

Low-Temperature Thermal Expansivities of Polyethylene, Polypropylene, Mixtures of Polyethylene and Polypropylene, and Polystyrene

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Synopsis

Length-temperature measurements on a series of polymer blends over the whole range of composition from pure polyethylene to pure polypropylene and one set of determinations on a 50:50 copolymer and on polystyrene are evaluated. The total crystallinity of the samples did not exceed 54%. The experimental procedure utilized a linear variable differential transformer without the use of a confining fluid, and the temperature ranged from about +20 to -185°C. A least-square numerical differentiation procedure based on moving arcs is applied to yield directly the coefficients of thermal expansion as a function of temperature. The linear voltage differential transformer (LVDT) technique can detect transitions in which the change in thermal expansion coefficients is less than $10^{-5}^{\circ}\text{C.}^{-1}$. In polypropylene as well as the blends, the principal glass transition is clearly seen in the range observed by others, namely at about -9 to -14°C. Its location varies only slightly with composition at polyethylene contents less than 88 mole-%. For polyethylene the transition region broadens noticeably. The results are suggestive of two transitions for $0 > T > -40^{\circ}\text{C.}$ A second transition region is observed for either pure component around -126°C. Its location varies somewhat with composition. However, our results do not indicate the appearance of an additional transition region characteristic of the mixture. The copolymer exhibits a major transition at -61°C. in good agreement with earlier workers. The thermal expansion decreases again around -150°C. In general our observations concerning transitions below T_g are consistent with dynamic results.

I. INTRODUCTION

Measurements of length-temperature curves for several polymers and mixtures of two of these were made at low temperatures. Polymers studied were polyethylene, polypropylene, their mixtures, a 50:50 copolymer, and for verification of the experimental techniques, polystyrene.

A general object of this work was to ascertain if transitions other than the main glass transition temperature exist and can be detected by means of length-temperature measurements. Thus the location and magnitude

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of the changes of the linear expansion coefficients were determined in the range of 20 to -185°C . The prior art has mainly limited itself to investigations of multiple glassy transitions by dynamic methods.^{1,2}

More specific objectives of this study were: (1) to compare the location and magnitude of any transitions noted in pure polyethylene and pure polypropylene with those found in their mixtures and copolymer, including the possibility of transitions not found in either pure polymer; (2) to investigate practical limitations of length-temperature measurements for finding the locations and magnitudes of glassy transitions; (3) to develop more refined methods for analyzing the experimental data; (4) to compare the locations of transitions as obtained by means of length-temperature measurements with reported results obtained by using other techniques.

II. EXPERIMENTAL

Materials

The polymer samples studied are described in Tables I and II. Additional details on their composition are given in reference 3.

TABLE I
Description of Systems Studied

Sample	Run number	Polymer
C	3	Polystyrene ^a
D	4, 5 ^b	Polypropylene (See Table II)
E, F, G H, I	6-11 ^{b,c}	Mixtures of polypropylene studied in runs 4 and 5 with polyethylene of run 12 (See Table II)
J	12 ^b	Polyethylene (See Table II)
K	13 ^b	Noncrystalline random copolymer of ethylene and propylene (See Table II)
L	14 ^d	Polyethylene test sample prepared by machining without heating or annealing of polymer
M	15 ^d	Same polyethylene polymer as run 14, but test sample prepared by casting

^a Prepared at the National Bureau of Standards, Sample 706, atactic, (with broad molecular weight distribution).

^b Prepared by Dr. E. G. Kontos, Naugatuck Chemical Company.

^c All mixture samples were prepared from the polyethylene (Sample J) and polypropylene (Sample D) by Dr. E. G. Kontos. The procedure consisted of coagulation in a 50:50 mixture of methanol and isopropanol, containing a small amount of stabilizer, and drying under vacuum for 12 hr. at 65°C .

^d Prepared by Union Carbide Corporation.

TABLE II
 Characteristics of Polyethylene-Polypropylene Systems Studied

Run number	Polymer designation	Polymer	Molar composition ^a		Crystallinity % by x-ray ^a		Density at 25°C., g./ml. ^a
			PP, %	PE, %	PP, %	PE, %	
4,5	D	Polypropylene	100	0	18	0	0.871
6	E	PP-PE mixture	91	9	16	8	0.870
7	F	PP-PE mixture	68	32	13	14	0.879
8,9	G	PP-PE mixture	52	48	12	23	0.888
10	H	PP-PE mixture	36	64	10	28	0.897
11	I	PP-PE mixture	12	88	6	42	0.906
12	J	Polyethylene	0	100	0	54	0.929
13	K	Copolymer PP-PE	50	50	0	0	0.854

^a Data obtained from Dr. Kontos, Naugatuck Chemical Company.

