Pressure–Volume–Temperature Studies of Amorphous and Crystallizable Polymers. I. Experimental

Olagoke Olabisi and Robert Simha*

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106. *Received November 18, 1974*

ABSTRACT: By means of instrumentation developed previously, three methacrylate polymers in the liquid and glassy states, a standard and a high molecular weight linear polyethylene, and a branched standard polyethylene are investigated between room temperature and about 200° and up to pressures of 2 kbar. Thus the liquid as well as the glassy and crystalline regions respectively are included. Analytical representations of the equation of state are obtained and the resulting thermal expansivities and compressibilities compared with each other and with the results of previous investigators for similar polymer systems, where possible.

As part of a series of dilatometric studies of amorphous polymers in the rubbery and glassy states we have determined the equation of state of several vinyl polymers at pressures up to 2 kbar.[1,2] These and other results[3] are summarized in terms of simple empirical relationships.[1,2,4] Finally we have analyzed the results in terms of liquid state theory.[5]

In continuing this series we consider two groups of systems, one encompassing several methacrylates, and the other polyethylenes above and below the melting range. As for the former, the most studied polymer is atactic poly(methyl methacrylate) (PMMA). But even here the data are limited in scope. Hellwege, *et al.*,[6] present two isotherms below T_g and their maximum temperature is 139°. Heydemann and Guicking[7] limit themselves to pressures below 1 kbar. A highly isotactic polymer was recently examined by Quach, *et al.*[2]

Dilatometric studies of other methacrylate polymers, including poly(*n*-butyl methacrylate) (PnBMA), at atmospheric pressure have been undertaken by several authors.[8-10] The latter investigators considered several degrees of stereoregularity in PMMA. Poly(cyclohexyl methacrylate) (PCHMA), a system of considerable interest in connection with low-temperature dynamic mechanical studies,[11,12] has not been investigated in our context.

The literature contains a number of studies on polyethylenes of various origins. The data are either limited in respect to the range of variables or accuracy, and in other instances are not given in a form suitable for numerical analysis. A study in a single laboratory with standard samples of the high and low density types is desirable.

The theoretical analysis of the measurements in the liquid range provides a further test of its basis, yields additional characteristic scaling parameters[1,2,4,5] for the diverse structures investigated, and offers a starting point for the characterization of their glasses. These are the subjects of the following paper.

I. Results

The design and calibration of the pressure dilatometer have been described previously.[1] PMMA was prepared by conventional free radical polymerization by Ms. S. Lee. The glass temperature of the sample is 105°. The PnBMA is identical with the polymer studied earlier.[9] The PCHMA was obtained through the courtesy of Dr. J. Heijboer and is identical with the polymer employed earlier in our dilatometric studies at atmospheric pressure.[12,13]

Three polymers of ethylene were used, namely the standard samples SRM 1475 and SRM 1476 issued by the National Bureau of Standards, which represent a linear (LPE) and branched (BPE) species, respectively. To these we have added the ultrahigh molecular weight linear polyethylene provided by the Allied Chemical Co. (HMLPE). In regard to sample preparation and thermal history we follow the procedures applied in previous work.[1,2]

The specific volumes of the three methacrylates in the liquid and glassy ranges are listed in Tables I–III and the results for the three ethylene polymers appear in Tables IV–VI.

II. Discussion

1. Methacrylate Polymers. We start with atmospheric pressure. The specific volumes can be represented by polynomials above and below the respective T_g's of 20, 105, and 107° for PnBMA, PMMA, and PCHMA, respectively, and the coefficients are listed in Table VII. The thermal expansivities α_l and α_g at $T = T_g$ are compared with previous observations in Table VIII.[8,9,13,14] For PnBMA the good agreement with the values of Haldon and Simha[9] is noted. In PMMA the agreement between two α_l's obtained in our laboratory with different instruments is satisfactory, but the relative difference in α_g is greater. In the α_g of PCHMA a still larger difference but with the opposite sign is noted. Unfortunately different molding procedures were employed in the two sets of experiments and instruments. The α_l's are in the order PnBMA > PCHMA > PMMA, although the difference between the first two is not large. This sequence is reasonable, considering the nature of the side groups. The inversion in the α_g's between PMMA and PCHMA may result from a restriction of the side-group motion by the ring in the glassy state.[13] The enlarged value of α_g in polymers with flexible side chains is again illustrated by PnBMA. Finally a detailed examination of the data[15] reveals once more a subglass relaxation located at 60° in PMMA, independently of pressure.[7]

We turn next to the analytical representation of the results at elevated pressures. Again we make use of the Tait equation in the form employed earlier.[1,2,4]

$$1 - V(P, T)/V(0, T) = 0.0894 \ln[1 + P/B(T)] \quad (1)$$

Some theoretical rationalization of this expression and of the near universality of the numeric has been offered by a comparison of first and second derivatives with results of cell theory, but it represents an essentially empirical, yet practically useful, relation.

Figures 1–3 illustrate the performance of eq 1 in the liquid as well as the glassy state. The transition pressures pertaining to a given isotherm were obtained by locating the minima in the isothermal pressure derivatives of the bulk moduli.[1] We recall that these transition data refer to the systems generated by pressurizing the liquid along a given isotherm and hence represent so-called high pressure or variable formation glasses.

