Determining Basic Thermodynamic Properties for Some Poly(*n*-alkyl methacrylates)

Kwang Hyun Song, Kyung Wook Kwon, and Junhan Cho*

Department of Polymer Science and Engineering, and Center for Photofunctional Energy Materials, Dankook University, Gyeonggi-do 448-701, Korea

Introduction

Polymethacrylates have been known to belong to an intermediate class of materials between commodity and engineering plastics. Those materials are used mainly for glass and molding compounds, and also for dispersions, adhesives, additives, and binders.[1] In addition, block copolymers from polymethacrylates and polystyrene are widely used as passive electronic materials and as templates.[2-4] Therefore, there is a need for studying the bulk thermodynamic properties of those polymethacrylates and also the phase behavior of block copolymers from them. Basic thermodynamic data such as volumetric properties for the methacrylate polymers are then essential to suffice the need. Once the volume data for given polymeric materials are given, other thermodynamic properties of the materials can be obtained by various thermodynamic relations.

Meanwhile, such volume data for poly(*n*-alkyl methacrylates) with ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, and *n*-dodecyl pendant groups were measured and tabulated by Zoller using his high pressure dilatometer.[5,6] It is the objective of this note to present a genuine scheme to obtain a priori volumetric properties as a function of temperature and pressure for poly(*n*-alkyl methacylates) in between those measured. The tabulated volume data for polymethacrylates with the number (n_c) of carbon atoms in the pendant group of 2, 3, 4, 6, and 12 are first cast into the form of the isothermal Padé equation of state, which satisfies the temperature-pressure superposition concept.[6-9] The Lagrange polynomials[10] with n_c's are then constructed to produce interpolated volume for the methacrylate polymers in between those tabulated. This method has once used by one of the authors to provide volume of poly(*n*-pentyl methacrylate) to study the phase behavior of loop-forming polystyrene-*b*-poly(*n*-pentyl methacrylate).[11-13]

*Corresponding Author. E-mail: jhcho@dankook.ac.kr

In this note, a more challenging attempt is made to obtain volume for poly(*n*-heptyl methacrylate) and poly(*n*-octyl methacrylate) while there is no experimental data between those for poly(*n*-hexyl methacrylate) and poly(*n*-dodecyl methacrylate).

Procedure

The compression behavior of polymeric liquids has been shown to satisfy the principle of temperature-pressure (T-P) superposition.[6-9] The compression strain, V/V_0, where V and V_0 are volumes at a given P and at ambient pressure P_0, respectively, is described universally by a composite variable, $(P-P_0)/B_0$ with B_0 implying bulk modulus at P_0, which combines the effects of pressure and temperature on the strain. Through the bulk thermodynamic argument, the so-called isothermal Padé equation of state has been formulated to represent the principle of T-P superposition:[6-8]

$$\ln(V/V_0) = \{\omega/(1-\omega)B_1\}[1-(1+B_1\{P-P_0\}/\omega B_0)^{1-\omega}] \tag{1}$$

where the symbols B_1 and ω respectively indicate the first-order pressure coefficient and the measure of the negative curvature of the series expansion of bulk modulus B in ($P-P_0$). It was shown that B_1=10.2 and ω=0.9 best correlate various polymer volume data. Zoller reported the tabulated volume data for vast number of polymers including poly(*n*-alkyl methacrylates) with ethyl, *n*-propyl, *n*-butyl, *n*-hexyl, and *n*-dodecyl side groups.[5,6] Table I lists V_0 and B_0 for those polymethacrylates.

Here, we offer a decent method to obtain volume data of polymethacrylates in between those given in Table I by interpolation based on Lagrange polynomials.[10] At each temperature and pressure, the known volumes of poly(*n*-alkyl methacylates) with n_c (the number of carbon atoms in the pendant groups)=2, 3, 4, 6, and 12 are regenerated by

Table I. Zoller's Volumetric Data for Various Poly(*n*-alkyl methacrylates) Expressed in the Padé form in Eq. (1)

Polymethacry-lates	B_0 at Ambient Pressure ($=a \cdot e^{-bT}$)		Density at Ambient Pressure ($=1/V_0=c+dT$)	
	b	$\ln a$	$d \times 10^4$	c
ethyl	0.0061	9.7384	-8.2191	1.3901
n-propyl	0.0049	9.1289	-6.7654	1.2848
n-butyl	0.0047	9.0834	-6.2635	1.2355
n-hexyl	0.0049	8.9897	-7.1308	1.2212
n-dodecyl	0.0054	9.2192	-6.6853	1.1436

The tabulated volume data for the polymethacrylates given above are taken only in the range of 370 K≤T≤480 K and 0.1 MPa≤P≤196 MPa.

using the isothermal Padé equation. The data points are matched with n_c as $(n_c, V(n_c))$. The Lagrange interpolating polynomial L_i is defined as

$$L_i(n) = \prod_{k \neq i} \frac{(n - n_k)}{(n_i - n_k)} \tag{2}$$

where n_i's are the selected numbers among all n_c's in making up a set of the Lagrange polynomials. The interpolated volume is estimated as the following equation:

$$V(n) = \sum_i V(n_i) \cdot L_i(n) \tag{3}$$

where $V(n_i)$ indicates the regenerated volume of the polymethacrylate having the pendant group with n_i carbon atoms.

