the CH decreases. Both of these effects may be attributed to a disruption of the domains on repeated deformation which allows greater relaxation of the flexible segments and greater orientation of the aromatic urethane segments. It should be noted, though, that while there is an effect of strain history on the orientation level, it is not great. A future publication will explore this observation in relation to intermolecular bonding.

Conclusions

It has been pointed out that there is a drastic change in orientation behavior in going from ET-24-1 to ET-28-1. Very little orientation is held in either segment in ET-24-1. In ET-28-1, ET-31-1 and ET-38-1, relatively high degrees of orientation are maintained, particularly in the hard segments. It is suggested that this is connected with the development of interlocking hard segment domains in ET-28-1 which do not exist in ET-24-1. In ET-24-1, the independent hard domains allow extensive relaxation of the orientation in both segments. In ET-28-1, relaxation of orientation is severely restricted by the interconnecting morphology of the hard segments. The flexible soft segments can relax to a greater degree, but they too are restrained by covalent bonding to the hard segments.

The first change in orientation behavior with composition thus occurs at the point where the morphology changes from independent hard domains to an interlocked structure. Once the interlocked subcrystalline hard regions are formed, only minor changes in orientation behavior due to the changing volume fraction of hard segment occur. The basic mechanism for these materials is an increasing orientation of both segments into the stretch direction (positive orientation) at all elongations. A similar conclusion based upon low-angle X-ray studies on comparable noncrystalline segmented polyurethanes was made by Wilkes.[15]

A fundamental change in orientation mechanism is observed when crystallinity (as determined by the existence of an intense high temperature DSC endotherm[12] is introduced into the hard blocks. While the noncrystalline segments present still orient as before, the crystalline regions show a transverse (negative) orientation of the segments at low elongations. This may be visualized as an orientation into the stretch direction of the crystalline regions themselves, pulling the chains transverse to the stretch direction. Low strain level hysteresis experiments show that this is a nearly reversible process. As the elongation is increased, however, the original crystallites are broken up and the segments orient positively. Orientation of the crystalline hard segments thus occurs in two steps. First the positive orientation of the crystalline region itself, followed by disruption of the region and increasing positive orientation of the segments. Crystalline and noncrystalline hard segment orientations are affected differently by temperature. Noncrystalline hard segment orientation shows a maximum value at about 90° for 38% MDI polyurethanes, all orientation being positive. For crystalline hard segments, lower orientation levels were observed and more negative orientation at low elongation was found at temperatures above 50°C. A two-step orientation mechanism still obtains, however, as the orientation becomes purely positive at about 100% elongation.

Acknowledgment. The authors acknowledge the assistance of Mr. Jeffrey T. Koberstein in carrying out some of the experimental work. The materials used in this study were kindly supplied by Dr. E. A. Collins of the B. F. Goodrich Chemical Co. We are also grateful to the National Science Foundation for support of this research through Grant GH-31747.

(15) C. E. Wilkes and C. S. Yusek, *J. Macromol. Sci., Phys.*, **7**, 157 (1973).

Thermal Expansion of Amorphous Polymers at Atmospheric Pressure. I. Experimental

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ABSTRACT: The design and calibration of a simple volume dilatometer are described. It overlaps and extends to about 250° the range of our cryogenic dilatometer and thus is suitable for expansivity studies of some polymeric high-temperature glasses, the corresponding liquids, and rubbery polymers. Measurements of specific volume are accurate within $\pm 1.3 \times 10^{-4}$ cm^3/g. The results for three methacrylate polymers are given, namely, cyclohexyl, cyclopentyl, and a highly isotactic methyl. The thermal expansivities and derived free-volume quantities are compared with each other and with previous results for homologous series of poly(alkyl methacrylates) and poly(vinyl ethers). The typical effects in systems with linear side chains, which are reflected in reduced values of the characteristic product $\Delta\alpha T_g$, are not encountered in the present systems. They retain "normal" values, not withstanding the enhanced mobility of the rings.

In the past several years we have undertaken studies of the pressure–volume–temperature (PVT) surface of amorphous polymers in the liquid and glassy domains.[1] At atmospheric pressure the range between room temperature and about 10°K has been investigated for a variety of polymeric structures, primarily as a low-frequency tool in mechanical relaxation spectroscopy and in connection with certain free-volume ideas. At elevated pressure ($P \leq$ 2 kbar) the PVT surface has been determined in the range between about 10 and 200°.

It has been possible to compare experimental results in the equilibrium liquid ($T > T_g$) successfully with the statistical theory[2-5] and, continuing on this basis, to explore

(1) Extensive literature references are found in P. S. Wilson, Ph.D. Thesis, Case Western Reserve University, 1973.

(2) R. Simha and T. Somcynsky, *Macromolecules*, **2**, 342 (1969).

(3) A. Quach and R. Simha, *J. Appl. Phys.*, **42**, 4592 (1971).

(4) R. Simha, P. S. Wilson, and O. Olabisi, *Kolloid-Z. Z. Polym.*, in press.

(5) A. Quach, P. S. Wilson, and R. Simha, *J. Macromol. Sci., Phys.*, in press; *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, in press.

the behavior of the characteristic hole fraction in the nonequilibrium glass and in the transition region for several polymers.[5-7]

From all points of view it becomes desirable to extend the temperature range for at least atmospheric pressure dilatometry, so as to (a) overlap with our cryogenic dilatometer, (b) permit investigation of a sufficient range in the glassy and liquid region for high T_g systems, and (c) provide accurate thermal expansivities in rubbery polymers above T_g. In this connection, it will be recalled that the cryogenic dilatometer employs length measurements and because of mechanical loading is unsuitable in the liquid (rubbery) range. Results so obtained may then be compared with theoretical predictions in the liquid state and may be used to explore corresponding approaches to the glassy state.