The smoothed B values derived from the isotherms in

Table I

Specific Volume (cc/g) of Poly(methyl methacrylate)

P,bar t,°C	1	100	200	300	400	600	800	1000	1200	1400	1600	1800	2000
17.2	.8442	.8420	.8399	.8378	.8358	.8319	.8281	.8246	.8212	.8180	.8149	.8119	.8091
31.9	.8466	.8443	.8420	.8399	.8378	.8337	.8298	.8261	.8226	.8192	.8160	.8129	.8100
45.9	.8492	.8467	.8444	.8421	.8399	.8357	.8316	.8278	.8242	.8206	.8173	.8141	.8110
56.8	.8513	.8488	.8463	.8440	.8417	.8373	.8331	.8292	.8255	.8219	.8185	.8152	.8121
67.7	.8537	.8510	.8485	.8461	.8437	.8392	.8351	.8309	.8270	.8233	.8198	.8165	.8133
80.1	.8566	.8539	.8512	.8487	.8462	.8415	.8371	.8329	.8289	.8252	.8216	.8181	.8148
90.8	.8595	.8567	.8539	.8513	.8487	.8439	.8393	.8350	.8308	.8269	.8234	.8199	.8164
100.9	.8620	.8591	.8563	.8536	.8509	.8460	.8412	.8368	.8327	.8287	.8249	.8213	.8179
113.5	.8677	.8635	.8595	.8557	.8524[a]	.8474	.8439	.8404	.8369	.8333	.8292	.8256	.8220
124.5	.8728	.8684	.8642	.8602	.8565	.8494	.8437	.8393	.8362	.8332	.8311	.8276	.8239
135.1	.8780	.8733	.8690	.8648	.8609	.8535	.8469	.8408	.8356	.8314	.8285	.8260	.8243
146.7	.8838	.8789	.8743	.8700	.8658	.8581	.8512	.8449	.8388	.8333	.8289	.8250	.8212
159.0	.8902	.8850	.8801	.8756	.8712	.8632	.8559	.8492	.8431	.8373	.8319	.8270	.8222

a - Line under number(s) indicates onset of T_g.

Table II

Specific Volume (cc/g) of Poly(cyclohexyl methacrylate)

P,bar t, °C	1	100	200	300	400	600	800	1000	1200	1400	1600	1800	2000
18.6	.9083	.9060	.9039	.9018	.8997	.8957	.8920	.8881	.8845	.8815	.8784	.8753	.8723
30.3	.9109	.9085	.9063	.9041	.9020	.8978	.8938	.8901	.8865	.8831	.8796	.8764	.8735
41.0	.9133	.9108	.9085	.9062	.9040	.8998	.8957	.8918	.8881	.8846	.8811	.8779	.8750
52.0	.9158	.9134	.9109	.9085	.9063	.9018	.8976	.8936	.8899	.8862	.8828	.8794	.8763
64.0	.9185	.9159	.9134	.9110	.9085	.9040	.8998	.8956	.8918	.8881	.8844	.8809	.8778
74.3	.9208	.9181	.9155	.9130	.9105	.9058	.9014	.8972	.8932	.8894	.8856	.8821	.8788
84.5	.9232	.9203	.9177	.9150	.9123	.9074	.9026	.8982	.8942	.8903	.8865	.8828	.8793
97.7	.9268	.9237	.9207	.9180	.9151	.9100	.9048	.9003	.8959	.8914	.8874	.8834	.8798
109.6	.9321	.9282	.9246[a]	.9215	.9188	.9131	.9077	.9028	.8977	.8935	.8888	.8844	.8801
122.7	.9394	.9341	.9291	.9245	.9200	.9141	.9111	.9073	.9026	.8978	.8933	.8889	.8847
134.3	.9458	.9401	.9347	.9299	.9251	.9165	.9084	.9028	.9000	.8970	.8928	.8881	.8840
147.3	.9533	.9473	.9415	.9361	.9312	.9219	.9136	.9058	.8989	.8925	.8889	.8857	.8830
158.2	.9596	.9532	.9471	.9415	.9361	.9263	.9178	.9098	.9025	.8960	.8898	.8841	.8786
169.3	.9674	.9604	.9539	.9480	.9423	.9323	.9231	.9148	.9074	.9003	.8943	.8884	.8830
179.9	.9727	.9654	.9586	.9523	.9465	.9359	.9262	.9179	.9099	.9029	.8962	.8895	.8848
189.2	.9786	.9708	.9636	.9571	.9507	.9399	.9298	.9210	.9130	.9053	.8986	.8926	.8870
198.9	.9845	.9763	.9688	.9619	.9554	.9439	.9337	.9245	.9164	.9087	.9018	.8954	.8890

a - Line under number(s) indicates onset of T_g.

