Effects of sequence length distribution on heat capacity and glass transition temperature of styrene–methyl methacrylate copolymers

Hidematsu Suzuki*, Yoshiyuki Nishio and Noritaka Kimura
Department of Bioengineering, Nagaoka University of Technology, Nagaoka, Niigata-Ken 940-21, Japan

and V. B. F. Mathot and M. F. J. Pijpers
DSM, Research and Patents, PO Box 18, 6160 MD Geleen, The Netherlands

and Yoji Murakami
Film Research Laboratories, Teijin Ltd, Sagamihara, Kanagawa-Ken 229, Japan
(Received 24 January 1994)

Heat capacities of alternating, statistical and diblock copolymers of styrene and methyl methacrylate were measured with a differential scanning calorimeter from 200 to 450 K to examine the additivity of heat capacity. In both solid and liquid regions, the heat capacity was found to be additive, in most cases within $\pm 2\%$ error irrespective of sequence length distribution. The glass transition temperatures, determined from enthalpy–temperature plots, depended on sequence length distribution as well as composition. This behaviour, although theoretically expected, was found to be complicated by another factor, tacticity.

(Keywords: heat capacity; alternating copolymer; sequence length distribution)

INTRODUCTION

Since the advent of computer-controlled differential scanning calorimetry (d.s.c.), measurements of (constant pressure) heat capacity, C_p, of polymers have become more familiar. It is now possible to obtain C_p values with a high accuracy by d.s.c., by setting appropriate operational conditions[1]. Then, using the C_p results, thermodynamic functions such as enthalpy can be calculated and used to discuss thermodynamic states of the polymer system. For example, glass transition temperature, T_g, formerly read directly from a thermogram, can now be determined, as a temperature independent of heating rate, from enthalpy–temperature plots[2].

Published heat capacity data of about 100 homopolymers have been collected, critically evaluated and analysed by Wunderlich and colleagues[3,4], and are available in tabular form, where several thermal properties, including C_p and T_g, can be seen together with references. Heat capacity data have also been published for copolymers and blends of homopolymers, bringing out the interesting information that heat capacity may be additive in those systems[5,6]. Thus the heat capacity of a given copolymer can be predicted by the sum of those, weighted by the given composition, of the homopolymer constituents. Furthermore, the heat capacity of a homopolymer can be seen as the sum of the heat capacity contributions of the smaller chemical groups of which the repeating unit is composed[7,8]. It has been found that such an additivity can hold empirically, with an accuracy of at worst $\pm 5\%$, ordinarily $\pm 2.5\%$, for copolymers, homopolymers and their blends both in the solid and in the liquid states[5–8].

The copolymers used so far for tests of the empirical additivity rule were exclusively statistical and block copolymers. For more crucial investigations, there are two reasons why alternating copolymers should be used. First, most physical properties, such as unperturbed dimensions[9] of a single copolymer chain and glass transition temperature[10] of solid copolymer, are known to depend not only on overall chemical composition but also on monomer arrangement. Second, by use of alternating copolymers as samples, a full variation in monomer arrangement can be realized for a given copolymer system.

In this study, on alternating, statistical and diblock copolymers of styrene and methyl methacrylate, heat capacity was measured by d.s.c. to examine the effects of monomer arrangement, i.e. sequence length distribution. The observed heat capacity will be compared, in the three temperature regions solid, transition and liquid, with that expected from additivity. The T_g results obtained were

* To whom correspondence should be addressed

0032-3861/94/17/3698–05

analysed, together with those for the corresponding homopolymers, after Barton[11] and Johnston[12], in a manner recently proposed[13–15].