Results and Discussion

Before proceeding to the prediction of volumetric properties of unknown polymethacrylates (n-heptyl and n-octyl), it should be conceived that there are two guiding principles. Firstly, the volume of the target polymethacrylates should be smoothly placed in between those of poly(n-hexyl methacrylate) and poly(n-dodecyl methacrylate). Secondly, the interpolated compression data of the target polymers should satisfy the concept of T-P superposition.

Keeping these two principles in mind, let us start the estimation with all the polymers included. In this case, L_0 (for n_0=2) to L_4 (for n_4=12) comprise the set of Lagrange polynomials. However, this procedure yields the volume of poly (n-octyl methacrylate) (n_c=8) at 370 K and at 0.1 MPa too close to that of poly(n-dodecyl methacrylate). Moreover, if the volume of this polymer at 0.1 MPa is plotted against temperature, it surpasses that of poly(n-dodecyl methacrylate) at T>420 K. This situation contradicts the guiding principle. Certainly, the increasing trend in volume for polymethacrylates from n_c=2 to 6 is reflected too strongly on the volume of n-octyl case.

Our next step is then to utilize only four polymethacrylates (L_0 to L_3) in the interpolation procedure. There are number of such ways. For example, one can take ethyl, n-propyl, n-hexyl, and n-dodecyl cases to interpolate poly(n-octyl methacrylate) volume. After the volumetric data are obtained through interpolation, those data are cast into the T-P superposable form, i.e., the isothermal Padé form. In Table II, V_0 and B_0 of the Padé equation for the polymer are given, where the Lagrange polynomials are constructed only with n_c=2, 3, 6, and 12. All the other possible choices of n_c in constructing the Lagrange polynomial are tested together. The average difference between the scattered interpolated volume data and the smoothed ones with the Padé equation is then compared in Table III. As seen in this table, the concept of T-P superposition is well preserved in the interpolated data. The best choice among them is that with n_c=2, 3, 6, and 12 to perform the interpolation procedure, where the

Table II. Interpolated Data in the Padé Form for Poly(n-heptyl methacrylate) and Poly(n-octyl methacrylate) by Constructing Lagrange Polynomials with n_c=2, 3, 6, and 12

New Polymetha-crylates	B_0 at Ambient Pressure $(=a \cdot e^{-bT})$		Density at Ambient Pressure $(=1/V_0=c+dT)$	
	b	$\ln a$	$d \times 10^4$	c
n-heptyl	0.0054	9.1687	-7.8053	1.2345
n-octyl	0.0058	9.3596	-8.4063	1.2480

Table III. Comparison of Interpolated Tabulated Volume Data Using Various Choices of n_c's and Correspondingly Smoothed Padé Equations for Poly(n-heptyl methacrylate) and Poly(n-octyl methacrylate)

Various Choices of n_c's	Average Error (cm³/g)	
	n-heptyl	n-octyl
2, 3, 4, 12	4.968×10^{-4}	8.484×10^{-4}
2, 3, 6, 12	3.114×10^{-5}	6.757×10^{-5}
2, 4, 6, 12	6.105×10^{-5}	1.431×10^{-4}
3, 4, 6, 12	1.128×10^{-4}	2.904×10^{-4}

average error of the smoothed volume function is merely 6.76×10^{-5} cm³/g. Encouraged by the success of the n-octyl case, the same method was used to interpolate the volume data for poly(n-heptyl methacrylate). The resultant smoothed Padé equation is given in Table II, which shows that the average error is again minimized as 3.11×10^{-5} cm³/g. In Figure 1, the smoothed volumes of polymethacrylates with n_c=2 to 12 at ambient pressure are all plotted against temperature. As seen in this figure, the isotherms for n-heptyl and n-octyl cases, where the Padé equation adopts the parameters in Table II, are well placed in between those for the n-hexyl and
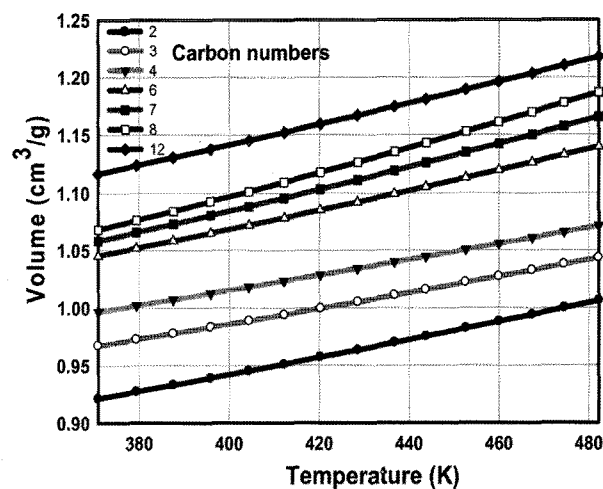