Table III

Specific Volume (cc/g) of Poly(n-butyl methacrylate)

P,bar t,°C	1	100	200	300	400	600	800	1000	1200	1400	1600	1800	2000
12.2	.9435	.9400	.9366	.9333	.9302	.9242	.9189	.9135	.9085	.9038	.8996	.8954	.8916
22.0	.9474	.9436	.9401[a]	.9366	.9334	.9273	.9214	.9161	.9109	.9062	.9013	.8968	.8931
33.9	.9536	.9492	.9449	.9409	.9370	.9306	.9251	.9197	.9147	.9096	.9049	.9004	.8961
46.0	.9607	.9560	.9515	.9473	.9432	.9357	.9287	.9223	.9167	.9117	.9071	.9031	.8991
59.7	.9692	.9641	.9593	.9548	.9505	.9424	.9346	.9278	.9215	.9155	.9103	.9053	.9019
73.5	.9781	.9726	.9674	.9626	.9579	.9494	.9417	.9345	.9278	.9217	.9161	.9105	.9057
82.3	.9840	.9782	.9728	.9676	.9627	.9537	.9457	.9381	.9310	.9247	.9188	.9129	.9079
94.5	.9921	.9858	.9800	.9743	.9692	.9598	.9511	.9432	.9358	.9291	.9231	.9173	.9121
105.6	.9999	.9932	.9871	.9813	.9759	.9660	.9571	.9490	.9415	.9346	.9282	.9222	.9166
118.7	1.0097	1.0025	.9960	.9898	.9839	.9735	.9639	.9554	.9476	.9407	.9341	.9280	.9220
133.1	1.0200	1.0121	1.0051	.9982	.9920	.9807	.9707	.9617	.9531	.9457	.9390	.9323	.9264
146.4	1.0300	1.0215	1.0140	1.0067	.9999	.9884	.9778	.9681	.9596	.9517	.9447	.9375	.9312
160.2	1.0404	1.0312	1.0229	1.0151	1.0081	.9956	.9841	.9741	.9653	.9568	.9496	.9432	.9365
174.3	1.0513	1.0414	1.0321	1.0239	1.0161	1.0024	.9906	.9799	.9707	.9627	.9545	.9479	.9412
187.5	1.0614	1.0505	1.0408	1.0319	1.0237	1.0098	.9974	.9864	.9770	.9683	.9590	.9515	.9448
199.5	1.0713	1.0599	1.0493	1.0400	1.0314	1.0163	1.0032	.9919	.9817	.9727	.9641	.9565	.9492

a - Line under number(s) indicates onset of T_g.

Figures 1–3, excluding the transition regions, can be represented by an exponential temperature function,[1,2,4,16,17] *viz.*

$$B = B_0 e^{-B_1 t} \qquad (2)$$

where t represents the temperature in degrees Celsius. Table IX lists the numerical values of the coefficients. Equation 2 predicts the average B's with a maximum deviation of only 1.5% (PnBMA at 33.9°).[15] Equations 1 and 2 together with the polynomial representation of V_0, see Table VII, represent the complete equation of state of the liquid polymers and of their high-pressure glasses.

The parameter B_1 represents the derivative $(\partial \ln \kappa/\partial T)_P$ of the isothermal compressibility κ for $P \ll B$. As one might expect, and is also seen here, B_1 is usually observed to be smaller in the glass. PnBMA represents an exception. Although the numerical difference is not large, the departure from the normal pattern appears to be real. Unless this results from the presence of low molecular weight impurities, an obvious suggestion is the presence of relatively mobile side groups. On comparing PCHMA with PMMA, we find the former to be somewhat less compressible in the glassy state as is seen from the numerical values of B, *viz.*, $B \approx$ 3570 at 18.6 *vs.* 3380 at 17.2°. This is reversed in the liquid; 1300 at 158.2 vs. 1490 at 159°C. A smaller and larger excluded volume below and above T_g respectively in the polymer with the bulky side group[13] would be in qualitative accord with such an observation. At a corresponding temperature above T_g, PnBMA has about the same isothermal compressibility as PMMA.

The detailed agreement between experimental and computed (eq 1 and 2) volumes and the by now familiar pattern in the transition region of the VT plane (see, for example, Figures 5 and 6 in ref 1) will not be produced here but may be inspected in ref 15.

The glass temperatures of the high-pressure glasses vary linearly with pressure in our range. The derivatives dT_g/dP are of a very similar magnitude, namely 20.4, 22.4, and 23.6°C/kbar for PnBMA, PCHMA, and PMMA, respectively. The latter value is close to the 23.0 reported by Hellwege, *et al.*[6] The similarity of these numbers and the spread of the coefficients for PMMA given in the literature[6,7,18] precludes any attempt at a correlation with the structure of the methacrylates. We recall also, that for isotactic PMMA the pressure coefficient equals 21.2°C/kbar, notwithstanding the considerably lower T_g (47°) than for the atactic species and differences in the compressibilities of the glasses (but not the liquids).[2]