EXPERIMENTAL

Materials

Out of each series of previously described[9] fractions, three statistical and two alternating styrene (S)–methyl methacrylate (M) copolymer samples were selected for this study. A diblock copolymer sample of the same constituents was a kind gift of Dr T. Fukuda of Institute for Chemical Research, Kyoto University[16]. The characterization data, i.e. the S mole fraction (m_S) and the weight- and the number-average molecular weights (M_w and M_n) are given in *Table 1*. In addition, several laboratory samples were used only for glass transition temperature determinations: an unfractionated statistical copolymer ($m_S = 0.10$, $M_w = 3 \times 10^5$), polystyrene (Pressure Chemical, $M_w = 6.7 \times 10^5$), and three poly(methyl methacrylate)s (anionic: $M_w = 1.2 \times 10^6$; free radical: $M_w = 1.0 \times 10^6$; and emulsion: $M_w = 2.2 \times 10^7$). For the last poly(methyl methacrylate) sample[17], the tacticity was determined with a Jeol JNM-EX-400 proton magnetic resonance spectrometer: isotactic, syndiotactic and heterotactic triads were, respectively, 3, 65 and 32%.

D.s.c. apparatus

Heat capacity measurements were performed at DSM with a Perkin–Elmer DSC-2 controlled by a computer: both measuring and temperature signals were coupled to a Tektronix 4052 graphical computer via a multiplexer (model 3497A Hewlett-Packard) and a 6(1/2) analogue/digital converter (model 3455A Hewlett-Packard). The data points were read at increments of 0.1 K. The crude data were stored on a TransEra Winchester disk with a capacity of 20 Mbyte. The d.s.c. measuring block was kept at a temperature of 153 K by a Cryoson TRL5 unit with liquid nitrogen. The furnace and a Perkin–Elmer dry box used were purged with dry nitrogen. The temperature and energy calibrations were carried out as described previously[18,19]. For glass transition temperature determinations of the additional samples, a Rigaku DSC was also used.

Measurements

Prior to the measurements, the samples in a fibrous form were dried under reduced pressure at 60°C for at least 24 h. Afterwards, the samples were compressed with a manually operated press, to obtain small discs of sufficient mass (13–18 mg) for accurate heat capacity measurements. Blank, sapphire and sample runs were made successively using the following procedure: fast heating to 450 K, 5 min pause, cooling to 200 K at 10 K min^{-1}, pause for another 5 min and reheating for measurement to 450 K at 10 K min^{-1}. The first heating to the highest temperature in a fixed range was necessary to erase the prior thermal history of both the sample and the apparatus[1].

Glass transition temperature was determined according to the method of Richardson and Savil[2]; in enthalpy–temperature plots an extrapolation was performed with a second-degree polynomial from temperatures above and below the transition, to determine the point of intersection.

Table 1 Molecular characteristics and glass transition temperatures of styrene–methyl methacrylate copolymer samples used

Code	m_s	M_w ($\times 10^{-4}$)	M_n ($\times 10^{-4}$)	R	T_g (K)
Statistical					
SM3-8	0.294	44.7	27.6	51	384.5
SM5-11	0.553	13.7	9.6_6	66	375.5
SM7-8	0.703	27.0	21.0	51	374.1
Alternating					
ALII-2	0.504	23.3[a]	17.9	100	370.1
ALII-3	0.490	18.6[a]	14.3	100	367.5
Diblock					
74B	0.47	82.8	73.9	0	374.8/400.0

[a] Product of experimental values of M_w/M_n and M_n

RESULTS

Figures 1 and *2* show the heat capacity results (open circles) of SM3-8 and SM7-8 statistical copolymers, respectively, over the entire temperature range of measurements. From these figures it can be seen that the temperature range 200–450 K covers three states of these copolymer samples: glass, transition and liquid. In

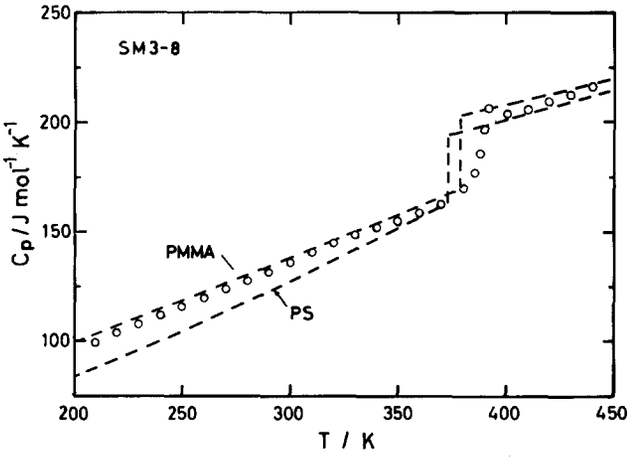

Figure 1 Plots of C_p against T for statistical copolymer SM3-8. (○) Results; (---) recommended data for the corresponding homopolymers[20,21]

