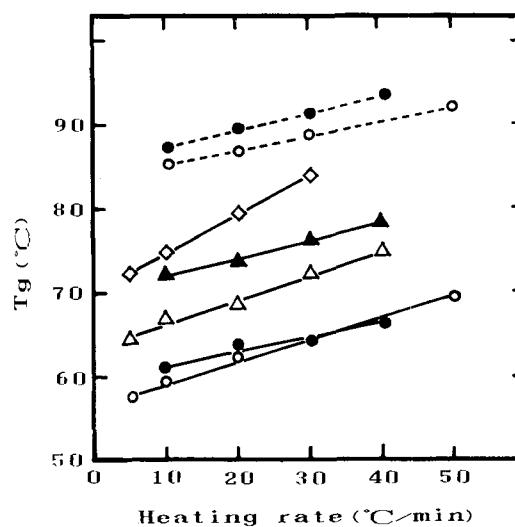


Figure 4 Glass transition temperature vs. heating rate of VBE terpolyesters with V/B/E ratios: (○) 0/60/40; (●) 0.5/60/39.5; (△) 5/60/35; (▲) 5/65/30; (◇) 5/75/20.

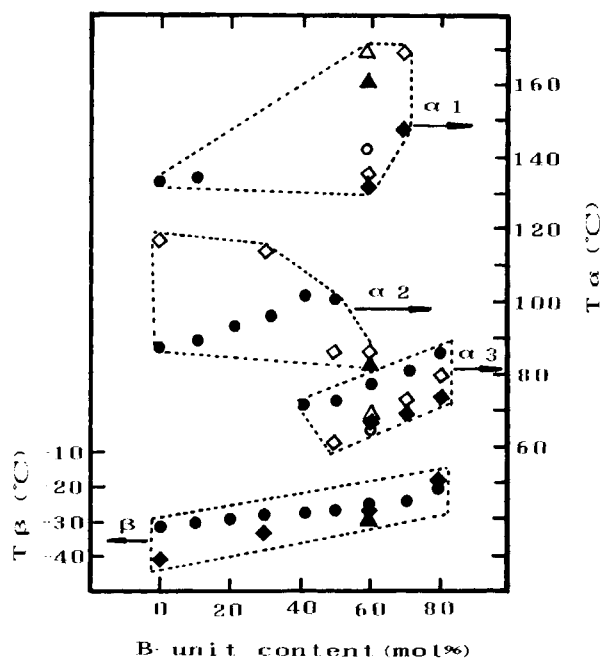


Figure 5 Temperature of α and β relaxation or transition peaks from $\tan \delta$ -temperature spectra for BE binary copolyesters by DMA measurements: (○) this study; (●) ref. 20; (Δ) ref. 7; (\blacktriangle) ref. 21; (\diamond) ref. 22, (\blacklozenge) ref. 23.

temperature increases with increasing B content. By DMA we can also detect two relaxation processes for the VBE terpolyesters. Figure 6 shows the temperature dependence of the tangent of mechanical loss for as drawn VBE terpolyester films. One relatively sharp maximum at 68–77°C (α_3 transition) and one very broad maximum centered at 136–140°C (α_1 transition) are observed. As listed in Table I, with decreasing V-unit content, the lower T_g (α_3) increases but the higher T_g (α_1) decreases. The lower T_g might be related to the motion of E segment found in the E-rich phase¹⁸ and the higher T_g may be assigned to relaxation of E segment in oriented E-rich phase and/or the local mobility of the B component in the B-rich phase.⁷ Antipov et al. observed a weak maximum at approximately 120°C in studies on B-unit-containing thermotropic polyester fiber.²⁴

Glass Transition and Thermal Expansion of VBE Terpolyester Observed with TMA

The T_g for the VBE terpolyester was also verified with a TMA.²⁵ Typical TMA plots of the VBE terpolyester as-drawn rod with V/B/E ratio of 0.05/60/39.95 are shown in Figure 7. There are two obvious inflection points at approximately 41 and 71°C (41 and 60°C) on curve A (curve B) and the third