The purpose of this paper is first, to describe the design, experimental procedure, and calibration of a volume dilatometer operative at atmospheric pressure between −35 and +250°. Secondly, thermal expansivities for three methacrylate polymers, *viz.*, cyclohexyl, cyclopentyl, and isotactic methyl, are discussed. The former two are of interest in connection with low-temperature dilatometric[8,9] and dynamic mechanical[10] investigations. The PVT properties of the third have been recently compared with those of conventional poly(methyl methacrylate) (PMMA).[5]

These measurements, together with others carried out previously in this laboratory or described otherwise in the literature, will be considered in the following paper in terms of theory for the liquid and glassy regions.

I. Experimental Section

A. Instrument. The glass dilatometer, conventional in design, is shown schematically in Figure 1. It consists of two main parts: a U-shaped sample chamber with cap and a calibrated column. The sections of the instrument are connected by ground-glass joints.

The cleaned glassware is dried in a vacuum oven for several days prior to assembly and the prepared sample placed in the sample chamber. A *small* amount of a special high-vacuum grease is applied to the two male joints. As lubricant we use Dow Corning FS-3452 which is not soluble in the silicone oil of the high-temperature bath. The ground-glass joints are slowly pressed together with a forceful twisting motion. When the dried surfaces appear to be properly wetted, the male joints are wiped clean of excess grease. This procedure is repeated several times so that a minimal amount of lubricant is used. Ideally, only a very thin layer is needed so that the joints may be easily separated at the end of the experiment by the application of heat.

Small springs are attached to the glass hooks shown in Figure 1 to keep the joint between the cap and the sample chamber in compression. They compensate for the slight pressure head (≤ 0.5 atm) developed by the column of mercury and by the buoyancy of the polymer sample. The assembled dilatometer is then attached to a glass support rod. The bent portion of the sample chamber slips between three hooks on the support rod and is fastened in place by light copper wire.

A mercury-filling apparatus is connected to the top of the calibrated column by means of a third ground-glass joint. It consists of a glass reservoir which contains a known mass of mercury and is mounted above a three-way stopcock. The entire assembly is then attached to a ring stand for support and the dilatometer is evacuated overnight by means of a small diffusion pump.

A vacuum of not less than 10^{-5} mm is obtained which seals the ground-glass joints. The stopcock is turned so that the vacuum line is closed off and the mercury is permitted to flow into the dilatometer. The mercury is triple distilled and fresh mercury is used for each experiment. The filling apparatus is then disconnected from the instrument.

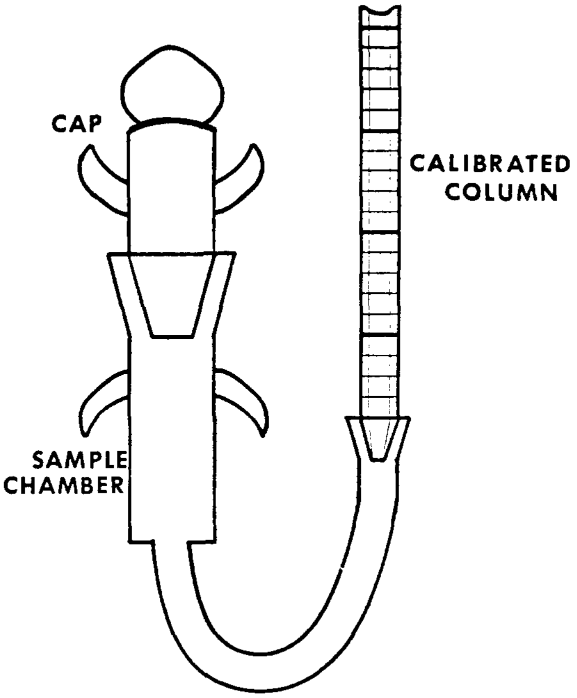

Figure 1. Schematic of dilatometer.

The dilatometer is suspended from the support rod and immersed in one of two liquid baths such that the level of mercury in the column is always below that of the heat-transfer fluid. One bath contains a water-antifreeze solution and is used in the temperature range −35 to +85°. The other bath uses Dow Corning 210H silicone oil and is operated from room temperature to 250°.

The temperature is regulated by a Lauda controller equipped with a linear programmer for both increasing and decreasing the temperature at rates varying from 0.05 to 3.0° per min. The heating rates used in this study were 12 and 18° per hr. All samples were first run at 18°/hr for about 2 hr. The controller was then set to maintain a constant temperature. The mercury level was monitored for at least 1 hr to see if it held constant. If it continued to increase, the heating rate was too fast, thus the thermal gradient too large, and the run was started over using the 12°/hr rate. This procedure was repeated at the slower heating rate and it was never found necessary to reduce the rate to less than 12°/hr. The controller has a short-range stability of $\pm 4 \times 10^{-3\circ}$ and a long-range stability of $\pm 7 \times 10^{-3\circ}$.

The temperature is measured by a set of secondary reference thermometers (±0.01°, −35 to +100°, and ±0.02°, 100-250°). The thermometer is placed in the "U" formed by the column and the sample chamber and is in contact with the sample compartment.

The mercury level in the calibrated column is recorded as a function of temperature, and the largest error is associated with the reading of this level. Instead of reading (and estimating) the height of the mercury in the column at equal temperature intervals, the following procedure was adopted. The temperature was recorded whenever the top of the miniscus of the mercury just appeared above a given line on the column and the outer edges of the miniscus were still below that line. This served to minimize the error.