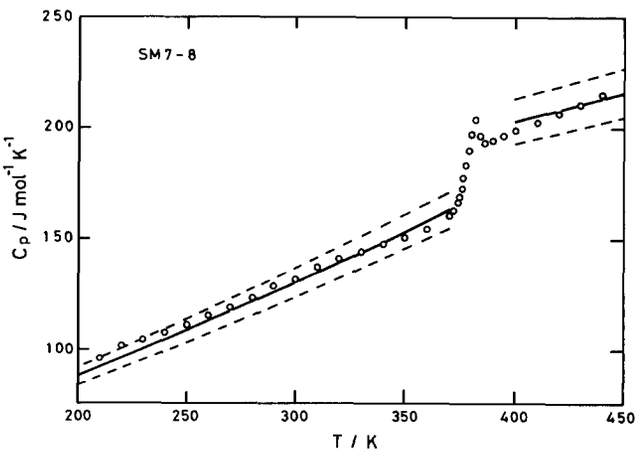

Figure 2 Plots of C_p against T for statistical copolymer SM7-8. (○) Results; (——) prediction using the additivity rule; (---) ±5% deviation from prediction

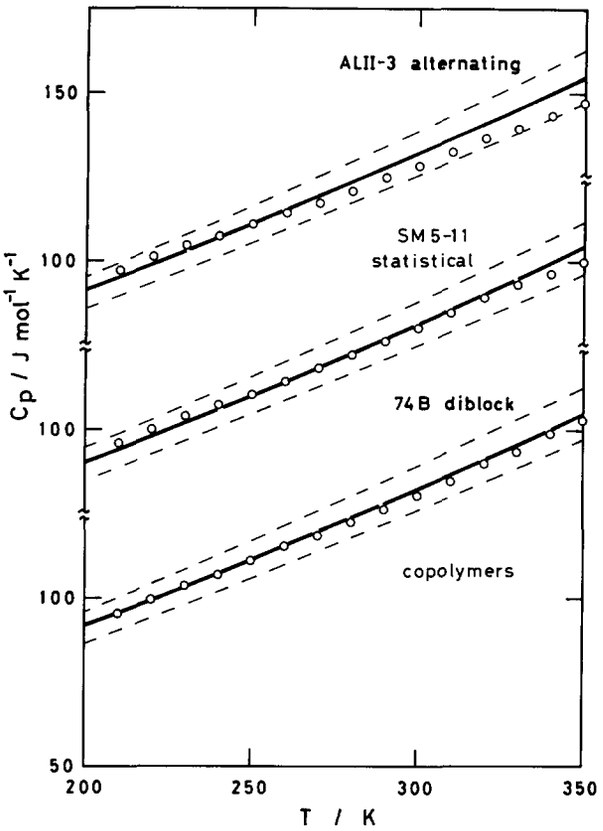

Figure 3 Plots of C_p against T, in the glassy state, for three copolymers similar in composition but different in sequence length distribution. For symbol and lines, see *Figure 2*

Figure 1, the recommended C_p data[20,21] of the two corresponding homopolymers are presented as broken lines for comparison. The C_p results obtained are located between the two C_p lines for the homopolymers both in the glass and liquid states, qualitatively suggesting the additivity of heat capacity of copolymer.

In *Figure 2*, a comparison is made between the C_p results obtained and those expected from the additivity rule: the expected copolymer heat capacties, denoted by solid lines, were calculated, with the recommended data, by a linear relation

$$C_p(A, B) = m_A C_p(A) + m_B C_p(B) \quad (1)$$

Here, $C_p(A, B)$ and $C_p(I)$ are, respectively, the heat capacity of copolymer composed of monomers A and B, and that of homopolymer I (I = A or B), and m_I the mole fraction of monomer I in the copolymer. In the figure, broken lines denote $\pm 5\%$ deviation from the expected heat capacity. It is seen that the heat capacity results obtained are in accordance with those expected, to an accuracy of much better than $\pm 5\%$.

