isopropyl alcohol to *p*-(*n*-butyl methacrylate) and poly(propylene oxide) in carbon tetrachloride. They concluded that at the low polymer concentrations used, hydrogen bonding between isoproyl alcohol and these polymers occurs to about the same extent as it would in solutions of corresponding monomer molecules. Higher polymer concentrations might reduce the number of hydrogen bonds formed due to coiling effects. Further quantitative spectrosopic studies of hydrogen bonding between polar additives and polymers in solution should provide considerable insight into the nature of interactions between these species. If coupled with adsorption experiments, such data may be a particularly fruitful means of establishing the influence of various additives on polymer adsorption.

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# Thermal Expansivities of Polymers at Cryogenic Temperatures[1]

**Robert A. Haldon[2] and Robert Simha[3]**

*Department of Chemistry, University of Southern California, Los Angeles, California 90007 and Division of Polymer Science, Case Western Reserve University, Cleveland, Ohio 44106.*

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ABSTRACT: In an extension of earlier work the linear expansion coefficients between about 20 and 120°K have been measured for ten poly(alkyl methacrylates) (PAMA), poly-4-methylpentene-1 (P4MP1), and a 49:51 ethylene–propylene (E–P) copolymer. The methacrylates exhibit an increasing expansion coefficient up to $\sim$40°K, except for PMMA, followed by a plateau and a relaxation region located between 80 and 110°K. The magnitude of this transition increases with flexibility in the alkyl side group. The existence of this region is consistent with both dynamic mechanical and proton spin lattice relaxation data for the higher members of the series. P4MP1 behaves similarly to the methacrylates, but with larger expansion coefficients. The E–P copolymer exhibits a relaxation around 56°K, lower than that ascribed to supposedly similar molecular motions in alkyl side chains. There are indications of possible further transitions in the higher methacrylates and P4MP1 below the temperature range studied.

We have recently carried out thermal expansion measurements for polyalkyl methacrylates between approximately 90°K and the glass transition temperature which show the existence of multiple transitions or relaxations in the glass.[4] With increasing length of the side chain, these could not be resolved by means of mechanical low frequency measurements. The results moreover suggested the presence of a transition around the lower limit of this temperature range for polymers with a fairly flexible side group. Such a relaxation would be consistent with audiofrequency dynamic measurements for poly(*n*-alkyl methacrylates)[5,6] in which a transition is observed at about 120°K, and also for similar systems such as poly(alkyl acrylates),[7] poly(alkyl vinyl ethers),[7] and poly-α-olefins,[8] all possessing flexible side chains.

In the present work, the temperature range has been extended to liquid helium temperatures for a series of poly(*n*-alkyl methacrylates), the isomers of poly(butyl methacrylate), poly-4-methylpentene-1, and a random copolymer of ethylene and propylene.

## Experimental Section

**Materials.** The ten poly(alkyl methacrylates) (PAMA) studied are the same samples used in ref 4. Poly-4-methylpentene-1 (P4MP1) was kindly supplied by ICI Plastics Division. It had a melt flow index of 2 (260°/5 kg), representing a fairly high molecular weight. The ethylene–propylene copolymer (E–P) was kindly furnished by Drs. Kontos and Nudenberg of the U. S. Rubber Co. It contains 49% ethylene with 2.6% ethylene and 1.6% propylene crystallinity and intrinsic viscosity of 3.34 at 135° in tetralin. The latter two polymers were molded to shape at room temperature and a pressure of 5000 psi. Neither polymer appeared altered on this treatment as evidenced by differential scanning calorimetry.

**Procedures.** The linear expansion coefficients were measured in a recording quartz dilatometer similar to that previously described.[4] For the present temperature range, however, it was necessary to keep the sample under vacuum during a run. The sensitivity of the dilatometer was about $2 \times 10^{-4}$ in. of sample expansion per inch of recorder deflection and the recorder chart could be read to ±0.01 in. corresponding to a length change of $2 \times 10^{-6}$ in. Temperature was measured with a copper–constantan thermocouple which could be read to $\pm 10^{-3}$ mV. The thermocouple was found to be very close at both liquid nitrogen and liquid helium temperatures to values given by Powell, Bunch, and Corruccini[9] and intermediate values were taken from their

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(2) Research Department, ICI Fibres Ltd., Pontypool, Monmouthshire, U. K.

