

Heat Capacity of Random Copolymers of Styrene and Methacrylates

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Synopsis

Differential scanning calorimetry has been used to investigate the thermal behavior of random copolymers of styrene and hexyl methacrylate and of styrene and glycidyl methacrylate in the temperature range of 20° to 150°C. Heat capacities of the copolymers and homopolymers, poly(hexyl methacrylate), poly(glycidyl methacrylate), and polystyrene have been measured. It is found that the heat capacities of the homopolymers from 60°K to the glass transition temperatures can be adequately obtained by Wunderlich's empirical method. It is also found that the copolymer heat capacities can be adequately represented by addition of homopolymer heat capacities.

INTRODUCTION

The use of thermoanalytical methods to investigate the thermal behavior of polymers is well known. Heat capacities, glass transition phenomena, and melting of polymers can be studied conveniently by differential thermal analysis (DTA) and differential scanning calorimetry (DSC). Although many studies on heat capacities of linear homopolymer have been reported,¹ data on copolymer heat capacities have been relatively scarce. In this communication, we report the results of our DSC study on poly(styrene-co-hexyl methacrylate) and poly(styrene-co-glycidyl methacrylate) of several different compositions in the temperature range of 20° to 150°C. Heat capacities of the random copolymers and the homopolymers poly(hexyl methacrylate), poly(glycidyl methacrylate), and polystyrene have been measured. It was found that the heat capacities of the homopolymers from 60°K to the glass transition temperatures can be adequately obtained from Wunderlich's empirical method.² It was also found that the copolymer heat capacities can be adequately represented by addition of homopolymer heat capacities.

EXPERIMENTAL

The copolymers poly(styrene-co-hexylmethacrylate) (PSCH) and poly(styrene-co-glycidyl methacrylate) (PSCG) were synthesized in a toluene solution at 61°C using AIBN (2,2-azobisisobutyronitrile) as a free-radical initiator. Styrene and AIBN were obtained from Eastman Kodak Company, Rochester, New York. Hexyl methacrylate was obtained from Polysciences, Inc., Warrington, Pennsylvania. Both poly(glycidyl methacrylate) (PGM) and poly-

TABLE I
Physical Chemical Properties of Polymers

Polymer	Intrinsic viscosity $[\eta]_{25^\circ}$	Composition styrene, mole-%	Molecular weight \bar{M}_n
PS		100	87,000
PHM-I		0	149,000
PHM-II	0.12 ^a	0	
PSCH-I	0.58 ^a	67.4	108,000
PSCH-II	0.28 ^a	56.4	26,000
PSCG-I	0.26 ^b	26.7	
PSCG-II	0.24 ^b	34.9	52,000
PGM		0	49,000

^a Solvent: toluene.

^b Solvent: methyl ethyl ketone.

(hexyl methacrylate)-I (PHM-I) were also synthesized by the same method. Poly(hexyl methacrylate)-II (PHM-II) and polystyrene (PS) were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin.

The synthesized polymers were twice precipitated from toluene with methanol and finally freeze-dried from benzene solutions. The chemical composition of the copolymers was determined by UV spectrophotometry.³ The data on the sample were obtained by use of a Beckman Model 25 spectrophotometer. The styrene content was determined by comparing absorption intensity of copolymer at 2690 Å with that of polystyrene in dichloromethane. Solution viscosities were measured in toluene or methyl ethyl ketone at 25°C with Cannon-Ubbelohde viscometers. A Wescan Model 231 Recording Membrane Osmometer was used to measure the osmotic pressures of the polymer solutions. Number-average molecular weights of the polymers, \bar{M}_n , were derived from the osmotic pressure-versus-concentration data using the standard method. The intrinsic viscosity $[\eta]_{25^\circ}$, chemical composition of the copolymers, and number-average molecular weight of the polymers are shown in Table I.

The technique for measuring specific heat by differential scanning calorimetry has been described.⁴ In the present work, a du Pont Model 990 differential scanning calorimeter was used for all heat capacity measurements. A sapphire (Al₂O₃) standard provided by du Pont was used for calibration. Heating rate was 10°C/min for all of the runs.