Figures 3–5 show similar comparisons in the three separate temperature regions: glass, transition and liquid. The three samples used, ALII-3, SM5-11 and 74B, are almost equimolar copolymers, but they differ significantly in sequence length distribution. This is most conveniently characterized by the run number, R[22].

The run number is defined as the average number of both A and B monomer sequences (runs) occurring in a copolymer per 100 monomer units[13,22]. For instance, homopolymers and diblock copolymers with a large degree of polymerization take R values of effectively zero, while alternating copolymers take an R value of 100. Statistical copolymers are predicted to have R values given by

$$R = 400 m_A m_B / \{1 + [1 + 4 m_A m_B (r_A r_B - 1)]^{0.5}\} \quad (2)$$

Here, r_A and r_B are monomer reactivity ratios[23] under the given copolymerization conditions. For the present S–M system, r_S and r_M are, respectively, 0.52 and 0.46[10], and the estimated R values for the samples used are given

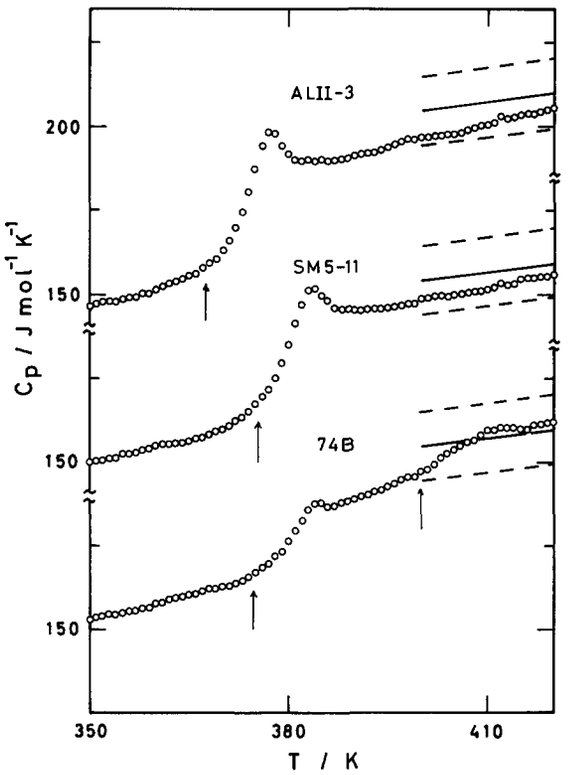

Figure 4 Plots of C_p against T for the three copolymers in the transition region. Arrow: T_g point determined by Richardson's method. For symbol and lines, see *Figure 2*

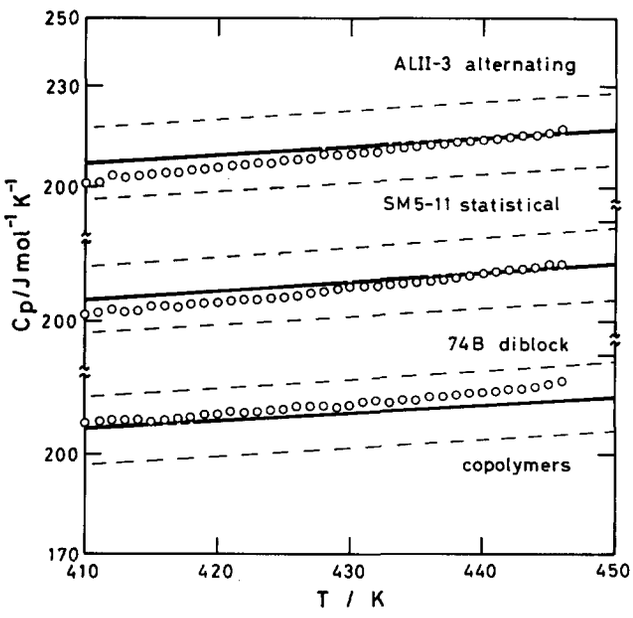

Figure 5 Plots of C_p against T for the three copolymers in the liquid region. For symbols and lines, see *Figure 2*