Procedures

The preparation of test specimens, description of the linear voltage differential transformer (LVDT) (Physical Sciences Transducer, Physical Sciences Corp., 314 East Live Oak Avenue, Arcadia, California), and the rest of the test apparatus and the test procedure are described in reference 3. Samples were about 1½ in. in length and ½ in. in diameter.

The LVDT was calibrated with a micrometer readable to 0.0001 in. LVDT output could be read to 0.001 mv. with a potentiometer. A length change of 0.0050 in. was equivalent to about 1.000 mv. for all but the polystyrene run, where the sensitivity was doubled. The average deviation from linearity was about ±3.0%.

The test runs reported here were performed by cooling the samples from room temperature to about -185°C. by the slow introduction of liquid nitrogen over a period of about 7 hr. The output length voltage from the LVDT and the thermocouple voltages were read by a potentiometer to 0.001 mv. and recorded manually to avoid any recorder error. Readings of the output of a copper-constantan thermocouple were taken at intervals of 0.050 mv. corresponding to temperature intervals of about 1.2°C. at room temperature and 2.8°C. at -185°C. About 120 data points were required to cover this range. LVDT output differences were generally greater than 0.040 mv. (0.0002 in.). In the analysis of the data, the use of alternate points (0.100 mv. thermocouple output inter-

vals) gave smoother results (see Section III). Thus, the minimum length difference used in the data analysis was 0.0004 in.

III. ANALYSIS OF DATA

Analysis Techniques

Most of the previous data of this type, i.e., length or volume versus temperature, have been analyzed by passing a series of straight lines through the data and utilizing the slopes and intersections of the lines for any further calculations.

This procedure is subject to bias, in that different observers may fit the data in different ways. Furthermore, in some cases, the slopes are nearly equal above and below the suspected transition region, and a minor change in the positioning of a line can have a major effect on the positions of its intersections as well as on its slope. This will be particularly true in the case of apparently "minor" transitions.

In order to obtain the derivative of the length-temperature data directly, a moving arc method was selected.⁴⁻⁶ This yields a more accurate measure of the changes in slopes as a function of temperature. The method is based on fitting local data points with orthogonal least-square polynomials and can be used most conveniently on any data equispaced in one variable. The arc is moved through all of the data to obtain midpoint slopes. The last few points at each end are also obtained by a similar procedure.

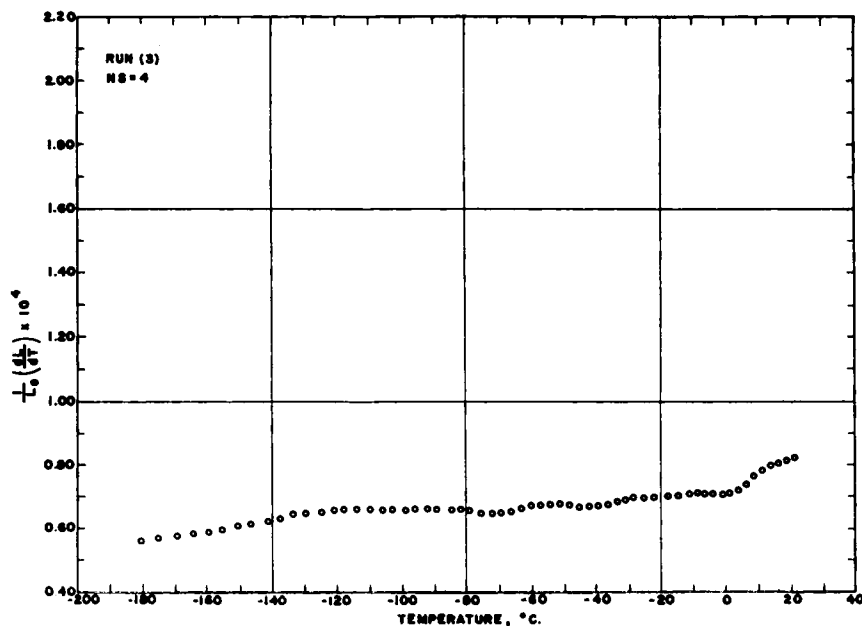


Fig. 1. Linear expansion coefficient as a function of temperature for polystyrene, sample C, run 3 (see Table I).