(3) Senior Visiting Research Fellow, The University of Manchester, 1967–1968. To whom correspondence should be addressed at Case Western Reserve University.

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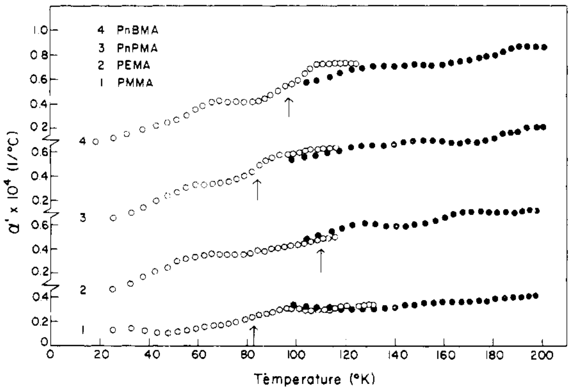

Figure 1. Linear expansion coefficient as a function of temperature for poly(methyl methacrylate), poly(ethyl methacrylate), poly(*n*-propyl methacrylate) and poly(*n*-butyl methacrylate): O, this work; ●, ref 4.

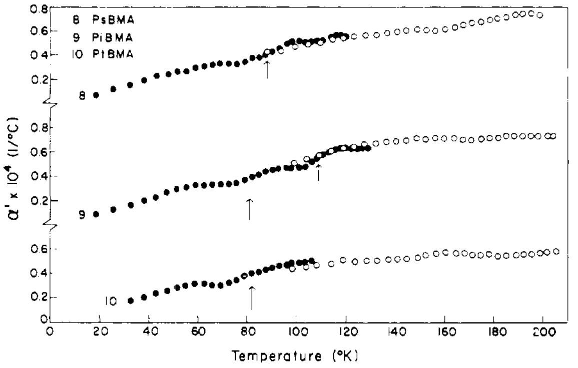

Figure 2. Linear expansion coefficient as a function of temperature for poly(*sec*-butyl methacrylate), poly(isobutyl methacrylate) and poly(*t*-butyl methacrylate): ●, this work; O, ref 4.

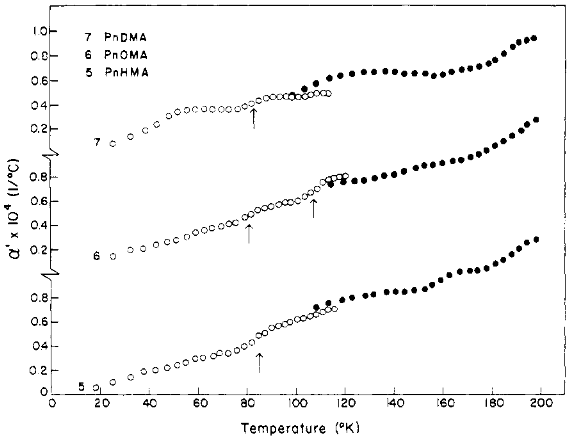

Figure 3. Linear expansion coefficient as a function of temperature for poly(*n*-hexyl methacrylate), poly(*n*-octyl methacrylate), and poly(*n*-decyl methacrylate): O, this work; ●, ref 4.

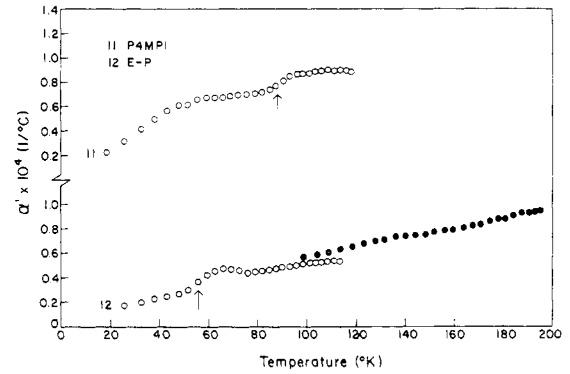

Figure 4. Linear expansion coefficient as a function of temperature for poly(4-methylpentene-1) and the random ethylene (49%)-propylene copolymer: ●, liquid nitrogen temperatures.