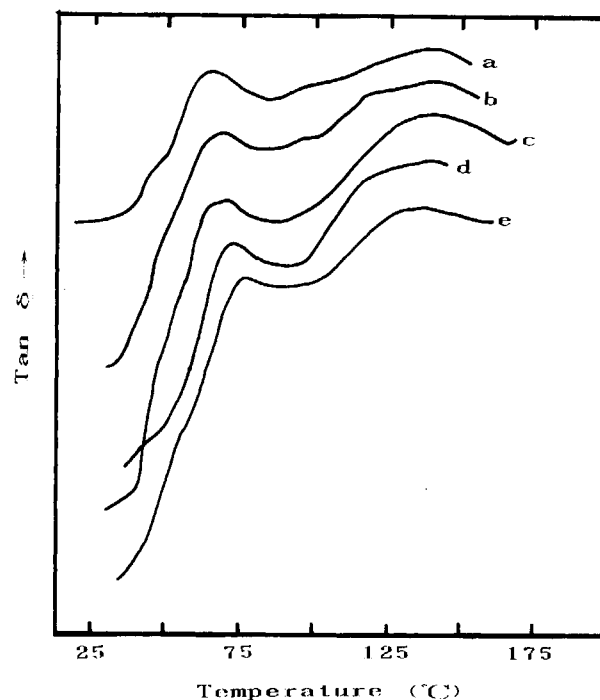


Figure 6 $\tan \delta$ vs. temperature spectra at 11 Hz and heating rate of 2°C/min for VBE terpolyesters with the V/B/E ratios: (a) 0/60/40; (b) 0.5/60/39.5; (c) 1.5/60/38.5; (d) 5/60/35; (e) 5/65/30.

weak inflection point at about 92°C. Apparently, these three points all stem from the glass transition of the terpolyester. This result would be analogous to the inflection points at 40, 70, and 87°C of B/E (60/40) polyester-oriented fiber observed with TMA.⁷ TMA helps to confirm the results obtained by DSC and DMA methods.

The thermal linear expansion coefficients for the terpolyester in parallel or perpendicular to the rod axis are estimated from Figure 7 to be -1.22×10^{-4} or $1.49 \times 10^{-4} \text{ deg}^{-1}$ in the temperature range from 42 to 55°C and 9.2×10^{-5} or $5.81 \times 10^{-4} \text{ deg}^{-1}$ in the range from 105 to 115°C. Note that the expansion coefficients in the rod axis change drastically from negative to positive values with increasing

Table I Glass Transition Temperatures of VBE Terpolyesters by DMA Method

V/B/E	$T_g \alpha_3$ (°C)	$T_g \alpha_1$ (°C)
0/60/40	67	141
0.5/60/39.5	68	140
1.5/60/38.5	70	140
5/60/35	74	138
5/65/30	77	136

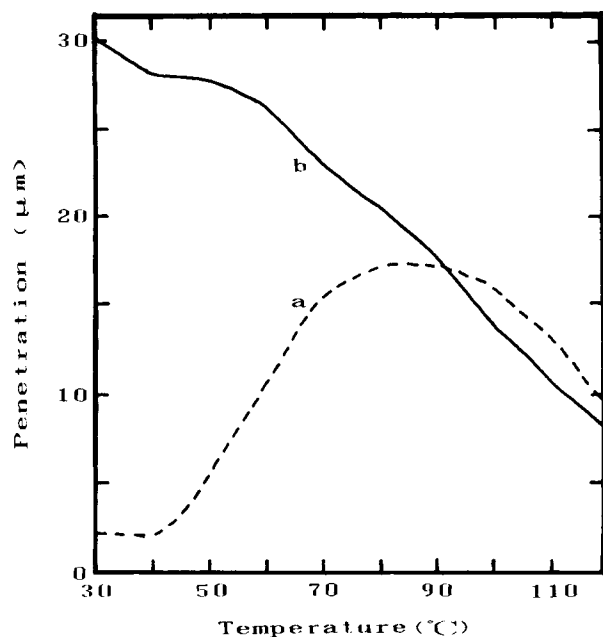


Figure 7 TMA plots of the VBE terpolyester as drawn rods with V/B/E ratio of 0.05/60/39.95 with a heating rate of 5°C/min; curves a and b are parallel and perpendicular to the drawn direction, respectively.

temperature from 40 to 120°C. These expansion coefficients are larger than that for the BE copolyester fiber^{7,26} and B homopolyester,²⁷ suggesting that the VBE terpolyester chains more highly fluctuate perpendicular to the chain axis. The high coefficient may be explained in terms of worse packing and lower orientation of the terpolyester chains. The torsional vibrations of the terpolyester chains must be less restricted in space, owing to the slightly large free volume.⁷ In the temperature range between 79 and 92°C, the expansion coefficient parallel to the rod axis levels off at a value equal to zero. Thus, these thermotropic liquid crystalline polyesters

could serve as a coating material for optical fibers to diminish fiber microbending loss.