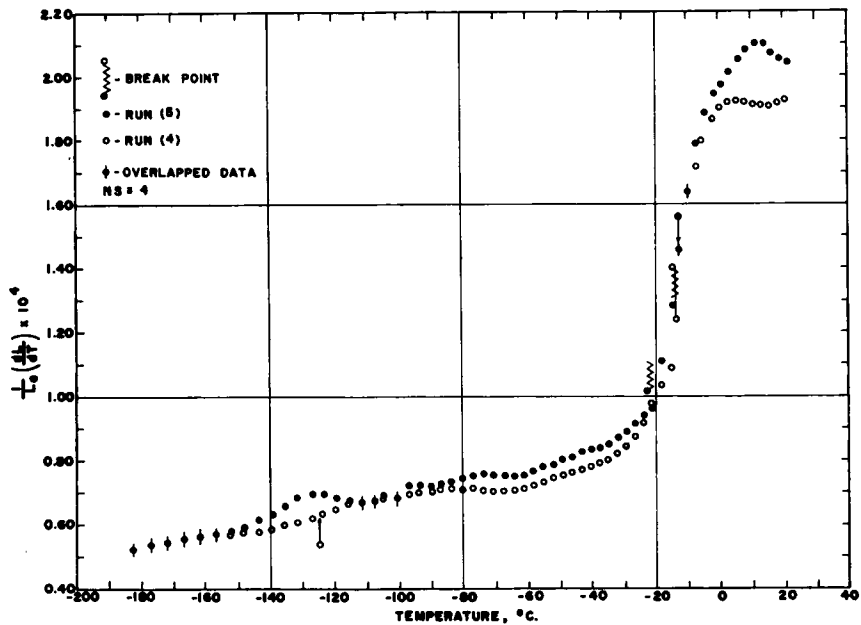


Fig. 2. Linear expansion coefficient as a function of temperature for polypropylene, sample D, runs 3 and 4 (see Tables I and II).

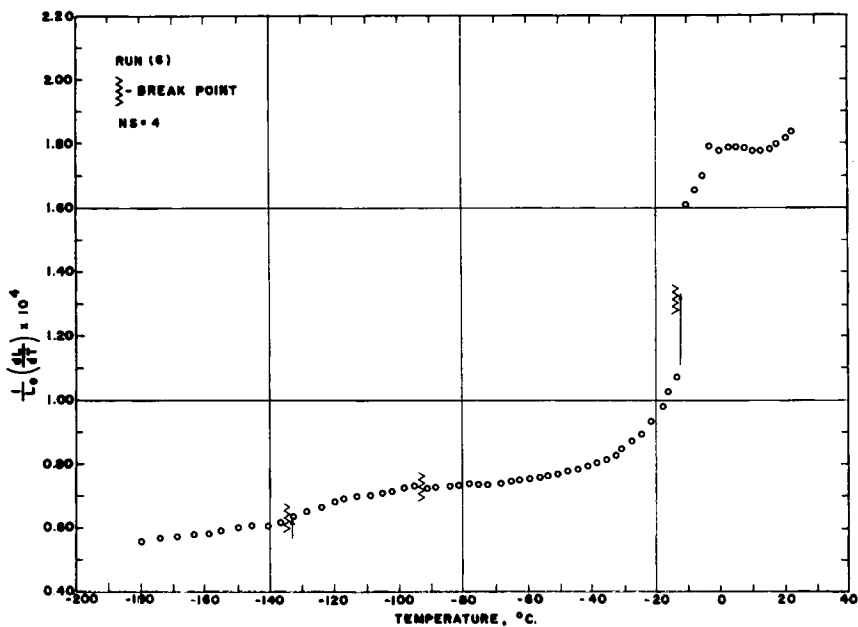


Fig. 3. Linear expansion coefficient as a function of temperature for a polyethylene (9 mole %)-polypropylene blend, sample E, run 6 (see Tables I and II).