Table 2 Comparison of calculated heat capacities with experimental results

Sample	T (K)	Heat capacity (J (mol K)$^{-1}$) Experimental	Calculated	Deviation (%)
SM3-8	250	115.5	114.6	−0.8
	360	158.5	160.9	1.5
	410	205.8	208.4	1.3
	430	212.3	213.3	0.5
SM5-11	250	110.7	110.8	0.1
	350	150.3	154.8	3.0
	400	198.9	204.2	2.7
	430	210.2	211.8	0.8
SM7-8	250	111.2	108.7	−2.2
	349	150.4	153.3	1.9
	399	199.1	202.9	1.9
	430	211.1	210.9	−0.1
ALII-3	250	111.0	111.7	0.6
	342	144.0	151.6	5.3
	392	192.6	202.6	5.2
	430	209.6	212.1	1.2
74B	250	110.8	112.0	1.1
	350	153.1	155.4	1.5
	410	209.6	207.3	−1.1
	430	214.9	212.3	−1.2

in *Table 1*. This table also lists, in the right-hand column, the T_g values obtained. As for the diblock copolymer sample, two glass transition temperatures were observed, reflecting the two-phase structure induced by the segregation of one type of blocks from the others[24]. The total heat capacity jump of this sample, when measured at 400 K, was 32.0 J (mol K)$^{-1}$ while those at T_g of the others were 30.0 J (mol K)$^{-1}$. The T_g values obtained, not listed in the table, were 384 K for statistical copolymer ($R=22$), 374 K for polystyrene, and 391, 394 and 399 K for free-radical, emulsion and anionic poly(methyl methacrylate)s, respectively.

DISCUSSION

Solid state

Table 2 shows a comparison of heat capacities calculated by the additivity rule with those experimentally obtained. First we take a close look at the C_p values at 250 K, a temperature well below T_g. It is seen that they accord with each other, for most samples, within ±1% error. The additivity rule holds for these copolymers. It has been reported that crystallinity and chain conformation in crystal structure affect heat capacity. For example, semicrystalline polyethylene shows a linear crystallinity dependence of C_p, and in polyoxides, the C_p contribution of oxygen, as obtained by eliminating that due to methylene groups, is about 40% higher in a planar zig-zag than in a helical crystal structure[25]. As the copolymers used here are amorphous, C–C backbone linear polymers, larger deviations from additivity for the aforementioned reasons are not expected.

Sample 74B is a two-phase system but it is seen from *Table 2* that the deviation is only 1.1% at 250 K, irrespective of the presence of interfaces. Indeed, an effect of microphase separation is obvious in the broadened glass transition region, but is not significant in the additivity of heat capacities at this temperature, as is the case with another block copolymer of styrene and α-methylstyrene[26]. In general, the heat capacity of a solid consists practically fully of vibrations. The observed additivity of heat capacities at 250 K must mean approximate additivity of vibration spectra.

Next, at a temperature 25 K lower than the T_g of each sample, we compare the experimental and the calculated heat capacities. It is seen from the table that deviations are larger at this temperature than at 250 K and they increase in the order: diblock, statistical and alternating copolymers. It seems at a first sight that sequence length distribution affects the actual C_p values at this temperature. As is clear from *Figure 4*, however, an apparent peak after glass transition (hysteresis effect) increases in the order mentioned above. Accordingly, the larger, systematically positive deviations observed could be due mainly to the hysteresis effect, not directly to the effect of sequence length distribution.

Liquid state

Comparison is made, in *Table 2*, at two temperatures, 430 K and a temperature 25 K higher than T_g of each sample. For sample 74B, 410 and 430 K were used for the presence of higher second glass transition. It is seen that the deviations are generally small and the largest one is for the alternating sample at 392 K. Again, this largest deviation could be due to the hysteresis effect, because deviation becomes smaller at higher temperatures. On the whole, the heat capacities of the samples in the liquid state are additive within ±2% error. This additivity is purely empirical but has been confirmed on other homo- and copolymers. This study added a new result on alternating copolymers.