The volume and density of the sample are obtained directly and the volumetric thermal expansivity, $\alpha \equiv (1/V)(\mathrm{d}V/\mathrm{d}T)$ is calculated by the method of moving arcs.[11] We use a seven-point least-squares parabola which begins at one end of the data set and indexes through point by point. The derivative is calculated for data points 4 to $(n - 4)$ and the first and last three points are lost. Parabolas of less than seven may yield unstable derivatives due to even slight fluctuations in the data. Nine and eleven point parabolas showed little improvement and were not used because of the increased computer time necessary. It should be noted, that as the number of data points used per arc is increased, the temperature interval increases and eventually the volume-temperature relation might not be well fitted by a quadratic function.

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(6) T. Somcynsky and R. Simha, *J. Appl. Phys.*, **42**, 4545 (1971).
(7) A. Quach and R. Simha, *J. Phys. Chem.*, **76**, 416 (1972).
(8) R. Simha, J. M. Roe, and V. S. Nanda, *J. Appl. Phys.*, **43**, 11 (1972).
(9) J. M. Roe, Ph.D. Thesis, Case Western Reserve University, 1973.
(10) J. Heijboer, Ph.D. Thesis, University of Leiden, 1972. See also *J. Polym. Sci., Part C*, **16**, 3413 (1968).
(11) J. L. Zakin, R. Simha, and H. C. Hershey, *J. Appl. Polym. Sci.*, **10**, 1455 (1966).

Table I
Density and Thermal Expansivity of *n*-Docosane as a Function of Temperature

T (°C)	ρ (g/cm^3)	α (10^{+4}/°K)	T (°C)	ρ (g/cm^3)	α (10^{+4}/°K)
45	0.7789	8.53	125	0.7259	9.22
50	0.7754	8.55	130	0.7225	9.28
55	0.7725	8.58	135	0.7190	9.34
60	0.7692	8.61	140	0.7156	9.41
65	0.7655	8.64	145	0.7121	9.48
70	0.7622	8.68	150	0.7091	9.55
75	0.7588	8.72	155	0.7058	9.62
80	0.7560	8.76	160	0.7021	9.70
85	0.7527	8.81	165	0.6989	9.77
90	0.7491	8.85	170	0.6953	9.85
95	0.7459	8.89	175	0.6921	9.93
100	0.7426	8.94	180	0.6888	10.01
105	0.7392	8.99	185	0.6851	10.10
110	0.7360	9.05	190	0.6816	10.19
115	0.7327	9.10	195	0.6780	10.28
120	0.7297	9.16	200	0.6746	10.37

In addition, the derivative dα/dT is also calculated by this method in order to further pinpoint the location of transition regions. A maximum in a dα/dT *vs.* T curve corresponds to the midpoint of the transition. This is a less ambiguous value than that obtained by the intersection of asymptotic lines in a V-T curve or by estimating the middle of the step change in an α − T figure.

B. Sample Preparation. All materials were dried in a vacuum oven for several days. Some were then compression molded into bars. The excess and edge material was trimmed and the bars were inspected under a microscope for voids. Each sample was dried again in a vacuum oven for at least 1 day and its room temperature density was determined by hydrostatic weighing. It was then returned to the vacuum oven for several days prior to running the experiment. Most of the materials were received in the form of bars. These were trimmed, inspected, and dried, but did not need to be remolded.

The sample weights were normally of the order of 2.5-3.0 g so as to maintain a mercury to polymer volume ratio of three to one. The one exception was isotactic PMMA, where only a 1-g sample was available. Therefore, a smaller sample chamber was used to preserve the volume ratio.

C. Calibration. The column is made of Trubore precision glass tubing from the Ace Glass Co. and has an inside diameter of 1.4986 ± 0.00127 mm. It was calibrated with mercury in two different ways. The first involved the calibration for variations in cross-sectional area and in the marking of the column. Known masses of mercury were filled at 23° into the dilatometer, and the height of the mercury in the column was recorded for each mass. From the known density of mercury,[12] the change in volume, ΔV_{23}, was calculated as a function of the change in height, Δh. This was then compared with the ΔV predicted from the cross-sectional area and the distance between marks on the column (1.0 ± 0.02 mm). The average ΔV predicted was 1.7638 × 10^{-3} cm^3/mark. It was found that the actual volume between marks was 1.7710 × 10^{-3} cm^3 and this value was used for all calculations.

The second procedure involved the calibration of the column for the volumetric expansivity of the glassware. The literature value for this quantity in the temperature range of interest is 9.75 × 10^{-6}/°K.[13] The dilatometer was filled with a known mass of mercury and an experimental run was made in the temperature range −25 to +220°. From the density of mercury[12] and the volume of the column as a function of height at 23°, the thermal expansivity of the glassware was found to vary almost linearly from 9.64 × 10^{-6} to 9.88 × 10^{-6} per °K in this temperature range. However, this change is at the limit of the accuracy of the instrument and the literature value of 9.75 × 10^{-6}/°K was used to correct the experimental data. It should be noted, that any slight contribution to the expansion of the system due to the small amount of lubricant on the ground-glass joints is also compensated for by this latter calibration.

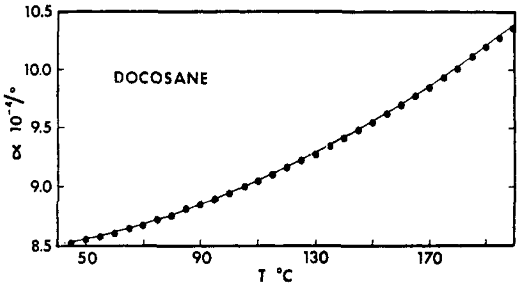

Figure 2. Thermal expansivity of *n*-docosane as a function of temperature. Solid circles, this work; line, ref 14.