TABLE I

SUMMARY OF TRANSITION AND EXPANSIVITY DATA

| Polymer | Transition temp (*T*), °K | —Value × $10^4$, $deg^{-1}$— $\alpha'$ (<*T*) | $\alpha'$ (>*T*) | $\Delta\alpha'$ |
|---|---|---|---|---|
| PMMA | 83 | 0.16 | 0.33 | 0.17 |
| PEMA | 110 | 0.35 | 0.60 | 0.25 |
| PnPMA | 84 | 0.33 | 0.62 | 0.29 |
| PnBMA | 97 | 0.41 | 0.73 | 0.32 |
| PnHMA | 85 | 0.35 | 0.65 | 0.30 |
| PnOMA[a] | 81 | 0.41 | 0.58 | 0.17 |
| | 107 | 0.58 | 0.78 | 0.20 |
| PnDMA | 83 | 0.36 | 0.47 | 0.11 |
| PsBMA | 88 | 0.32 | 0.51 | 0.19 |
| PiBMA[a] | 81 | 0.33 | 0.47 | 0.14 |
| | 109 | 0.47 | 0.63 | 0.16 |
| PtBMA | 82 | 0.30 | 0.46 | 0.16 |
| P4MP1 | 88 | 0.69 | 0.89 | 0.20 |
| E-P(PPR 5317) | 56 | 0.26 | 0.45 | 0.19 |

[a] Two apparent transitions.

extensive Table 2, as were values for ($dE/dT$) necessary to compute the coefficient of linear expansion, $\alpha'$. Thermocouple scatter was greatest at the lowest temperatures and the error in the temperature interval is maximally 0.7°. Therefrom the maximum error in the expansion coefficient is about 9%.

The cryostat and aluminum block housing the sample were precooled with liquid nitrogen to 77°K and approximately 2 l. of liquid helium was required to lower the temperature to 4.2°K and leave a little in the dewar. The system was heated up at a rate of approximately 1°/min below 20°K after which a rate of ≤0.5°/min was maintained for the duration of the run.

### Results and Discussion

Thermal expansivities *vs.* temperature for the poly(alkyl methacrylates) are given in Figures 1–3 and for poly-4-methylpentene-1 and the ethylene-propylene copolymer in Figure 4. Numerical data are summarized in Table I. A feature of the graphs, apart from those of the higher methacrylates, is the overlap obtained between runs started at liquid helium and liquid nitrogen temperatures. The liquid nitrogen results shown are those previously published[4] apart from that for PsBMA in the temperature range 90–150°K, where repeat runs on more carefully annealed polymer gave a somewhat lower expansion coefficient than previously obtained. Overlap is less satisfactory with the higher methacrylates and this is believed to be due to slight differences in sample thermal history between runs. We have previously demonstrated that $\alpha'$ for these polymers is critically dependent on rates of cooling.[4] For all polymers studied the length–temperature data are more scattered below ~40°K and this, coupled with the low sensitivity of the copper–constantan thermocouple in this region, makes the absolute values of $\alpha'$ somewhat more suspect. In any case, $\alpha'$ obviously increases up to ~40°K, with the exception of PMMA. After this initial increase most samples show a plateau region followed by a very obvious transition, the location of which depends on the particular polymer.