Table IV

Specific Volume (cc/g) of Branched Polyethylene

P, bar t,°C	1	100	200	300	400	600	800	1000	1200	1400	1600	1800	2000
19.1	1.0720	1.0686	1.0653	1.0621	1.0589	1.0533	1.0477	1.0425	1.0377	1.0334	1.0292	1.0249	1.0209
29.0	1.0776	1.0739	1.0704	1.0668	1.0636	1.0573	1.0513	1.0458	1.0405	1.0359	1.0317	1.0278	1.0231
41.4	1.0847	1.0806	1.0766	1.0727	1.0693	1.0619	1.0555	1.0499	1.0448	1.0394	1.0351	1.0305	1.0258
51.2	1.0923	1.0877	1.0833	1.0791	1.0751	1.0673	1.0604	1.0541	1.0482	1.0425	1.0375	1.0330	1.0279
68.5	1.1115	1.1056	1.1002	1.0947	1.0899	1.0805	1.0721	1.0642	1.0572	1.0510	1.0447	1.0394	1.0345
79.5	1.1270	1.1198	1.1132	1.1068	1.1005	1.0893	1.0795	1.0708	1.0629	1.0562	1.0496	1.0439	1.0386
97.9	1.1595	1.1502	1.1417	1.1333	1.1259	1.1131	1.1016	1.0916	1.0811	1.0723	1.0652	1.0584	1.0522
109.6	1.1940	1.1788	1.1659	1.1544	1.1439	1.1259	1.1109	1.0976	1.0854	1.0752	1.0658	1.0567	1.0497
116.4	1.2327	1.2068	1.1857	1.1683	1.1535	1.1322	1.1164	1.1027	1.0923	1.0826	1.0721	1.0632	1.0553
125.1	1.2570	1.2462	1.2363	1.2272	1.2188	1.1610[a]	1.1458	1.1320	1.1189	1.1075	1.0974	1.0887	1.0809
135.1	1.2692	1.2577	1.2473	1.2377	1.2288	1.2130	1.1993	1.1535	1.1396	1.1268	1.1146	1.1037	1.0948
142.7	1.2762	1.2642	1.2532	1.2433	1.2341	1.2179	1.2036	1.1909	1.1533	1.1415	1.1284	1.1163	1.1043
149.5	1.2827	1.2703	1.2591	1.2488	1.2395	1.2228	1.2082	1.1952	1.1836	1.1731	1.1427	1.1287	1.1145
160.5	1.2930	1.2799	1.2681	1.2575	1.2477	1.2304	1.2153	1.2019	1.1899	1.1790	1.1693	1.1601	1.1516
172.0	1.3037	1.2899	1.2775	1.2664	1.2561	1.2381	1.2225	1.2089	1.1965	1.1853	1.1751	1.1658	1.1571
184.8	1.3157	1.3009	1.2877	1.2759	1.2652	1.2463	1.2298	1.2155	1.2028	1.1913	1.1809	1.1714	1.1624
198.0	1.3270	1.3110	1.2970	1.2845	1.2730	1.2531	1.2362	1.2210	1.2080	1.1961	1.1852	1.1756	1.1662

a - Line under number(s) indicates onset of T_m.

Table V

Specific Volume (cc/g) of Linear Polyethylene

P,bar t,°C	1	100	200	300	400	600	800	1000	1200	1400	1600	1800	2000
19.5	1.0210	1.0188	1.0167	1.0147	1.0126	1.0088	1.0049	1.0015	0.9981	0.9949	0.9920	0.9891	0.9863
32.3	1.0255	1.0232	1.0210	1.0189	1.0169	1.0128	1.0091	1.0052	1.0017	0.9984	0.9951	0.9919	0.9889
47.6	1.0308	1.0283	1.0259	1.0236	1.0213	1.0169	1.0127	1.0086	1.0048	1.0011	0.9975	0.9941	0.9908
55.8	1.0341	1.0315	1.0289	1.0264	1.0240	1.0192	1.0148	1.0105	1.0064	1.0028	0.9993	0.9957	0.9922
66.1	1.0382	1.0354	1.0326	1.0299	1.0273	1.0224	1.0179	1.0135	1.0091	1.0050	1.0011	0.9974	0.9938
76.4	1.0429	1.0398	1.0368	1.0339	1.0312	1.0258	1.0208	1.0160	1.0117	1.0074	1.0033	0.9994	0.9956
84.8	1.0470	1.0437	1.0405	1.0374	1.0343	1.0289	1.0237	1.0188	1.0139	1.0090	1.0051	1.0010	0.9970
94.5	1.0530	1.0494	1.0460	1.0426	1.0394	1.0333	1.0278	1.0225	1.0174	1.0128	1.0082	1.0039	0.9997
104.5	1.0605	1.0566	1.0528	1.0493	1.0457	1.0390	1.0332	1.0273	1.0221	1.0171	1.0124	1.0083	1.0042
115.5	1.0719	1.0674	1.0631	1.0590	1.0551	1.0476	1.0407	1.0346	1.0290	1.0241	1.0194	0.0146	1.0095
128.9	1.1027	1.0931	1.0842	1.0761	1.0691	1.0574	1.0482	1.0398	1.0337	1.0284	1.0234	1.0189	1.0146
142.1	1.2692	1.2573	1.2467	1.2369	1.2279	1.0801[a]	1.0570	1.0582	1.0499	1.0433	1.0367	1.0316	1.0273
152.9	1.2787	1.2662	1.2549	1.2446	1.2352	1.2185	1.2038	1.0645	1.0519	1.0452	1.0389	1.0339	1.0298
165.4	1.2915	1.2783	1.2664	1.2557	1.2458	1.2284	1.2131	1.1995	1.1876	1.0737	1.0446	1.0373	1.0320
171.1	1.2970	1.2834	1.2710	1.2601	1.2498	1.2320	1.2163	1.2026	1.1903	1.1793	1.1693	1.0499	1.0429
180.9	1.3075	1.2930	1.2802	1.2687	1.2582	1.2395	1.2235	1.2093	1.1968	1.1855	1.1753	1.1660	1.1577
189.6	1.3165	1.3013	1.2879	1.2756	1.2648	1.2455	1.2290	1.2147	1.2015	1.1900	1.1794	1.1694	1.1610
199.7	1.3271	1.3112	1.2971	1.2846	1.2734	1.2534	1.2362	1.2213	1.2081	1.1966	1.1857	1.1756	1.1666

a - Line under number(s) indicates onset of T_m.