Figure 1. Volume at ambient pressure for poly(n-alkyl methacrylates) plotted against temperature.
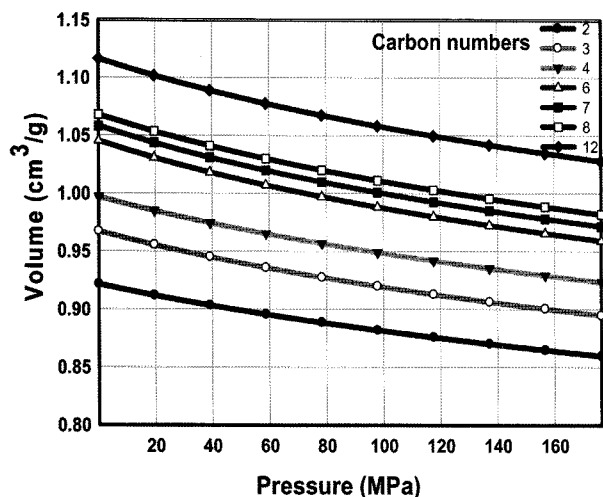
Figure 2. Compression response of volumetric properties for poly(n-alkyl methacrylates).

n-dodecyl cases. Figure 2 depicts the compression responses of all the polymethacrylates to pressure at 371 K. Poly(n-heptyl methacrylate) and poly(n-octyl methacrylate) reveal the compression behavior in a desirable way, as seen in Figure 2.

It is necessary to compare our result with any relevant published data in the literature. In 1957, Rogers and Mandelkern reported the volume data for polymethacrylates with n_c=2, 3, 4, 6, 8, and 12 at ambient pressure in the limited temperature range.[14] In the case of poly(n-octyl methacrylate), volume data were measured only up to ~300 K. Later, Simha and Wilson tried to fit the data by Rogers and Mandelkern to offer volume at ambient pressure based on the hole theory of Simha and Somcynsky.[15,16] In Table IV, the projected volumes at ambient pressure and at 373 K, and also thermal expansion coefficients for the series of poly(n-alkyl methacrylates) are listed along with those obtained in this study. Even though the volume data for poly(n-octyl methacrylate) were measured at lower temperatures, the projected volume at 393 K for the polymers is quite close to

ours. The results on the thermal expansion coefficients (α), however, reveal discrepancy from each other. According to Rogers and Mandelkern, the reported α increased with the increase of carbon atoms in the pendant groups, if $n_c \leq 6$. Otherwise, α showed some fluctuations exhibiting the lowest α for n-octyl case. Although Simha and Somcynski fitted the experimental data made in the former work to their theoretical isotherm, α's of poly(n-alkyl methacrylates) predicted by the hole theory were monotonically increasing with n_c. In Zoller's work, α's of poly(ethyl methacrylate), poly(n-hexyl methacrylate), and poly(n-dodecyl methacrylate) are similar to each other. The n-butyl case reports the lowest α. From our interpolation scheme, the increasing tendency from n-butyl case to n-hexyl case is extended to n-heptyl case, and then its speed slows down in the n-octyl case to reach α of poly(n-dodecyl methacrylate).

The variation in the volumetric properties for poly(n-alkyl methacrylates) is caused by molecular factors such as excluded volume and van der Waals interaction strength of pendant groups. As the pendant group size increases, the van der Waals interaction should also increase. However, the correspondingly increased excluded volume of those groups requires more free space between them, which diminishes the interaction strength between the monomers. This action explains the trends of increasing α's of polymethacrylates from ethyl to n-octyl side groups. In the n-dodecyl case, the strengthened van der Waals interaction takes over separation effects due to large excluded volume, which then yields more tightly binding interaction between monomers than adjacent polymethacrylates with smaller side groups. Therefore, α of poly(n-dodecyl methacrylate) is to be diminished from that of poly(n-octyl methacrylate) and become similar to that of poly(n-hexyl methacrylate).