RESULTS AND DISCUSSION

A typical thermogram is shown in Figure 1. Heat capacities calculated from the thermograms of amorphous polystyrene, poly(hexyl methacrylate), poly(glycidyl methacrylate), and the copolymers are shown in Table II and in Figures 2 to 8. Since in the glass transition range heat capacity is strongly heating-rate and thermal-history dependent, heat capacity data in these ranges generally are not shown. Except for polystyrene, heat capacity data of the polymers studied in the present work have not been reported. Heat capacities of atactic polystyrene have been measured by many workers and have been summarized by Wunderlich and Baur.¹ Our results, plotted in

TABLE II
Heat Capacity of Polymers

Polymer	Heat capacity at indicated temperature, cal deg ⁻¹ mole ⁻¹			
	300° K	340° K	380° K	420° K
PS	28.8	33.5	45.2	50.2
PHM	77.0	82.5	87.7	90.2
PSCH-I	41.7	54.3	58.3	62.7
PSCH-II	52.0	63.1	67.0	70.5
PSCG-I	46.0	55.0	65.6	69.3
PSCG-II	45.0	51.6	62.5	65.3
PGM	55.0	71.0	74.0	

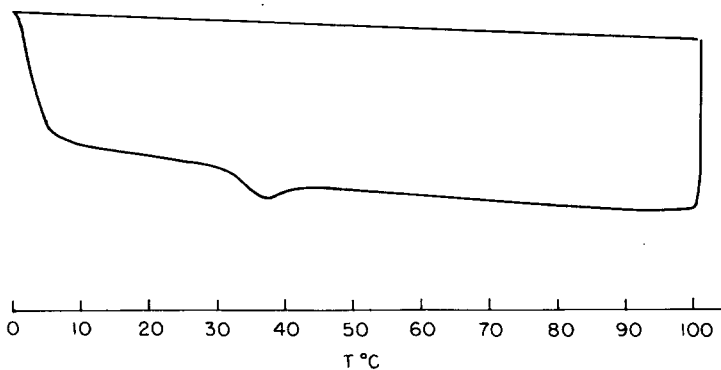


Fig. 1. Typical thermogram for poly(styrene-co-hexyl methacrylate)-II.

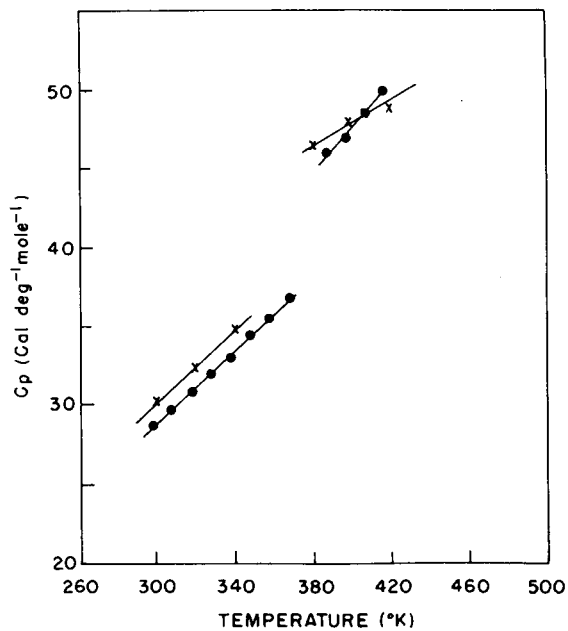


Fig. 2. Heat capacity of polystyrene: (●) present work; (x) Wunderlich and Baur.