Table VI

Specific Volume (cc/g) of High Molecular Weight Linear Polyethylene

P,bar t,°C	1	100	200	300	400	600	800	1000	1200	1400	1600	1800	2000
18.7	1.0783	1.0748	1.0714	1.0682	1.0650	1.0590	1.0535	1.0482	1.0435	1.0382	1.0339	1.0300	1.0262
33.4	1.0870	1.0832	1.0797	1.0763	1.0730	1.0664	1.0605	1.0551	1.0499	1.0447	1.0402	1.0357	1.0316
44.0	1.0933	1.0893	1.0855	1.0818	1.0783	1.0716	1.0653	1.0594	1.0537	1.0484	1.0438	1.0393	1.0349
56.8	1.1016	1.0973	1.0931	1.0891	1.0852	1.0780	1.0714	1.0652	1.0598	1.0542	1.0490	1.0441	1.0397
68.8	1.1108	1.1060	1.1014	1.0970	1.0928	1.0849	1.0780	1.0715	1.0654	1.0596	1.0544	1.0493	1.0445
79.2	1.1200	1.1147	1.1096	1.1047	1.1004	1.0919	1.0845	1.0773	1.0704	1.0644	1.0588	1.0534	1.0480
91.5	1.1326	1.1268	1.1213	1.1160	1.1110	1.1020	1.0933	1.0859	1.0783	1.0722	1.0663	1.0607	1.0554
103.4	1.1470	1.1405	1.1342	1.1284	1.1228	1.1126	1.1037	1.0951	1.0877	1.0812	1.0749	1.0689	1.0632
113.4	1.1620	1.1544	1.1472	1.1406	1.1344	1.1229	1.1130	1.1036	1.0954	1.0888	1.0825	1.0764	1.0710
124.5	1.1900	1.1795	1.1700	1.1611	1.1530	1.1393	1.1272	1.1169	1.1080	1.1002	1.0931	1.0863	1.0802
136.7	1.2737	1.2621	1.2516	1.1860[a]	1.1649	1.1394	1.1217	1.1094	1.0982	1.0897	1.0817	1.0745	1.0679
147.2	1.2856	1.2735	1.2625	1.2525	1.2433	1.2269	1.1445	1.1257	1.1110	1.0990	1.0900	1.0823	1.0751
157.5	1.2970	1.2841	1.2726	1.2619	1.2523	1.2350	1.2200	1.2068	1.1323	1.1155	1.1023	1.0923	1.0840
167.9	1.3084	1.2951	1.2829	1.2721	1.2622	1.2444	1.2291	1.2155	1.2033	1.1922	1.1273	1.1135	1.1013
178.3	1.3204	1.3063	1.2937	1.2824	1.2719	1.2536	1.2378	1.2238	1.2114	1.2007	1.1904	1.1812	1.1197
187.8	1.3306	1.3156	1.3022	1.2902	1.2792	1.2603	1.2439	1.2294	1.2168	1.2049	1.1941	1.1845	1.1759
199.5	1.3435	1.3278	1.3138	1.3013	1.2899	1.2701	1.2533	1.2385	1.2250	1.2132	1.2023	1.1922	1.1832

a - Line under number(s) indicates onset of T_m.

Table VII
Coefficients of Polynomials $V = \Sigma_{i=0}^{3} a_i t^i$ at Atmospheric Pressure[a]

Polymer	Temp range, deg C	a_0	$a_1 \times 10^4$	$a_2 \times 10^6$	$a_3 \times 10^{10}$
PnBMA	25–200	0.9341	5.5254	6.5803	1.5691
PCHMA	110–200	0.8793	4.0504	0.7774	−7.7534
PMMA	110–160	0.8254	2.8383	0.7792	0.0
PCHMA	18.6–84.5	0.9042	2.1978	0.0580	0.0
PMMA	67.7–100	0.8394	1.8365	0.4049	0.0
PMMA	17.2–56.8	0.8417	1.3711	0.5765	0.0

[a] Maximum error of fit less than 0.1% in V.

Table VIII
Thermal Expansion at T_g (P = 1 atm) for PnBMA, PMMA, and PCHMA from Different Sources

Polymer	Ref	T_g, deg C	$\alpha_1 \times 10^4$, deg C^{-1}	$\alpha_g \times 10^4$, deg C^{-1}
PnBMA	8	20	6.44	4.01
	9	18	6.00	4.44
	This work	20	6.05	4.36
PMMA	8	105	5.29	2.47
	9	103	4.80	2.25
	14	100	5.19	2.75
	This work	105	5.30	2.95
PCHMA	13	107	5.91	2.93
	This work	107	5.91	2.53