D. Testing. The material chosen for this purpose was a straight-chain hydrocarbon, *n*-docosane ($C_{22}H_{46}$), previously studied in the temperature range of 44-200° by Orwoll and Flory.[14] The thermal expansivity is shown in Figure 2 as a function of temperature. The agreement between our data, exhibited in 5° intervals, and the empirical polynominal given by these authors is within ±0.8%. They claim an error in density of ±0.07% (±6 × 10^{-4} g/cm^3) and an accuracy of their α equation of ±0.5%. The density and thermal expansivity of this material are given in Table I as a function of temperature.

E. Error Analysis. The total error in the volume of the system may be attributed to errors in three quantities: height of the mercury column, mass of the system, and temperature. The corresponding volume errors for our instrument were found to be 2.45 × 10^{-4}, 0.19 × 10^{-4}, and 0.65 × 10^{-4} cm^3, respectively. Therefore, if all of the errors were to be additive, the maximum cumulative error in the volume of the system would be ±3.29 × 10^{-4} cm^3. If all of this is attributed to the polymer sample taking, ρ_p = 1.1 g/cm^3 and using a typical sample of 2.5 cm^3, the maximum error in specific volume is ±1.27 × 10^{-4} cm^3/g. This corresponds to a percentage error in specific volume of ±0.014%. Analysis of a large number of polymer systems[1] has shown that the corresponding error in the thermal expansivity will be 10-40 times as large. Therefore, the maximum α error should be ±0.14-0.56%.

II. Results and Discussion

The quantities to be presented include the specific volumes and thermal expansivities of each material as a function of temperature. As described in section I, the actual data are in the form of a dense net of irregularly spaced points. The interval between points ranges from about 1.2 to 0.4° as the temperature is increased. This is due to the accompanying increase in the thermal expansivity of the system, and the decreasing temperature change required for the mercury level to increase from one mark on the column to the next. To facilitate the presentation of the data and to put them into a more convenient form for future use by others, points have been read off the original curves, drawn on an expanded scale, at equal temperature intervals. The specific volume tables are given at 5° intervals, and so are the thermal expansivity curves, except in the transition regions where they are enriched by points at every 2.5°.

As said before, the derivative dα/dT has been obtained for all of the amorphous polymers as a function of temperature by the moving arc procedure. The maxima in the dα/dT curves are useful tools for pinpointing the location of sub-glass transitions, corresponding to low-frequency ($\simeq$10^{-3} Hz) dynamic results. Only one of the amorphous materials discussed here exhibits sub-glass relaxations in the temperature ranges studied and the dα/dT figure will be shown for that material only.

The additional quantities which are of interest include: the glass transition temperature, T_g; α_g and α_l, the glassy and liquid thermal expansivities extrapolated to T_g; the

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[12] P. H. Bigg, *Brit. J. Appl. Phys.*, **15,** 1111 (1964).

[13] Ace Glass Inc., Vineland, N. J., Cat. 600, 1968. See also Corning Glass Works, Corning, N. Y., Pyrex Labware, 10, 1971.

[14] R. A. Orwoll and P. J. Flory, *J. Amer. Chem. Soc.*, **89,** 6814 (1967).

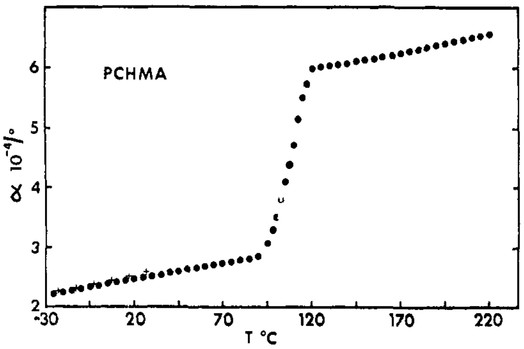

Figure 3. Thermal expansivity of PCHMA as a function of temperature. Solid circles, this work; crosses, ref 9.

product $\Delta\alpha T_g$, where $\Delta\alpha = (\alpha_l - \alpha_g)$; and $\alpha_l T_g$. The latter two quantities have been shown to be approximately constant for a large number of polymer systems without long side chains.[15-17] Finally we consider the corresponding expansivity intergrals.[16]

Table II and Figure 3 summarize the results for poly(cyclohexyl methacrylate) (PCHMA). We are indebted to Dr. Heijboer who provided both cyclic methacrylates. The T_g is found to be 107°, in qualitative accord with the dynamic mechanical work of Heijboer[10] who observed a T_g of about 125° at 1 Hz. The cryogenic work of Roe[9] indicates that the strong γ relaxation associated with the cyclohexyl ring is shifted by 43° on going from 1- to the $\simeq 10^{-3}$-Hz frequency, corresponding to dilatometry. This is consistent with the prediction of Heijober.[10] The corresponding shift in T_g would be less dramatic because of the much higher energy of activation associated with the glass transition. An estimation can be obtained from Boyer's analysis (Figure 34 of ref 18), which yields ΔT_g = 17°, in good accord with the 18° shift found here. The 107° value is also confirmed by the recent high-pressure study of Olabisi.[19]

We obtain for α_l and α_g 5.91×10^{-4} and 2.93×10^{-4} per °K, respectively. $\Delta\alpha T_g$ is 0.113, which agrees well with the Simha–Boyer[15,17] value. On the other hand, the quantity $\alpha_l T_g$ is 0.225, considerably larger than the average Simha–Boyer value of 0.164 or the Simha–Weil[16] average of 0.180. This difference may be related to the bulkiness of the side group. Other examples of this are polystyrene with $\alpha_l T_g$ = 0.206,[16] poly(*o*-methylstyrene) with 0.211,[3] and the value of 0.224 for poly(*tert*-butyl methacrylate).[16]