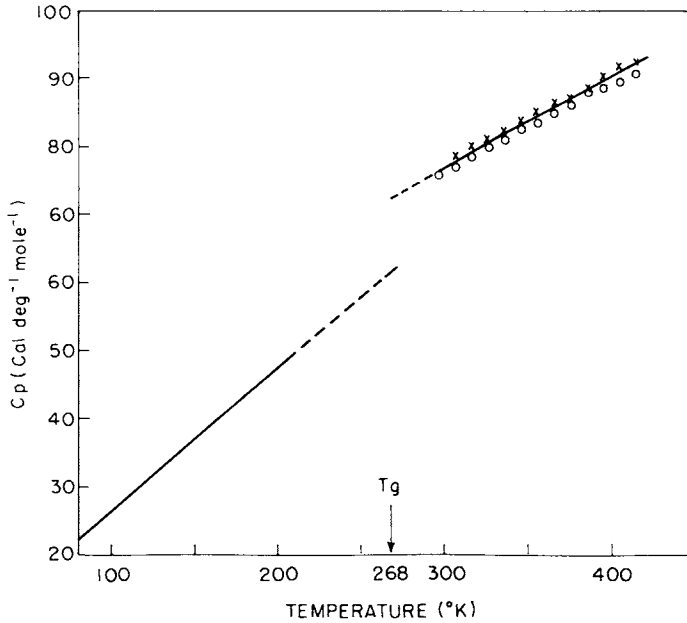


Fig. 3. Heat capacity of poly(hexyl methacrylate): (x) PHM-I; (o) PHM-II. Solid line between 80° and 210°K was obtained by the group contribution method of Wunderlich and Jones.

Figure 2, are seen to agree closely with the values tabulated by Wunderlich and Baur.

Motions in solids consist mainly of vibration of atoms around their equilibrium positions. These vibrations are usually coupled through intermolecular force. In most of the solids, the vibration is small and the motion can be as-

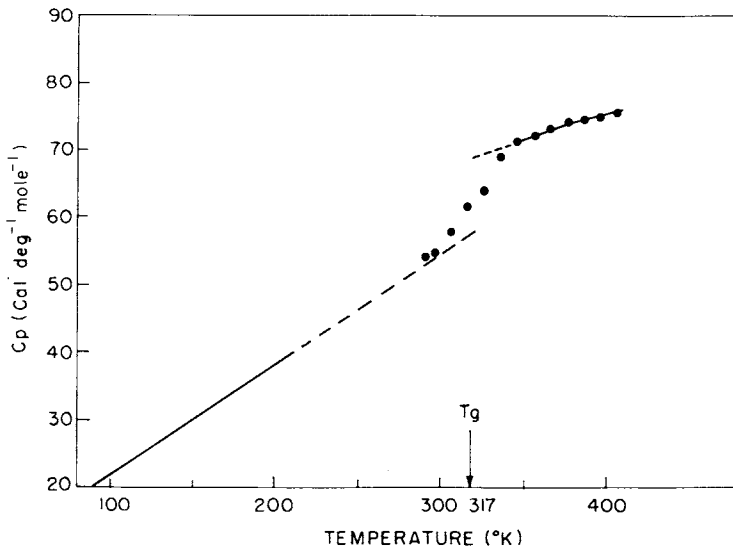


Fig. 4. Heat capacity of poly(glycidyl methacrylate): (●) present work. Solid line between 90° and 210°K was obtained by the group contribution method of Wunderlich and Jones.

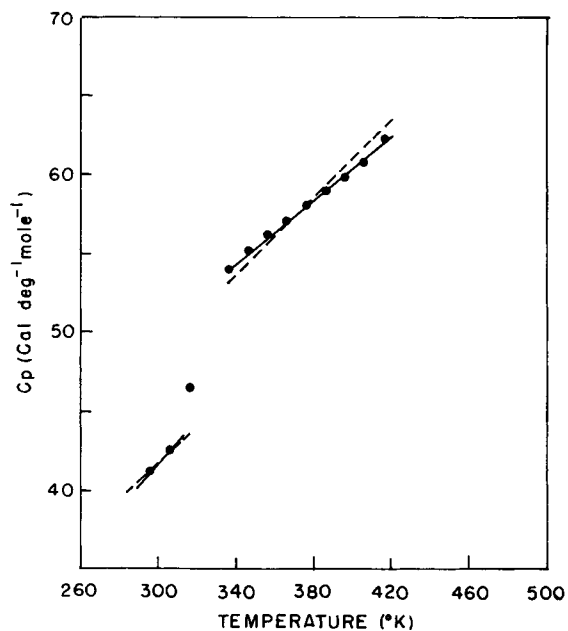


Fig. 5. Heat capacity of poly(styrene-co-hexyl methacrylate)-I. Closed circles and solid line represent experimental data; dotted line was obtained from the addition of homopolymer heat capacities.