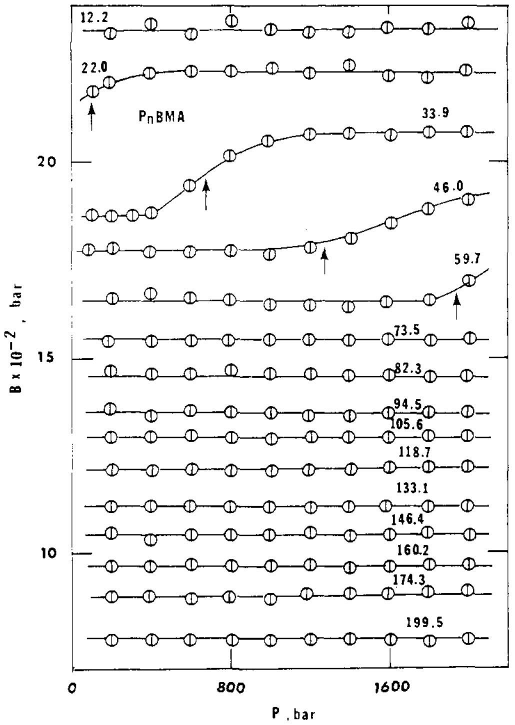

Figure 1. Tait parameter B of PnBMA as a function of pressure at a series of temperatures above and below T_g. Arrows indicate transition points.

Table IX
Coefficients in Equation 2

Polymer	Temp range, deg C	B_0, bar	$B_1 \times 10^3$, deg C^{-1}
PnBMA, g	12.2–34	2509	5.580
l	34–200	2267	5.344
PCHMA, g	18.6–74	3762	2.983
l	122.7–200	2952	5.220
PMMA, g	17.2–91	3564	3.229
l	113.5–160	2875	4.146

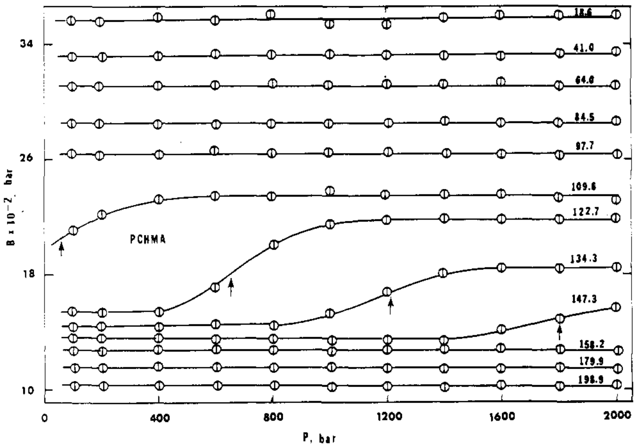

Figure 2. Tait parameter B of PCHMA as a function of pressure at a series of temperatures above and below T_g. Arrows indicate transition points.

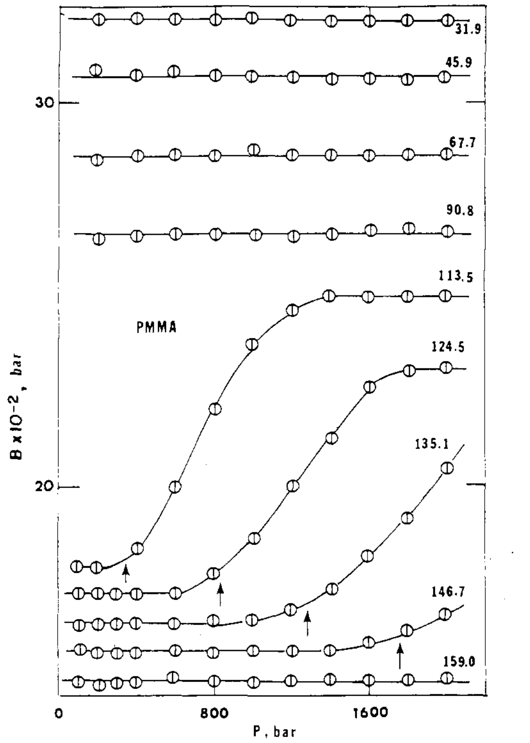

Figure 3. Tait parameter B of PMMA as a function of pressure at a series of temperatures above and below T_g. Arrows indicate transition points.

2. **Polyethylenes.** Our analysis follows the preceding pattern, except for the element of crystallinity present here. The ratios V_T/V_{20} at atmospheric pressure are depicted in Figure 4 for our polymers and the high and low density samples of Hellwege, *et al.*[6] The former is a Marlex polymer and appears to be similar to the linear standard sample, judging from its density (0.9726 g/cm^3). The latter has a lower density (0.9183 g/cm^3) than its counterpart. Below the melting range, the results are close for the two LPE's, in accord with their room-temperature densities. Above 175°, however, our densities are significantly lower. The differences between the two crystalline BPE's are in

Table X
Coefficients for VT Equations for Polyethylenes[a] (Atmospheric Pressure)

Polymer	T_m	a_0	$a_1 \times 10^3$	$a_2 \times 10^6$	V_0	$\alpha_1 \times 10^4$, deg K^{-1}	Range
HMLPE	403	1.4098	−2.6322	5.1421	0.8992	8.50_2	292–386 413–473
LPE	403	1.2556	−1.7743	3.3368	0.9172	7.80_6	293–388 415–473
BPE	386	1.8778	−5.7855	10.3720	0.9399	7.34_1	292–371 398–473

[a] Maximum error of fit less than 0.1% in specific volume.