PMMA (Figure 1) has an expansion coefficient of $\sim 0.1 \times 10^{-4}$ deg$^{-1}$ between 20 and 60°K, increasing to $\sim 0.3 \times 10^{-4}$ deg$^{-1}$ over a relatively large temperature interval of about 35°, with the midpoint location at ~83°K. No other transition is obvious up to at least 200°K. PEMA, PnPMA and all the butyl isomers (Figure 2) exhibit an increase in $\alpha'$ between 20 and 50°K, followed by a plateau region. Thereafter a transition region is obvious for each polymer with its midpoint location varying between 80 and 110°K depending on the polymer. PiBMA apparently has two transitions, and this was a reproducible feature although conceivably it could represent one particularly broad transition region. PnHMA and PnOMA (Figure 3) have no horizontal plateau regions but PnHMA obviously has a relaxation at about 85°K and PnOMA apparently two, but not clear-cut. PnDMA exhibits a fairly small transition at ~83°K. The previous results,[4] combined with the current data, are suggestive of a second relaxation region around 100°K. However, the present observations in the overlap region do not provide an adequate basis for such an assignment.

There are no mechanical loss peaks in the literature corresponding to the relaxations we observe in PMMA and PEMA. Woodward[10] shows a peak at ~5°K for PMMA and 50°K for PEMA, both at a frequency of $\sim 10^4$ Hz. Sinnott[11] observed loss peaks at <4.2 and 41°K for PMMA and PEMA, respectively, at a frequency of less than 10 Hz. The dynamic results for PEMA may correspond to the initial increase of $\alpha'$ in Figure 1. Dilatometric measurements of PMMA below the present temperature range are pertinent in this connection. Moreover, proton spin lattice relaxation results show a $T_1$ minimum for PMMA[12] at ~100°K ($5 \times 10^7$ Hz) and for PEMA at ~135°K ($3.5 \times 10^7$ Hz).[13,14] The results of Hoff, Robinson, and Willbourn[5] show no transition in the 120°K region for PEMA but other similar systems do. Poly-1-butene (PB),[8] poly(ethyl acrylate) (PEA),[7] and poly(ethyl vinyl ether) (PEVE)[7] all exhibit a $\gamma$-transition, in the latter two cases at slightly higher temperatures than the corresponding transition for the *n*-butyl polymer, similar to the relative order in Table I.

The observed transitions in PnPMA, PnBMA, and PsBMA all have a corresponding mechanical relaxation.[5,6] Damping maxima for the first two polymers at 1 Hz have been located at about 86 and 93°K, respectively,[15] *i.e.*, at lower temperatures than would be anticipated from our results (Table I). In PiBMA we separate two, with the upper one about 20° higher than the transition in PsBMA. We note that a similar difference was observed by Shen and coworkers[6] in dynamic measurements on the same systems.

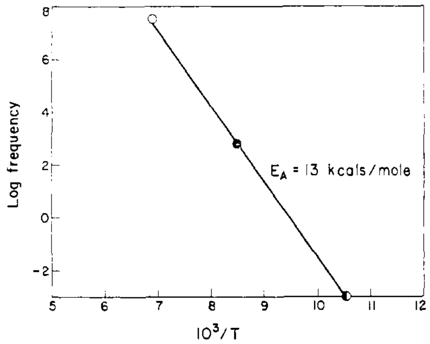

Figure 5. Arrhenius plot for the poly(*n*-butyl methacrylate) transition. Points indicate in descending order ref 13, 6, and this work.

The molecular motion associated with this relaxation has been attributed to reorientations of the alkyl side group[5] and is probably similar to the proposed crankshaft mechanism of the polyethylene $\gamma$-transition[16] for the higher members of the series.[17,18] For PMMA the nmr relaxation is associated with motion of the ester methyl group.[12] These interpretations are consistent with our observation, Table I, that the magnitude of the motion, as measured by the change in expansion coefficient, $\Delta\alpha'$, increases with increasing side chain length, at least to *n*-butyl, as more volume is required for reorientation. Insofar as $\alpha'$ nearly doubles at this transition, the independent motion of the side chain must be fairly vigorous. When the side chains get very long the motions become more complicated[12] and perhaps more diffuse, explaining the less clear behavior in PnOMA. We have suggested previously[4] that the lower expansion coefficients observed in PnDMA are due to side chain ordering, and the magnitude of the transition observed at ~83°K is indeed less than for the lower members of the series. In the butyl isomer series, $\Delta\alpha'$ appears to decrease with increasing side group bulk as the alkyl group requires less volume for reorientation.