One definite merit of the present scheme is to yield the complete pressure-volume-temperature properties of poly(n-heptyl methacrylate) and poly(n-octyl methacrylate). Even though there lacks any experimental report on those properties, the arguments given above suggest that the predicted compression results are genuine to be used in other studies,

Table IV. Volumes (V_0) at Ambient Pressure and at 393 K, and Thermal Expansion Coefficients (α) for the Series of Polymethacrylates in This Study and also in the Previous Works

Polymethacrylate with n_c	This Study		Rogers-Mandelkern		Simha-Wilson	
	V_0(393 K) (cm^3/g)	$\alpha \times 10^4$ (1/K)	V_0	$\alpha \times 10^4$	V_0	$\alpha \times 10^4$
2	0.9371	7.702	0.928	5.40	0.9283	5.717
3	0.9814	6.640	0.9815	5.80	0.9810	6.237
4	1.0108	6.331	1.0075	6.10	1.0081	6.550
6	1.0627	7.578	1.055	6.60-7.00	1.0568	7.109
7	1.0779	8.413				
8	1.0897	9.161	1.089	5.80-6.20	1.09935	7.339
12	1.1353	7.590	1.141	6.80	1.1565	8.045

where finite compressibility of those polymethacrylates are required.

Conclusions

It has been shown that the experimentally determined volume data for poly(*n*-alkyl methacrylates) with pendant groups having 2, 3, 4, 6, and 12 carbon atoms were used to interpolate the volume of the intermediate poly(*n*-heptyl methacrylate) and poly(*n*-octyl methacrylate) by employing Lagrange interpolation method. The interpolated volume data for the two polymethacrylates were smoothly placed between the true experimental ones, as the number of carbon atoms increases at given temperatures and pressures. The newly determined volume data in the octyl case were compared with previous reports made in a limited way (only at low temperatures and ambient pressure) by Rogers and Mandelkern and theoretically by Simha and Somcynski. It was found that our results were in part harmonious with those earlier works.

We presented here basic thermodynamic properties such as volume data of poly(*n*-alkyl methacrylates) with *n*-heptyl and *n*-octyl pendant groups. For those polymers, experimental results in a proper range of temperature and pressure have never been given in the literature. In particular, the determination of the compression response of those polymethacrylates is the main outcome of our proposed procedure. It was shown that these newly determined thermodynamic data are genuine and can be readily converted to any valuable information through thermodynamic relations. One of such possibilities is to use the volumetric properties of poly(*n*-heptyl methacrylate) and poly(*n*-octyl methacrylate) in order to investigate baroplastic phase behavior of block copolymers from polystyrene and them, which should be the subject of our future study.

References

(1) M. Sticker and T. Rhein, in *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH Verlag GmbH & Co., KGaA, 2000.
(2) T. Thurn-Albrecht, J. Schotter, G. A. Kastle, N. Emley, T. Shibauchi, L. Krusin-Elbaum, K. Guarini, C. T. Black, M. T. Tuominen, and T. P. Russell, *Science*, **290**, 2126 (2000).
(3) C. T. Black, K. W. Guarini, K. R. Milkove, S. M. Baker, T. P. Russell, and M. T. Tuominen, *Appl. Phys. Lett.*, **79**, 409 (2001).
(4) D. Y. Ryu, K. Shin, E. Drockenmuller, C. J. Hawker, and T. P. Russell, *Science*, **308**, 236 (2005).
(5) P. Zoller and D. Walsh, *Standard Pressure-Volume-Temperature Data for Polymers*, Technomic Publishing Co., Inc., Lancaster, 1995.
(6) J. Cho and I. C. Sanchez, in *Polymer Handbook*, 4 ed., J. Brandrup, E. H. Immergut, and E. A. Grulke, Eds., Wiley Interscience, New York, 1999, p VI/591.
(7) I. C. Sanchez, J. Cho, and W.-J. Chen, *Macromolecules*, **26**, 4234 (1993).
(8) I. C. Sanchez and J. Cho, *Polymer*, **36**, 2929 (1995).
(9) J. Cho and I. C. Sanchez, *Macromolecules*, **31**, 6650 (1998).
(10) R. Seroul, *Programming for Mathematicians*, Springer-Verlag, Berlin, 2000.
(11) J. Cho, *Macromolecules*, **37**, 10101 (2004).
(12) D. Y. Ryu, U. Jeong, J. K. Kim, and T. P. Russell, *Nature Mater.*, **1**, 114 (2002).
(13) D. Y. Ryu, D. H. Lee, J. K. Kim, K. A. Lavery, T. P. Russell, Y. S. Han, B. S. Seong, C. H. Lee, and P. Thiyagarajan, *Phys. Rev. Lett.*, **90**, 235501 (2003).
(14) S. S. Rogers and L. Mandelkern, *J. Phys. Chem.*, **61**, 985 (1957).
(15) R. Simha and P. S. Wilson, *Macromolecules*, **6**, 908 (1973).
(16) R. Simha and T. Somcynsky, *Macromolecules*, **2**, 342 (1969).