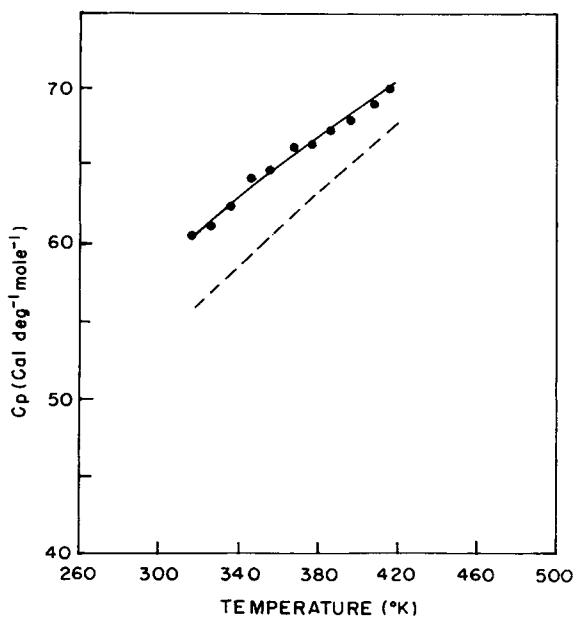


Fig. 6. Heat capacity of poly(styrene-co-hexyl methacrylate)-II. Closed circles and solid line represent experimental data; dotted line was obtained from the addition of homopolymer heat capacities.

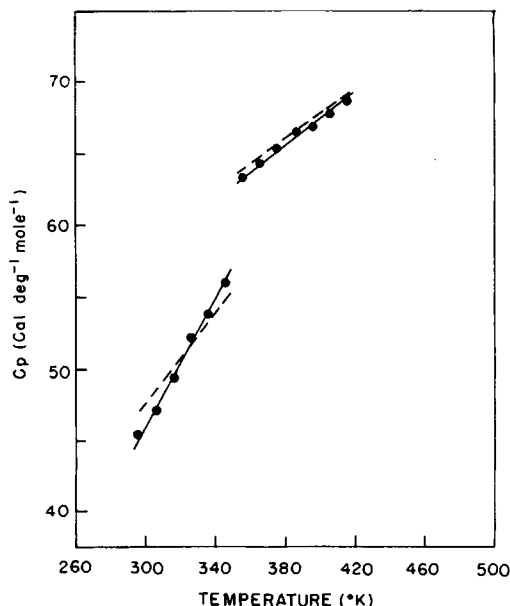


Fig. 7. Heat capacity of poly(styrene-co-glycidyl methacrylate)-I. Closed circles and solid line represent the experimental data; dotted line was obtained from the addition of homopolymer heat capacities.

sumed to be harmonic. It is known that small harmonic vibration can be decomposed into some normal modes of vibration and each normal mode is independent. The molar heat capacity is simply the sum of all normal modes.⁵

The heat capacity of the polymer can be calculated if the detailed frequency spectrum of the polymer is available. Theoretical attempts have been made to explain the temperature dependence of the heat capacity of simple, linear polymers such as polyethylene.^{6,7}