In connection with this latter material, the results of Simha–Weil[16] illustrate the effects of increasing the bulkiness of the side group upon both $\int(\alpha_l - \alpha_g)\mathrm{d}T$ and $\int\alpha_l\mathrm{d}T$ (from 0 to T_g) for polymers of butyl methacrylate. In passing the series *n*-, *sec*-, iso-, *tert*-butyl methacrylate, the $\Delta\alpha$ integral increases from 0.051 to 0.090 and the α_l integral from 0.116 to 0.149, with the largest change in both cases being associated with the iso to tertiary step. In terms of $\alpha_l T_g$, the change is from 0.174 to 0.224. Above the glass transition, the increased bulkiness results in a larger excluded volume. Below T_g, however, this bulk hinders the motion of the side group and results in a lower excluded volume. The net effect is an enlarged free volume defined by the $\Delta\alpha$ integral. To avoid confusion, it should be recalled that $\int(\alpha_l - \alpha_g)\mathrm{d}T$ (from 0 to T_g) cannot be directly converted to $\Delta\alpha T_g$.[16]

Table II
Specific Volume of PCHMA as a Function of Temperature[a]

T (°C)	V_{sp} (cm^3/g)	T (°C)	V_{sp} (cm^3/g)
−30	0.8884	100	0.9272
−25	0.8900	105	0.9290
−20	0.8913	110	0.9312
−15	0.8929	115	0.9345
−10	0.8942	120	0.9371
−5	0.8959	125	0.9400
0	0.8972	130	0.9430
5	0.8989	135	0.9461
10	0.9002	140	0.9490
15	0.9018	145	0.9520
20	0.9032	150	0.9548
25	0.9049	155	0.9579
30	0.9063	160	0.9607
35	0.9079	165	0.9638
40	0.9092	170	0.9669
45	0.9108	175	0.9700
50	0.9122	180	0.9731
55	0.9138	185	0.9762
60	0.9151	190	0.9793
65	0.9163	195	0.9825
70	0.9181	200	0.9857
75	0.9197	205	0.9888
80	0.9212	210	0.9920
85	0.9228	215	0.9952
90	0.9245	220	0.9983
95	0.9261		

[a] Dashed line indicates location of T_g.

Also included in Figure 3 are the upper limits of the results from our cryogenic dilatometer.[9] The agreement is quite good but the data are diverging with increasing temperature. Samples for the low-temperature instrument are in the form of thin rectangular strips which are held taut by a counter-balance weight. Therefore, as the glass transition is approached, these samples may yield slightly. This effect would be magnified for materials with high α_g values, as is the case here. This will become more evident in the discussion of the next system.

Table III and Figure 4 present the findings for poly(cyclopentyl methacrylate) (PCPMA). This material has a T_g of 75°, in accord with Heijboer's $T_g \simeq$ 95° at 1 Hz.[10] From Boyer[18] we would estimate this shift to be 22°. Comparing the six- and five-membered rings, we note the lower T_g, and higher thermal expansivity of the latter, at cryogenic temperatures[9] as well as in our range. The characteristic α_l and α_g at T_g are also larger, *viz.*, 5.98 and 3.10 *vs.* 5.91 and 2.93×10^{-4}. These results suggest a lower cohesive energy and higher flexibility in PCPMA. The five-membered ring can assume four conformations in contrast with only two for the other,[10] and the activation energies for the predominant γ relaxations are respectively 3.1 and 11.4 kcal per mol. The enhanced ring motions should also reduce effective cohesive interactions. In this connection it is of interest to make comparative estimates of the apparent energies of activation ΔH_a for the glass transition. Lewis[20] offers two alternative relations. For sterically restricted polymers (bulky groups and/or stiff chains), he writes

$$\Delta H_a = (46.4\times T_g - 955)/(1.048 - 2.35\times10^{-3}\times T_g)$$

This yields values of $\simeq$108 and $\simeq$66 kcal per mol for the hexyl and pentyl polymer, respectively. The ΔH_a for

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(15) R. Simha and R. F. Boyer, *J. Chem. Phys.*, **37**, 1003 (1962).
(16) R. Simha and C. E. Weil, *J. Macromol. Sci., Phys.*, **1**, 215 (1970).
(17) R. F. Boyer and R. Simha, *J. Polym. Sci., Part B*, **11**, 33 (1973).
(18) R. F. Boyer, *Rubber Rev.*, **36**, 132 (1963).
(19) O. Olabisi, Ph.D. Thesis, Case Western Reserve University, 1973.
(20) A. F. Lewis, *J. Polym. Sci., Part B*, **1**, 649 (1963).

Table III
***Specific Volume of PCPMA as a Function of Temperature*[a]**

T (°C)	V_{sp} (cm^3/g)	T (°C)	V_{sp} (cm^3/g)
−30	0.8769	95	0.9164
−25	0.8781	100	0.9193
−20	0.8795	105	0.9222
−15	0.8810	110	0.9251
−10	0.8820	115	0.9281
−5	0.8831	120	0.9310
0	0.8845	125	0.9339
5	0.8859	130	0.9369
10	0.8872	135	0.9400
15	0.8885	140	0.9430
20	0.8899	145	0.9461
25	0.8911	150	0.9492
30	0.8925	155	0.9522
35	0.8939	160	0.9555
40	0.8952	165	0.9588
45	0.8966	170	0.9621
50	0.8980	175	0.9653
55	0.8994	180	0.9688
60	0.9008	185	0.9722
65	0.9022	190	0.9758
70	0.9040	195	0.9792
75	0.9060	200	0.9828
80	0.9082	205	0.9862
85	0.9108	210	0.9899
90	0.9137		

[a] Dashed line indicates location of T_g.