Transition region

As is seen from *Table 1*, the glass transition temperatures observed vary with sequence length distribution as well as monomer composition. This phenomenon has been described theoretically by Barton[11] and Johnston[12], based on configurational entropy and free volume theories, respectively. Barton's equation expressed with the run number is as follows[13]:

$$T_g = m_A T_{gAA} + m_B T_{gBB} + (R/100)(T_{gAB} - \bar{T}_g) \quad (3)$$

with

$$\bar{T}_g \equiv (T_{gAA} + T_{gBB})/2$$

Here, T_g is the glass transition temperature of a copolymer composed of monomers A and B, having composition and sequence length distribution specified by the values of m and R, respectively. T_{gXY} (X, Y=A or B) is the T_g value of a polymer composed of XY dyads only, i.e. T_{gAA} and T_{gBB} are for homopolymers, while T_{gAB} is for alternating copolymer. Johnston's equation is expressed as[14]

$$1/T_g = W_A/T_{gAA} + W_A/T_{gBB} + (R/200\bar{M})[(M_A + M_B)/T_{gAB} - M_A/T_{gAA} - M_B/T_{gBB}] \quad (4)$$

with

$$\bar{M} \equiv m_A M_A + m_B M_B$$

Here, W is the weight fraction and M is the formula weight of monomer.

The T_g predictions derived from these equations are illustrated in *Figure 6*, where the T_g values obtained are

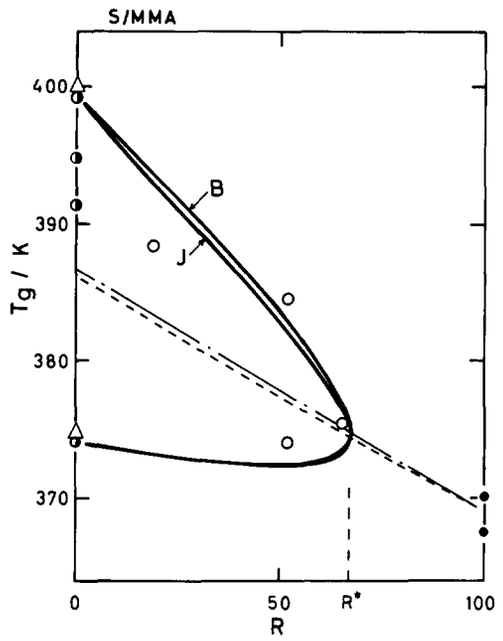

Figure 6 Plots of T_g against R for styrene–methyl methacrylate copolymers. (○) Statistical; (●) alternating; (△) block copolymer; (◑) homopolymers. (——) Theoretical predictions by Barton[11] (B) and by Johnston[12] (J); (–·–) (– – –) see text

also plotted against R. As is well known, poly(methyl methacrylate) shows marked tacticity dependence of glass transition temperature. This is clear from the variations in T_g seen in the figure. This problem is to be considered in another paper[27], and here the T_g value of anionic poly(methyl methacrylate) was taken as T_{gBB} for predictions. There is no problem with T_{gAA} for polystyrene. A mean of the two values observed on alternating copolymers was used for T_{gAB}.

It is seen from *Figure 6* that there is no substantial difference in prediction between the two equations for this copolymer system. The sequence length distribution dependence of glass transition temperature is obvious, for example, from the lines which are the loci of T_g predicted, respectively, by Barton (–·–) and by Johnston (– – –) for equimolar copolymers with various R values. The T_g values are seen at $R=100$ and $R=66$, close to R^*, the maximum of R for this system. At $R=0$ can be read the T_g value predicted for the equimolar *compatible* diblock copolymer. This is purely hypothetical, however. Since the actual diblock sample has a two-phase structure, one can see, instead of a single value, two distinct T_g values close to those of the homopolymers. In contrast, the composition dependence of glass transition temperature is seen from the two T_g values at $R=51$ in this figure. On the whole, only a fair agreement can be seen between experiment and theory. This could be because this system contains an additional problem of tacticity, which will be considered in another paper[27].

In conclusion, the heat capacities of alternating, statistical and diblock copolymers of styrene and methyl methacrylate were found to be additive, irrespective of sequence length distribution, in both regions of solid and liquid, in most cases within ±2% error. In contrast, the glass transition temperatures showed a marked dependence on sequence length distribution as well as composition. This behaviour, although theoretically predicted, was found to be complicated by another factor, tacticity.

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