Prediction of the T_g Based on Composition and Sequence Distribution of VBE Terpolyesters

The three simplest relationships that describe the effect of the mole or weight fractions of monomer units of linear terpolymers on their T_g are the Dimarzio-Gibbs, Pochan, and Fox equations.²⁸

For our VBE terpolyester system, the Dimarzio-Gibbs equation can be expressed as

$$T_g = F_V \times T_{gV} + F_B \times T_{gB} + F_E \times T_{gE} \quad (2)$$

where T_g is the glass transition temperature of a terpolyester composed of three monomer units V, B, and E; F_V , F_B , and F_E are the mole fractions of units V, B, and E in the VBE terpolyesters; T_{gV} , T_{gB} , and T_{gE} denote the glass transition temperature of V, B, and E homopolyesters, respectively.

The Pochan and Fox Equations can be written as

$$\ln T_g = W_V \times \ln T_{gV} + W_B \times \ln T_{gB} + W_E \times \ln T_{gE} \quad (3)$$

and

$$1/T_g = W_V/T_{gV} + W_B/T_{gB} + W_E/T_{gE} \quad (4)$$

where W_V , W_B , and W_E are the weight fractions of the components V, B, and E in the VBE terpolyesters. As can be seen from Table II, our experimental T_g deviates greatly from the above-said three simple relationships because these classical equations predict that T_g increases continuously (smoothly) and monotonically with composition. However, it has been observed that the T_g composition variation of

Table II Predicted and Experimental T_g 's (°C) of the VBE Terpolyesters

V/B/E	Predicted T_g						Experimental
	Dimarzio	Pochan	Fox	Couchman	Johnston	Uematsu	T_g^a
15/50/35	123	112	97	78	78	76	77
0.5/60/39.5	122	108	93	64	70	66	66
5/60/35	125	113	97	72	74	72	69
5/65/30	129	117	102	78	75	77	74
5/75/20	138	129	114	92	87	83	83
σ (%)	42.3	36.4	26.8	5.49	4.54	2.62	

^a Heating rate 20°C/min.

Table III Diad Sequence Distribution Parameters and T_g of the BE Binary Copolyesters^a

B/E	Uematsu Equation			Johnston Equation				T_g^a (°C)	
	F_{BB}	F_{EE}	F_{BE}	W_B/W_E	P_{BB}	P_{EE}	P_{BE}		P_{EB}
50/50	0.209	0.230	0.561	0.385/0.615	0.44	0.44	0.56	0.56	75
60/40	0.313	0.130	0.557	0.484/0.516	0.54	0.31	0.46	0.69	66
70/30	0.429	0.040	0.531	0.593/0.407	0.63	0.14	0.37	0.86	76

^a Heating rate 20°C/min.

the BE and VBE copolyester systems is not monotonic owing to their biphasic structure (Fig. 1 and Table I). The classical equations become invalid.

To describe more precisely the dependence of the VBE terpolyesters' T_g on composition, the effect of sequence distribution on T_g has to be considered. Equations that take into account sequence distribution are being used extensively^{13,29} because they can predict precisely T_g -composition relationship for a number of copolymer systems. So far there are three equations that describe the sequence distribution dependence of the T_g of copolymers, namely, modified Dimarzio-Gibbs equation (Uematsu equation), modified Pochan equation (Couchman equation), and modified Fox equation (Johnston equation).

Uematsu and Johnston added an empirical and ponderable extra term to consider diad sequence AB and BA influence on T_g of Dimarzio-Gibbs and Fox equations, respectively, considering binary copolymer as a blend of the two homopolymers and the alternating copolymer. Couchman described the dependence of T_g on monomer reactivity ratios in the copolymers.