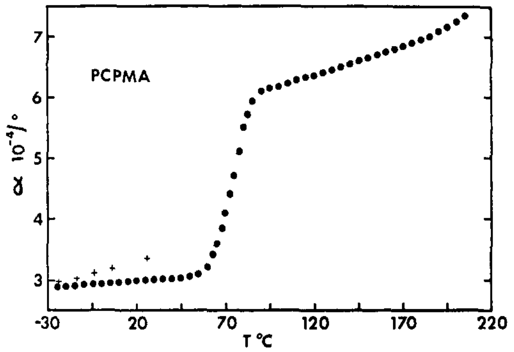

Figure 4. Thermal expansivity of PCPMA as a function of temperature. Solid circles, this work; crosses, ref 9.

Table IV
Specific Volume of I-PMMA as a Function of Temperature[a]

T (°C)	V_{sp} (cm^3/g)	T (°C)	V_{sp} (cm^3/g)
−35	0.8121	85	0.8440
−30	0.8127	90	0.8466
−25	0.8133	95	0.8492
−20	0.8139	100	0.8519
−15	0.8145	105	0.8544
−10	0.8152	110	0.8571
−5	0.8159	115	0.8597
0	0.8166	120	0.8622
5	0.8173	125	0.8649
10	0.8181	130	0.8674
15	0.8189	135	0.8701
20	0.8198	140	0.8728
25	0.8207	145	0.8753
30	0.8217	150	0.8779
35	0.8227	155	0.8805
40	0.8236	160	0.8832
45	0.8245	165	0.8858
50	0.8258	170	0.8883
55	0.8281	175	0.8910
60	0.8309	180	0.8934
65	0.8336	185	0.8960
70	0.8361	190	0.8988
75	0.8388	195	0.9014
80	0.8413	200	0.9040

[a] Dashed line indicates location of T_g.

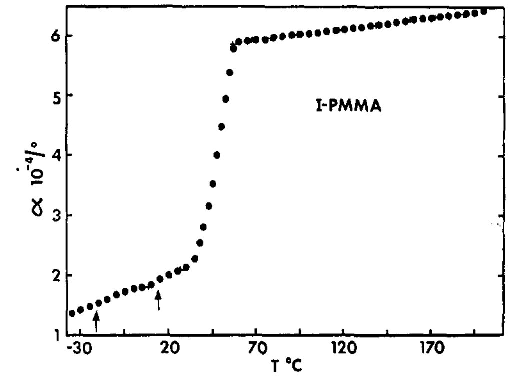

Figure 5. Thermal expansivity of I-PMMA as a function of temperature. Arrows indicate locations of sub-glass relaxations. Solid circles, this work; crosses, ref 5.

PCPMA, however, is quite low for a sterically restricted system. Lewis' second equation for nonrestricted materials (side groups absent or small, and flexible chains) is

$$\Delta H_a = (77.6 \times T_g + 3030)/(0.94 - 1.55 \times 10^{-3} \times T_g)$$

Now $\Delta H_a \simeq 75$ kcal/mol for the cyclopentyl polymer, a value which is quite high for a nonrestricted material. The conclusion is therefore, that PCPMA is more flexible than the normal restricted polymers and has too much bulk to act totally nonrestricted. This appears to be in accord with the previous discussion. Furthermore, $\Delta\alpha T_g$ is 0.100 and $\alpha_l T_g$ is 0.208. These quantities are both smaller than for PCHMA, reflecting the decrease in the bulkiness of the side group.

In Figure 4 it can be seen that the thermal expansivity begins to increase at an enhanced rate above ≃180°. This may be due to the onset of degradation or to a liquid–liquid transition. No evidence was found of degradation products in the dilatometer at the end of the experiment and spot checks of readings during the cooling process revealed no discrepancies from those obtained during heating. However, we are not aware of any literature reference to a liquid–liquid transition in PCPMA.

The data obtained from the cryogenic dilatometer[9] are also exhibited in Figure 4. It can be seen that the deviations between the two sets of results are magnified for this material. This is because the α_g of PCPMA is larger than that of PCHMA and the T_g is 32° lower. The data of the low-temperature instrument extend therefore much closer to the transition. The $d\alpha/dT$ for both of these materials do not indicate sub-glass relaxations in the temperature range studied.

We turn to a consideration of $\int(\alpha_l - \alpha_g)dT$ (from 0 to T_g) which represents approximately[16] one of the two free volume ratios defined by Boyer and Simha.[15] Similarly to the behavior of the product $\Delta\alpha T_g$ this integral is relatively small for polymers with long n-paraffinic side chains in the alkyl methacrylate and vinyl ether series, compared with those containing bulky and more rigid substituents.[16] However the variations are not as large.