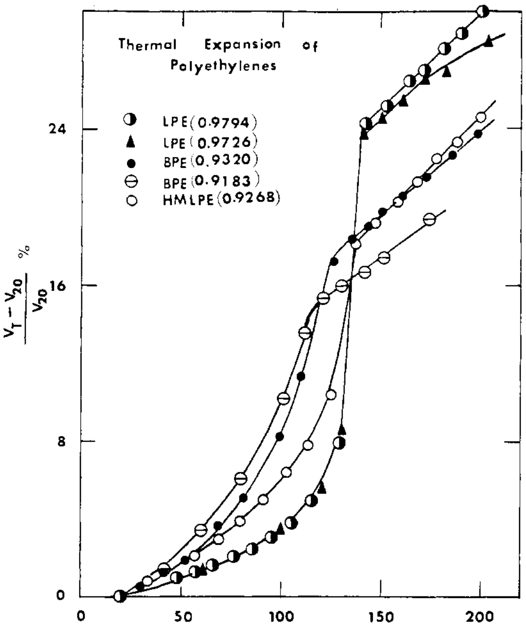

Figure 4. Volume change of polyethylenes at atmospheric pressure as a function of temperature including melting range.

accord with those in the degree of crystallinity. In the melt a more appreciable difference having an opposite sign is observed. The density of HMLPE is close to that of the BPE standard sample at room temperature. In the melt the differences between the BPE's and LPE's are comparatively minor, as is illustrated in Tables IV–VI. The breadth of the melting range of HMLPE is intermediate between that of the linear low molecular weight and the branched species.

The results can be fitted to second-order polynomials in the crystalline region, whereas we find constant thermal expansivities in the melt, thus

$$\begin{aligned} V &= a_0 + a_1 T + a_2 T^2 \qquad T < T_m \\ V &= V_0 \exp(\alpha_1 T) \qquad T > T_m \end{aligned} \tag{3}$$

with numerical values given in Table X. The expansivity α_1 of BPE agrees with values reported by previous investigators,[19] but these authors observe no difference between high and low density specimens, in contrast to our findings. The HMLPE has a significantly higher thermal expansivity than its low molecular weight counterpart. Whether this reflects the influence of temperature dependent entanglements, expected at such high molecular weights ($>5 \times 10^6$), or of a comparatively reduced short-range order, is uncertain. We should mention, however, that Wilson,[14] using a different volume dilatometer,[13] found α_1 to vary from 7.82 to 7.99×10^{-4} between 150 and 200°, the range in question, which is close to the value quoted here for LPE.

We continue with the pressure data in the melt. As indicated recently,[17] a previous analysis of Hellwege, *et al.*'s, experiments in terms of the Tait equation[20] contained an oversight. This does not affect qualitative conclusions for the amorphous polymers, but does so for the polyethylene melts. Equation 1 may again be shown to represent the isotherms satisfactorily.[15] Equation 2 can be fitted to the averaged experimental B's with a maximum deviation of 1.5%.[15] The coefficients B_0 and B_1 are listed in Table XI, which also contains the corrected values for Hellwege, *et al.*'s,[6] polymers; see the second and last rows. The previous suggestion of a pressure induced ordering effect, which was based on the apparent dependence of the Tait parameter B on pressure,[20] must be abandoned. We note the closeness of the B_1 coefficients with the exception of HMLPE. However, all the compressibilities are very similar, since the maximum difference between the B's of the five polymers at 175° amounts to only 4.3%.

Equations of state for semicrystalline polymers have been developed by several authors.[21–24] These are either of a correlative nature or attempt to derive properties of the amorphous fraction from characteristics of the crystal. We do not propose here to apply these results to our data. Our main theoretical concerns are the melt and the glass and we are looking here only for analytical representations of experimental data. In the light of the success of eq 1, it would be of interest to explore its performance below the melting range and the applicability of the Tait relation to the crystal. The proper starting point would be the usual relation

$$V(P, T) = xV_c(P, T) + (1 - x)V_a(P, T) \tag{4}$$

with x the degree of crystallinity, V_a the specific volume of the amorphous fraction extrapolated from the melt, and V_c that of the crystal. Appropriate Tait expressions for the two phases may be written, which involve temperature extrapolations of $V_a(0,T)$ and $B_a(T)$. Unfortunately the results are very sensitive to the numerical values assigned to these quantities. Particularly the use of the relationships for $V_a(0,T)$ established in the melt is questionable and we do not pursue this approach further at this time.

Since there is practical utility to obtaining an explicit PVT expression for purposes of interpolation and comparison, we have investigated the direct application of eq 1 to the semicrystalline polymers. The detailed results are given elsewhere.[15] The parameter B turns out to increase slowly with pressure, excluding of course the transition region. A simple averaging of each isotherm yields the result

$$B = B_0 - B_1 t \tag{2a}$$

with the numerical coefficients displayed in Table XII. We note a systematic trend of B_0 with the density at 20° and a maximum deviation of 5% in LPE at 19.5°. However, B_1 varies irregularly, so that at elevated temperatures this trend no longer affects the compressibility.