Our transition for PnBMA may be compared with both the spin lattice relaxation[13] and the audiofrequency loss peak.[6] Figure 5, a plot of log frequency vs. $1/T$, combines dynamic and dilatometric measurements, using an effective frequency of $10^{-3}$ Hz for the latter.[19] A straight line over 10 decades and an apparent activation energy of 13 kcal/mol are obtained. Although not to be taken too literally, this value is considerably larger than the 3.4–4.5 noted by Hoff, *et al.*,[5] and Shen, *et al.*,[5] over a more limited frequency range. Heijboer's[15] point for the ordinate value of zero would fall to the right of the line.

Because of its similar structure and by analogy with dynamic results,[8] P4MP1 would be expected to exhibit

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the transition observed at $\sim$88 °K (Figure 4). It is also interesting that the initial slope of $\alpha'$ is steeper than for the methacrylates, with the expansion coefficients somewhat larger. We recall in this connection that Crissman, Sauer, and Woodward[20] observed a fairly large mechanical relaxation at $\sim$24 °K (10 Hz) and much more pronounced than for PiBMA with its similar side group.

The results for the E–P copolymer (Figure 4) above 100 °K are similar to those of Zakin, *et al.*[21] The decrease in $\alpha$ between 190 and 90 °K could be indicative of an extremely broad relaxation region. It is also noteworthy that a slight plateau region appears around 140 °K, similar to that in Figure 9 of ref 21 at approximately 133 °K. On reducing the temperature further, the copolymer should exhibit an analogous relaxation, if the mechanism is indeed similar to that postulated for the polyethylene $\gamma$-transition. The observed transition lies considerably lower, $\sim$56 °K, and this may be related to the absence of crystallinity. Finally it may be worthy of note that infrared measurements of Shen and coworkers[22] indicate freezing out of $-CH_2-$ vibrations in polyethylene below 100 °K.

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# Matrix Method for Determining the Dimensions of Branched Random-Flight Chains[1]

**W. C. Forsman**

*The School of Chemical Engineering and The Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania 19104.*

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ABSTRACT: A new method is presented for mathematically characterizing branching in random-flight chains. The method is then used to calculate mean-square radii of gyration for a number of examples. For every mode of branching there can be defined a matrix, $[D]$, with eigenvalues that completely define the distribution of radii of gyration. The parameter $g$, the ratio of the mean-square radius of gyration of the branched chain to that of a linear chain with the same number of statistical segments $t$, is given by $g = (6/t^3)$ trace $[D]$. When applied to cruciform, star, and uniformly branched molecules the method gives values for $g$ in agreement with those obtained previously by other investigators using entirely different mathematics.

Because of the effect of branching on many of the physical properties of polymers, there has been a continuing interest in the configurational statistics of branched-chain molecules.[2–8] We present here a new method of mathematically characterizing chain branching that is completely general and requires only matrix algebra.

It will be shown that a matrix, $[D]$, is associated with any random-flight chain, whether linear or with any mode of branching, and that this matrix determines many of the important statistical features of the chain. In particular, we will show that the distribution of radii of gyration is determined by its eigenvalues and that the mean-square radius of gyration is simply related to trace $[D]$. Mean-square radii for the examples treated in this paper are in agreement with those of previous investigators.

It is always possible that the matrix method may give reasonable closed-form expressions for chain dimensions for classes of branched chains other than those reported here. Of more interest, however, is that this new approach is especially suitable for digital computer calculations and could be applied to branched chains far more complex than those usually treated by analytical methods. Furthermore, since so much structural information is contained in $[D]$, it is tempting to imagine that this matrix might also be directly related to various types of chain behavior. For example, we have established a simple relationship between $[D]$ and chain dynamics that will be presented in a subsequent publication.

Since the calculations presented in this paper are based on random-flight statistics, the results are assumed to apply to real polymer molecules at the Flory $\Theta$ temperature. We also assume, as has been done previously,[4] that this work could be extended to include polymer–solvent interactions.

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