We perform a graphical integration over α_g for the two

Table V
Experimental Volume-Temperature Quantities

Polymer	T_g (°K)	V_g (cm^3/g)	α_g (10^{+4}/°K)	α_l (10^{+4}/°K)	$\Delta\alpha T_g$	$\alpha_l T_g$	$\int(\alpha_l - \alpha_g)dT^a$	$\int\alpha_g dT^a$
PCHMA	380	0.9300	2.93	5.91	0.113	0.225	0.083	0.067
PCPMA	348	0.9060	3.10	5.98	0.100	0.208	0.052	0.087
I-PMMA	320	0.8248	2.34	5.83	0.112	0.187	0.090	0.035

[a] From 0 to T_g.

cyclic methacrylates by combining the low-temperature results of Roe[9] with ours. The two sets of data were connected at a temperature below which they coincided, which happened to be approximately at T_g = −115° for both polymers. Using the same procedure as previously for the α_l integration,[16] the results are 0.083 and 0.052 for PCHMA and PCPMA, respectively. The former is close to those for poly(*tert*-butyl methacrylate) and polystyrene, whereas the second is comparable to that observed for the normal series members of intermediate length or bulkiness. This difference is primarily due to the enhanced relaxational activity and thermal expansivity of PCPMA even at cryogenic temperatures.[9] The integral over α_g is 0.087, compared with 0.067 for the companion system. From the tabulated results of ref 16 one can compute the integral $\int\alpha_g dT$ (from 0 to T_g) for the two series. None of the polymers reach the above value for PCPMA, once again indicating its high degree of thermal activity in the glassy state. The hexyl material, on the other hand, behaves similarly to the butyl methacrylates.

Table IV and Figure 5 present the results for an isotactic poly(methyl methacrylate) (I-PMMA) which was prepared in this laboratory by Dr. Quach and found to have an isotacticity exceeding 99%. The synthesis technique, structural characterization, and elevated pressure results are published elsewhere.[5] The T_g was determined to be 47°. This compares well with the value of 49.7° obtained by Quach *et al.*[5] The α_l and α_g are 5.83×10^{-4} and 2.34×10^{-4} per °K, respectively. The $\Delta\alpha T_g$ is 0.112, in good accord with Simha-Boyer value.[15,17] The quantity $\alpha_l T_g$ is 0.187 compared with the average value of Simha-Weil[16] of 0.180. The much smaller value of $\alpha_l T_g$ for the I-PMMA, primarily a consequence of the reduction in T_g (see Table V), as compared to the two previous materials, is another illustration of the effect of a decrease in the bulkiness of the side group.

Recent measurements by Lee[21] enable us to compute the two expansivity integrals with the results 0.090 and 0.035. The first value seems unusually large compared with the 0.071 observed for conventional PMMA, and is reached otherwise only by *tert*-butyl methacrylate.[16] This is primarily a consequence of the unusually small value of the integral over α_g. Now the α_g's at their respective T_g's are not too different and sub-glass relaxational activity is limited and similar for both PMMA species.[21,22] Hence the difference in the α_g integral, 0.035 *vs.* 0.049, reflects largely the reduction in the range of integration from 378°K to 320°K. Simha and Weil were concerned primarily with the effect of side chains on the free volume. Similar low values of T_g for methacrylates are encountered only in the ethyl, *n*-propyl, and in the *sec*- and isobutyl isomers. These however have greater relaxational activity and thus values of the α_g integral than the methyl methacrylates.

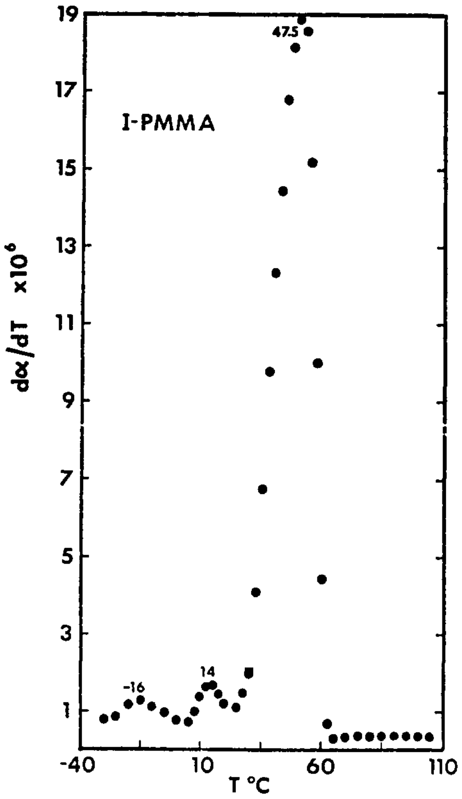

Figure 6. Temperature derivative of the thermal expansivity of I-PMMA as a function of temperature.

Figure 5 shows the excellent agreement with the atmospheric pressure results of Quach *et al.*[5] The arrows indicate the positions of sub-glass relaxations. These are better illustrated in Figure 6, where they appear centered at 14 and −16°. Wittman and Kovacs[23] reported a transition in I-PMMA at 8° and Heydemann and Guicking mention one at −7° in the atactic species.[24] The relaxation in the region of 10° has been observed in many methacrylate polymers[22] and is considered characteristic of the species.[10]

III. Conclusions

The pertinent experimental quantities for the three methacrylates are summarized in Table V.

There is a significant variation in respect to several primary and derived quantities. The glass temperature and volume decrease with decreasing bulkiness of the substituent. The thermal expansivity α_g assumes the "usual" value for I-PMMA, and is enhanced in the cyclic materials, as expected for systems with considerable sub-glass relaxational activity.[17] Close to the glass transition, the thermal expansivities in the liquid state are but slightly

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(21) S. Lee, M.S. Thesis, Case Western Reserve University, 1973.

(22) R. A. Haldon and R. Simha, *J. Appl. Phys.*, **39**, 1890 (1968).

(23) J. C. Wittmann and A. J. Kovacs, *J. Polym. Sci., Part C.*, **16**, 4443 (1969).

(24) P. Heydemann and H. D. Guicking, *Kolloid-Z. Z. Polym.*, **193**, 16 (1963).

larger in the ring compounds. With increasing temperature, however, the differences between the three polymers increase in the direction suggested by the α_l values in Table V. It is reasonable to associate this difference between the two types of polymers to differences in packing and in cohesive energy density.