As a first approximation, the heat capacity of polymers can be assumed equal to the sum of the contributions of the skeletal vibrations and group vibrations.^{5,8} The skeletal vibrations can be looked upon as the vibrations of a chain of rigid units. The group vibrations consist of the normal modes of the detailed structure of the units. A model which often is being used to describe the skeletal vibration of a polymer was first proposed by Tarasov.⁹ Tarasov assumed that at low temperature, when the vibrations are intermolecularly coupled, the heat capacity can be calculated according to three-dimensional Debye model. At a higher temperature, when vibrations at a higher frequency are excited, the vibrations are essentially one-dimensional and heat capacity can be calculated according to a one-dimensional Debye model. The heat capacity of polymers according to Tarasov's model is

$$C_v = R \left\{ D_1(\theta_1/T) - \frac{\theta_3}{\theta_1} [D_1(\theta_3/T) - D_3(\theta_3/T)] \right\} \quad (1)$$

where D_1 and D_3 are one-dimensional and three-dimensional Debye functions, respectively; $\theta_1 = h\nu_1/k$, $\theta_3 = h\nu_3/k$, where ν_1 and ν_3 are cut-off frequencies in one-dimensional and three-dimensional vibrations. The Tarasov ap-

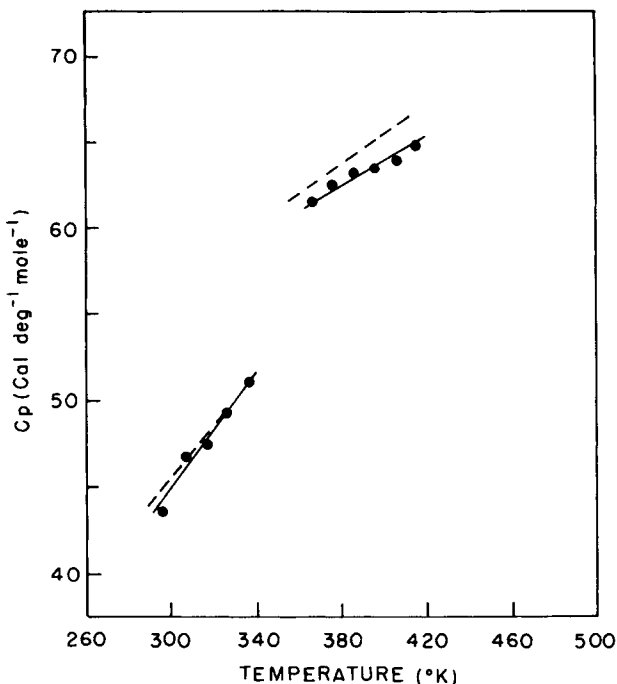


Fig. 8. Heat capacities of poly(styrene-co-glycidyl methacrylate)-II. Closed circles and solid line represent the experimental data; dotted line was obtained from the addition of homopolymer heat capacities.

proximation has been used successfully for a number of polymers.¹ Wunderlich and Jones² have tabulated θ_1 and θ_3 of some polymers evaluated by the use of eq. (1). By comparing the θ temperatures of polyethylene with other polymers of identical backbone chain, they have found that θ_1 temperatures are close to the ratio of the square root of the masses, while θ_3 values are not. This implies that in the temperature range where θ_1 determines heat capacity, the difference in heat capacity between polymers is largely determined by the difference in mass per carbon backbone atom and the difference in group vibrations. The available heat capacity data between 60°K and the melting transition temperature support the above conclusion.² In this temperature region, therefore, heat capacity can be derived by adding characteristic contributions arising from the different chemical groups in the polymer molecule. Tables of such contributions have been derived by Wunderlich and Jones.²

According to Wunderlich's addition scheme, the heat capacities of poly(hexyl methacrylate) (Fig. 9a) can be assumed to be equal to a sum of CH_2 and COO group contributions, i.e.,

$$C_p(\text{PHM}) = 2\text{I} + 5\text{II} + 2\text{III} + \text{COO}$$

where I stands for a CH_2 group in the polymer backbone, II for a CH_2 group in the side chain, and III for a CH_2 group which is part of a methyl group. Similarly, the heat capacities of poly(glycidyl methacrylate) (Fig. 9b) can be assumed to be equal to a sum of CH_2 , COO , and O_a group contribution, i.e.,