Table XI
Coefficients in Equation 2

Polymer ($\rho_{20°}$)	Temp range, deg C	B_0, bar	$B_1 \times 10^3$, deg C^{-1}
LPE (0.9794)	142–200	1767	4.661
LPE (0.9726)	150–203	1738	4.558
BPE (0.9320)	130–200	1771	4.699
HMLPE (0.9268)	140–200	1683	4.292
BPE (0.9183)	130–175	1879	4.796

III. Conclusions

In the liquid and in the glass, the normal side chain exerts a greater influence in enhancing the thermal expansivity at T_g than the cyclohexyl ring. Similarly, the temperature coefficients of the compressibility in liquid PnBMA and to a lesser degree PCHMA exceed that of PMMA. In the glassy state, a reversal between PCHMA and PMMA occurs. Whereas these coefficients are usually found to be larger in the liquid than in the glass, the two values are almost identical in PnBMA, which may be taken as a manifestation of a relative freedom of the side chain. Regardless of these differences, the varying compressibilities and locations of the glass temperature, the differences between the pressure coefficients dT_g/dP are minor, with the smallest value resulting for PnBMA.

In the melt we observe an increase of the thermal expansivity in the series BPE, LPE, HMLPE with the larger difference between the latter two. This may be caused by a temperature-dependent contribution of entanglements. Only small differences between the compressibilities exist, although HMLPE is distinguished by a lower temperature coefficient of the compressibility at low pressure.

The use of the Tait equation for the semicrystalline system cannot yield more than a rough average between crystalline and amorphous contributions. The compressibility extrapolated to 0° seems to increase with decreasing density of the five polyethylenes in Table XII, which is reasonable. However, as the temperature increases, a systematic trend is obliterated. At 100°, HMLPE still has the largest compressibility of the LPE's, but both BPE's are considerably more compressible.

Acknowledgment. This research was supported by the National Science Foundation under Grant GH-36124.

Table XII
Coefficients in Equation 2a

Polymer ($\rho_{20°}$)	Temp range, deg C	B_0, bar	B_1, deg C^{-1}
LPE (0.9794)	19.5–115	4758	22.7017
LPE (0.9726)	19.4–120	4479	21.7195
BPE (0.9320)	19.1–98	3233	22.6510
HMLPE (0.9268)	18.7–113	3051	14.7650
BPE (0.9183)	20–101	2758	17.4424

Miniprint Material Available. Full-sized photocopies of the miniprinted material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the miniprinted and supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for $4.00 for photocopy or $2.50 for microfiche, referring to code number *MACRO*-75-206.

References and Notes

(1) A. Quach and R. Simha, *J. Appl. Phys.*, **42**, 4592 (1971); *Macromolecules*, **4**, 268 (1971).
(2) A. Quach, P. S. Wilson, and R. Simha, *J. Macromol. Sci., Phys.*, **9**, 533 (1974).
(3) J. E. McKinney and M. Goldstein, *J. Res. Nat. Bur. Stand., Sect. A*, **78**, 331 (1974).
(4) J. E. McKinney and R. Simha, *Macromolecules*, **7**, 894 (1974).
(5) R. Simha and T. Somcynsky, *Macromolecules*, **2**, 342 (1969).
(6) K. H. Hellwege, W. Knappe, and P. Lehmann, *Kolloid-Z. Z. Polym.*, **183**, 110 (1962).
(7) P. Heydemann and H. D. Guicking, *Kolloid-Z. Z. Polym.*, **193**, 16 (1963).
(8) S. S. Rogers and L. Mandelkern, *J. Phys. Chem.*, **61**, 985 (1957).
(9) R. A. Haldon and R. Simha, *J. Appl. Phys.*, **39**, 1890 (1968).
(10) J. C. Wittman and A. J. Kovacs, *J. Polym. Sci., Part C*, **16**, 4443 (1969).
(11) J. Heijboer, *J. Polym. Sci., Part C*, **16**, 3413 (1968).
(12) J. M. Roe and R. Simha, *Int. J. Polym. Mater.*, **3**, 193 (1974).
(13) P. S. Wilson and R. Simha, *Macromolecules* **6**, 902 (1973).
(14) P. S. Wilson, Ph.D. Thesis, Case Western Reserve University, 1973.
(15) O. Olabisi, Ph.D. Thesis, Case Western Reserve University, 1973.
(16) G. Gee, *Polymer*, **7**, 177 (1966).
(17) R. Simha, P. S. Wilson, and O. Olabisi, *Kolloid-Z. Z. Polym.*, **251**, 402 (1973).
(18) W. Shishkin, *Sov. Phys.-Solid State*, **2**, 322 (1960).
(19) For example, M. J. Gubler and A. J. Kovacs, *J. Polym. Sci.*, **34**, 551 (1959).
(20) V. S. Nanda and R. Simha, *J. Chem. Phys.*, **41**, 3870 (1964).
(21) R. E. Barker, Jr., *J. Appl. Phys.*, **38**, 4234 (1967).
(22) D. J. Pastine, *J. Chem. Phys.*, **49**, 3012 (1968).
(23) Y. Wada, A. Itani, T. Nishi, and S. Nagai, *J. Polym. Sci., Part A*, **7**, 201 (1969).
(24) M. G. Broadhurst and F. I. Mopsik, *J. Chem. Phys.*, **52**, 3634 (1970).