As has already been noted, the differences in $\alpha_l T_g$ simply reflect those in T_g. The constancy of $\Delta\alpha T_g$ suggests that the side-chain effects which have been invoked to rationalize smaller numerical values in the n-alkyl methacrylate series,[15] either are not operative, or affect both the liquid and the glassy state in the two ring polymers. In contrast, the free volume integral is sensitive to the relaxational activity in the glass, as monitored by the last integral in Table V, with the value of the former being unusually large for I-PMMA. While the numerical values of the other quantities ultimately reflect structural differences, it is noteworthy to contrast this once again with the characteristic constancy of the product $\Delta\alpha T_g$.

In the following paper we will examine these and additional experimental results in the liquid and glassy states from the point of view of a theoretical equation of state.

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Thermal Expansion of Amorphous Polymers at Atmospheric Pressure. II. Theoretical Considerations

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ABSTRACT: We analyze a number of structurally diverse systems. A simple interpolation expression represents accurately the implicit form of the theoretical equation of state for the liquid derived previously, and facilitates numerical evaluations. The very good agreement between predicted and measured volumes is in accord with earlier observations. Thermal expansivities, α, are estimated with a maximum error, averaged over all systems investigated, of 3.7%. The theoretical temperature dependence of α is $\propto T^{1/2}$. However, the experimental results are better approximated by a linear function or by a proportionality factor which decreases with increasing T. The volume and temperature scaling parameters are compared for different polymers. The characteristic temperature T^* shows a parallel trend with T_g. But, not surprisingly, T_g is not strictly a corresponding temperature. Hence the hole fraction $1 - y$ at T_g is not constant, but increases with increasing reduced, and essentially actual glass temperature. A connection between the liquid and glassy states is provided by the temperature dependence of y, finite also in the glass, as shown earlier, and treated there as an adjustable quantity in the theoretical equation of state. From the difference between the experimental and theoretical y's for the glass and supercooled liquid, respectively, a characteristic frozen fraction can be deduced which increases with decreasing T_g. In accord with well-known macroscopic characteristics, the frozen fractions in the series of n-alkyl methacrylates are comparatively small and exhibit a minimum as a function of side-chain length.

We have previously shown the close agreement between master curves constructed from volume–temperature data at atmospheric pressure, encompassing oligomers and polymers,[1] and the predictions of our hole theory.[2] Such comparisons were subsequently extended to detailed data from our laboratory, including elevated pressures for polystyrene and poly(o-methylstyrene).[3] Finally, some high-pressure results taken from the literature, were also discussed.[4] The quantitative success of the theory has enabled us to proceed to the liquid–glass transition region and finally to explore the glassy state in terms of theoretical results, developed originally for the liquid equilibrium state.[3,5,6]

We are now in a position to investigate in detail the volume–temperature relations for series of structurally related as well as widely different polymers. This program is pursued here only at atmospheric pressure. Thus we obtain the specific characteristic volume (V^*) and temperature (T^*) scaling factors and define in quantitative detail the performance of the theory. Secondly, we examine the behavior of the hole fraction as a characteristic ordering parameter, in the glassy state of these polymers with their widely differing glass temperatures, and obtain semiempirical relationships. The accuracy of the experimental data with their different origins is not uniform. Nevertheless, the nature of our conclusions, as will be seen, is not affected by these differences.

Table I lists in order of decreasing T_g, except for the alkyl methacrylate series, the systems to be investigated and the sources of data.[3,7-19] These include earlier results from this laboratory and those reported in the foregoing paper[9] to which we added measurements[12] on a high mo-

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(1) R. Simha and A. J. Havlik, *J. Amer. Chem. Soc.*, **86**, 197 (1964).
(2) R. Simha and T. Somcynsky, *Macromolecules*, **2**, 342 (1969).
(3) A. Quach and R. Simha, *J. Appl. Phys.*, **42**, 4592 (1971); *Macromolecules*, **4**, 268 (1971).
(4) R. Simha, P. S. Wilson, and O. Olabisi, *Kolloid-Z. Z. Polym.*, in press.
(5) T. Somcynsky and R. Simha, *J. Appl. Phys.*, **42**, 4545 (1971).
(6) A. Quach and R. Simha, *J. Phys. Chem.*, **76**, 416 (1972).
(7) J. M. G. Cowie and P. M. Toporowski, *J. Macromol. Sci., Phys.*, **1**, 81 (1969).
(8) J. P. Mercier, J. J. Aklonis, M. Litt, and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **9**, 447 (1965).
(9) P. S. Wilson and R. Simha, *Macromolecules*, submitted for publication.
(10) S. S. Rogers and L. Mandelkern, *J. Phys. Chem.*, **61**, 985 (1957).
(11) K. H. Hellwege, W. Knappe, and P. Lehmann, *Kolloid-Z. Z. Polym.*, **183**, 110 (1962).
(12) P. S. Wilson, Ph.D. Thesis, Case Western Reserve University, 1973.
(13) L. Mandelkern, G. M. Martin, and F. A. Quinn, *J. Res. Nat. Bur. Stand., Sect. A*, **58**, 137 (1957).
(14) J. E. McKinney, National Bureau of Standards, U. S., private communication.
(15) M. Takahishi, M. C. Shen, R. B. Taylor, and A. V. Tobolsky, *J. Appl. Polym. Sci.*, **8**, 1549 (1964).
(16) G. Kraus and J. T. Gruver, *J. Polym. Sci., Part A-2*, **8**, 571 (1970).
(17) B. E. Eichinger and P. J. Flory, *Macromolecules*, **1**, 285 (1968).
(18) H. Shih and P. J. Flory, *Macromolecules*, **5**, 758 (1972).
(19) K. Polmanteer, Dow Corning Corp., Midland, Mich., private communication.