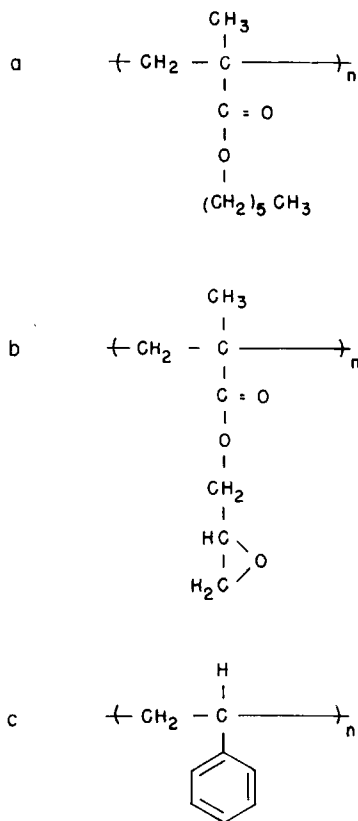


Fig. 9. (a) Poly(hexyl methacrylate); (b) poly(glycidyl methacrylate); (c) polystyrene.

$C_p(\text{PGM}) = 2\text{I} + 3\text{II} + \text{III} + \text{COO} + \text{O}_a$, where O_a stands for ether oxygen contribution and was derived from polyoxymethylene and polytetrahydrofuran heat capacity data. C_p versus T obtained by the addition method in the temperature range of 50° to 210°K is shown as a solid line in Figure 3 for PHM and in Figure 4 for PGM. The glass transition temperature T_g for PHM and PGM is 268°K and 317°K, respectively. If both the experimental C_p data and the C_p obtained by the addition method for PHM are extrapolated to its glass transition temperature, the heat capacity increase in the glass transition temperature, ΔC_p , is found to be 11.0 cal/deg mole. Similarly, ΔC_p for PGM has been found to be 11.5 cal/deg mole.

The phenomena that heat capacities of polymers increase substantially in the glass transition range are well known. Wunderlich has applied the hole theory of liquid^{10,11,12} to assume that such an increase in heat capacity is due to increase in the number of holes. The change in number of holes above the glass transition temperature contributes a part of heat capacity in addition to the contribution due to liquid lattice vibration. He has found that the increase in heat capacity of many polymers heating through T_g is 2.7 ± 0.5 cal/deg per mole of "bead." A bead has been defined as the basic unit of major motion in the liquid state. The number of beads in poly(methyl methacrylate), for example, has been assumed to be 3. If the number of beads in both

PHM and PGM is assumed to be 4, ΔC_p for PHM and PGM has been found to be 2.8 and 2.9 cal/deg per mole, respectively, in agreement with Wunderlich's observation. Since the side chain of poly(hexyl methacrylate) contains five more CH_2 groups than the side chain of poly(methyl methacrylate) and the side chain of poly(glycidyl methacrylate) contains an epoxide ring, it is reasonable to assume that both PHM and PGM have one more bead than poly(methyl methacrylate).

Existing data in the literature indicate that the copolymer heat capacity can be represented approximately by addition of the homopolymer heat capacities.¹ Although the side chains of the polymers studied in the present work are more complex, the data obtained also support this conclusion. In Figures 5, 6, 7, and 8, the heat capacities of the copolymers determined calorimetrically (solid lines) and obtained by the addition of homopolymer heat capacity (dotted lines) are shown as a function of temperature in the ranges of 290° and 420°K. The agreement between the two values is within 3% for PSCH-I, PSCG-I, and PSCG-II. For PSCH-II, the deviation from the additivity is somewhat larger, 2–8%. As is well known, the glass transition temperature of a copolymer lies intermediate between the glass transition temperature of the two homopolymers. In carrying out the addition scheme for the copolymers above and below their T_g , it became necessary to extrapolate the heat capacity data of polystyrene, poly(hexyl methacrylate), and poly(glycidyl methacrylate) to the appropriate temperature range. Among the four copolymers studied in the present work, PSCH-II has the lowest glass transition temperature, 40°C. To calculate its C_p , extrapolation of heat capacity data of polystyrene above the glass transition temperature to 40°C was required. Errors associated with the linear extrapolation of the data are partly responsible for the larger deviation from additivity for the copolymer PSCH-II.

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