According to the modified Dimarzio-Gibbs equation presented by Uematsu and Honda,¹³ the relationship between T_g s and diad sequence fractions of random terpolyesters could be expressed:

$$T_g = F_{VV} \times T_{gV} + F_{BB} \times T_{gB} + F_{EE} \times T_{gE} + F_{VB} \times T_{gVB} + F_{VE} \times T_{gVE} + F_{BE} \times T_{gBE} \quad (5)$$

where T_{gVB} , T_{gVE} , and T_{gBE} denote the glass tran-

sition temperatures of imaginary alternating copolymers, respectively; F_{VV} , F_{BB} , F_{EE} , F_{VB} , F_{VE} , and F_{BE} are the molar fractions of the corresponding diads in the random terpolyesters. We will designate eq. (5) as the Uematsu equation for brevity.

Another a relationship between T_g s and diad sequence probabilities of the random terpolyesters is also described by the Johnston equation:^{13,30}

$$\frac{1}{T_g} = \frac{W_V P_{VV}}{T_{gV}} + \frac{W_B P_{BB}}{T_{gB}} + \frac{W_E P_{EE}}{T_{gE}} + \frac{W_V P_{VB} + W_B P_{BV}}{T_{gVB}} + \frac{W_V P_{VE} + W_E P_{EV}}{T_{gVE}} + \frac{W_B P_{BE} + W_E P_{EB}}{T_{gBE}} \quad (6)$$

where P_{VV} , P_{BB} , P_{EE} , P_{VB} , P_{BV} , P_{VE} , P_{EV} , P_{BE} , and P_{EB} are the terpolyester distribution probabilities of the corresponding diads. Balachandar et al. and Fernandez-Garcia et al. have used the diad sequence- T_g relation for the BE binary copolyester with the B-unit content less than 43 mol % and methyl methacrylate/methylacrylate copolymer and obtained good agreement between predicted and experimental values.^{13,29}

The Couchman equation for the VBE terpolyester can be written as

$$\ln T_g = \frac{r_V f_V^2 \ln T_{gV} + r_B f_B^2 \ln T_{gB} + r_E f_E^2 \ln T_{gE} + 2 f_V f_B \ln T_{gVB} + 2 f_V f_E \ln T_{gVE} + 2 f_B f_E \ln T_{gBE}}{r_V f_V^2 + r_B f_B^2 + r_E f_E^2 + 2 f_V f_B + 2 f_V f_E + 2 f_B f_E} \quad (7)$$

Table IV Diad Sequence Fractions and T_g of Two Model VBE Terpolyesters for Uematsu Equation

V/B/E	F_{VV}	F_{BB}	F_{EE}	F_{VB}	F_{VE}	F_{BE}	T_g^a (K)
30/35/35	0.167	0.115	0.061	0.106	0.199	0.354	359
34/33/33	0.204	0.107	0.035	0.088	0.228	0.339	363

^a Heating rate 20°C/min.

Table V Diad Sequence Probabilities and T_g of Two Model VBE Terpolyesters for Johnston Equation³³

V/B/E	$W_V/W_B/W_E$	$P_{VV}/P_{VB}/P_{VE}$	$P_{BV}/P_{BB}/P_{BE}$	$P_{EV}/P_{EB}/P_{EE}$	T_g (°C) ^a
30/35/35	0.292/0.272/0.436	0.555/0.095/0.350	0.220/0.328/0.453	0.268/0.559/0.173	86
34/33/33	0.331/0.257/0.412	0.600/0.052/0.48	0.213/0.324/0.464	0.331/0.563/0.106	90

^a Heating rate 20°C/min.

in which r_V (6.97), r_B (0.78), and r_E (0.73) are the reactivity ratios of monomers V, B, and E in the terpolymerization system;³¹ f_V , f_B , and f_E are the molar fractions of monomers V, B, and E in the feed. The experimental T_{gV} , T_{gB} , and T_{gE} values of V, B, and E homopolymers have been found to be 142, 158, and 67°C, respectively by Kricheldorf et al.,³² Balachandar et al.,¹³ and Meesiri et al.⁵ The hypothetical T_{gBE} of the BE alternating copolymer can be calculated from model BE copolyesters according to eqs. (5) and (6). The sequence distribution parameter and T_g of the three model BE copolymers with three B/E monomer ratios are listed in Table III, from which the average T_{gBE}^U calculated is 297 K, and the average T_{gBE}^J calculated is 59°C. Similarly, according to eqs. (5) and (6), the respective T_{gVB}^U and T_{gVE}^U calculated from the sequence distribution parameters and the T_g s of the two model VBE terpolyesters shown in Table IV³³ are 336 and 395 K, and the respective T_{gVB}^J and T_{gVE}^J calculated from Table V are 76 and 154°C. The values of T_g predicted from eqs. (5)–(7) using these T_{gVB}^U , T_{gVE}^U , T_{gBE}^U , T_{gVB}^J , T_{gVE}^J , T_{gBE}^J and corresponding sequence distribution parameters (Tables VI and VII) are collected in Table II. The experimental values, T_{gex} , of the corresponding VBE terpolyesters are also listed in Table II. The standard deviation percentage σ (%) was calculated by $\sigma = 100d^{0.5}$, where

$$d = \frac{1}{n} \sum_{i=1}^n [(T_{gexi} - T_{gpri})/T_{gpri}]^2 \quad (8)$$

where T_{gexi} and T_{gpri} represent experimental and predicted values respectively, for the i experimental

point of a total of n experiment points. The results for the standard deviation percentage are gathered in Table II. It can be seen that the experimental T_{gex} of the terpolyesters show much lower value than the Dimarzio–Gibbs, Pochan, and Fox equations' prediction. Obviously, the three simple equations do not hold for the VBE terpolyester, because these equations do not take into consideration the effect of monomer sequence and reactivity ratio on the T_g of the terpolyesters. But the Uematsu, Johnston, and Couchman equations give a better fit with experimental results with an accuracy of 2.6–5.5% deviation. It can be said that the diad model seems to be sufficient to predict the dependence of terpolyester T_g on composition, sequence distribution and monomer reactivity ratio. From the knowledge of the monomer sequence and reactivity ratio of the VBE terpolyesters, their T_g s could be predicted with a deviation less than 5.5% without prior measurements other than those of the T_g of homopolymers.

CONCLUSIONS

Detailed DSC as well as DMA and TMA measurements of the thermotropic liquid crystalline BE and VBE copolyesters reveal the existence of two phases with two T_g s of approximately 66–83 and 136–140°C. The lower T_g is attributed to the E-rich phase and the higher T_g might be assigned to the B-rich phase. Both Uematsu and Johnston equations are able to predict precisely the T_g of the VBE terpolyesters on the basis of their composition and sequence distri-

Table VI Diad Sequence Fractions of the VBE Terpolyesters for Uematsu Equation^{9,33}

V/B/E	F_{VV}	F_{BB}	F_{EE}	F_{VB}	F_{VE}	F_{BE}
15/50/35	0.055	0.227	0.039	0.077	0.109	0.493
0.5/60/39.5	0.001	0.270	0.114	0.003	0.005	0.607
5/60/35	0.005	0.287	0.088	0.029	0.038	0.553
5/65/30	0.006	0.359	0.023	0.036	0.020	0.556
5/75/20	0.004	0.513	0.014	0.044	0.018	0.416

Table VII Diad Sequence Probabilities of VBE Terpolyesters for Johnston Equation^{9,33}

V/B/E	$W_V/W_B/W_E$	$P_{VV}/P_{VB}/P_{VE}$	$P_{BV}/P_{BB}/P_{BE}$	$P_{EV}/P_{EB}/P_{EE}$
15/50/35	0.150/0.401/0.449	0.364/0.300/0.330	0.064/0.452/0.484	0.170/0.718/0.112
0.5/60/39.5	0.005/0.485/0.510	0.103/0.345/0.552	0.002/0.467/0.531	0.002/0.727/0.271
5/60/35	0.051/0.491/0.458	0.104/0.443/0.442	0.009/0.449/0.492	0.043/0.729/0.228
5/65/30	0.052/0.545/0.403	0.170/0.569/0.261	0.014/0.553/0.433	0.027/0.919/0.074
5/75/20	0.055/0.662/0.283	0.101/0.703/0.196	0.009/0.690/0.290	0.032/0.910/0.058

bution. The thermal linear expansion coefficients for the VBE terpolyester rods parallel and perpendicular to the rod axis are estimated to be -1.22×10^{-4} and $1.49 \times 10^{-4} \text{ deg}^{-1}$ at 50°C , respectively.

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