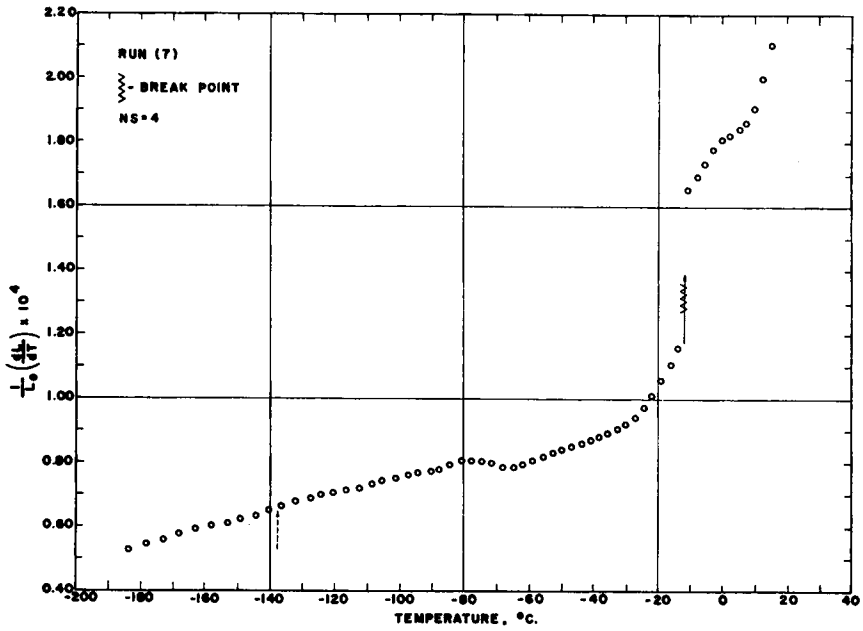


Fig. 4. Linear expansion coefficient as a function of temperature for a polyethylene (32 mole-%)-polypropylene blend, sample F, run 7 (see Tables I and II).

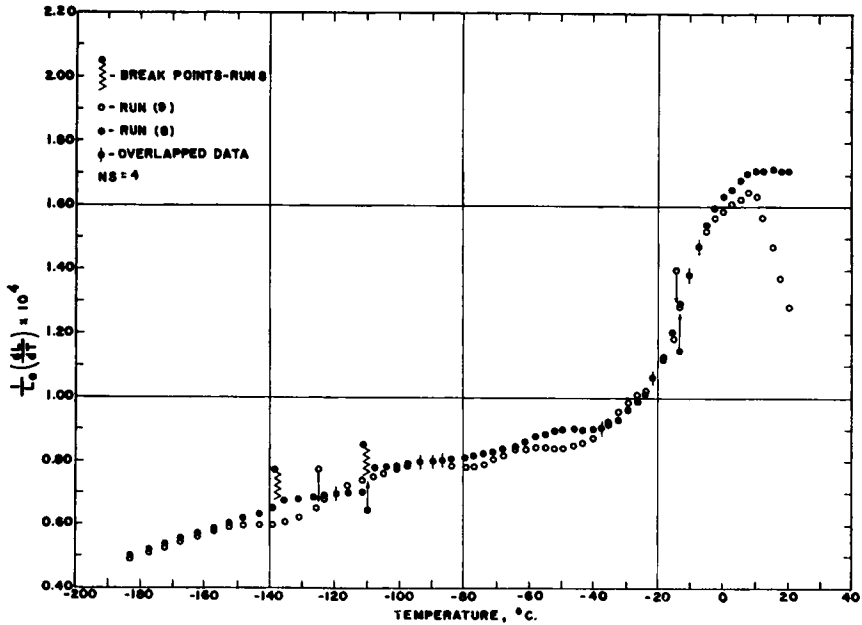


Fig. 5. Linear expansion coefficient as a function of temperature for a polyethylene (48 mole-%)-polypropylene blend, sample G, runs 8 and 9 (see Tables I and II).

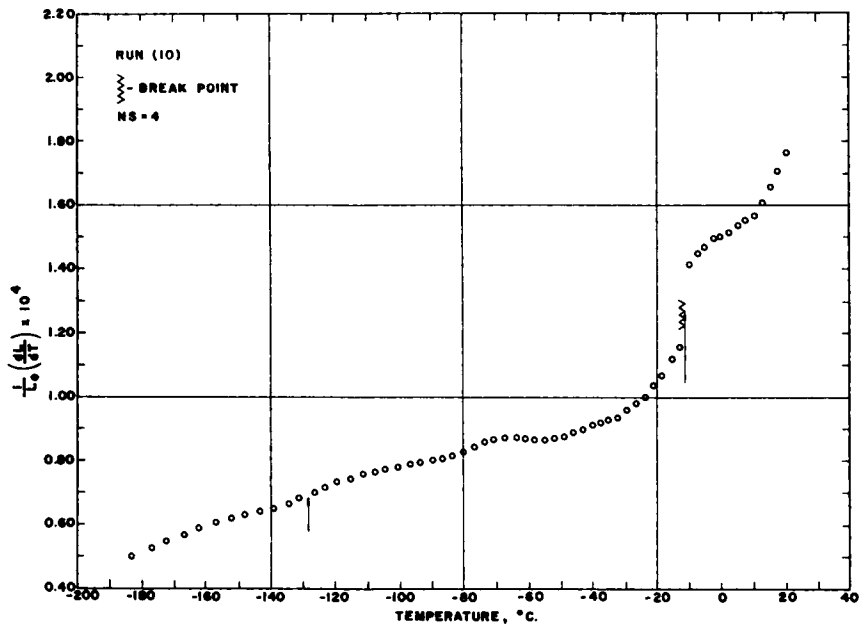


Fig. 6. Linear expansion coefficient as a function of temperature for a polyethylene (64 mole-%)-polypropylene blend, sample H, run 10 (see Tables I and II).

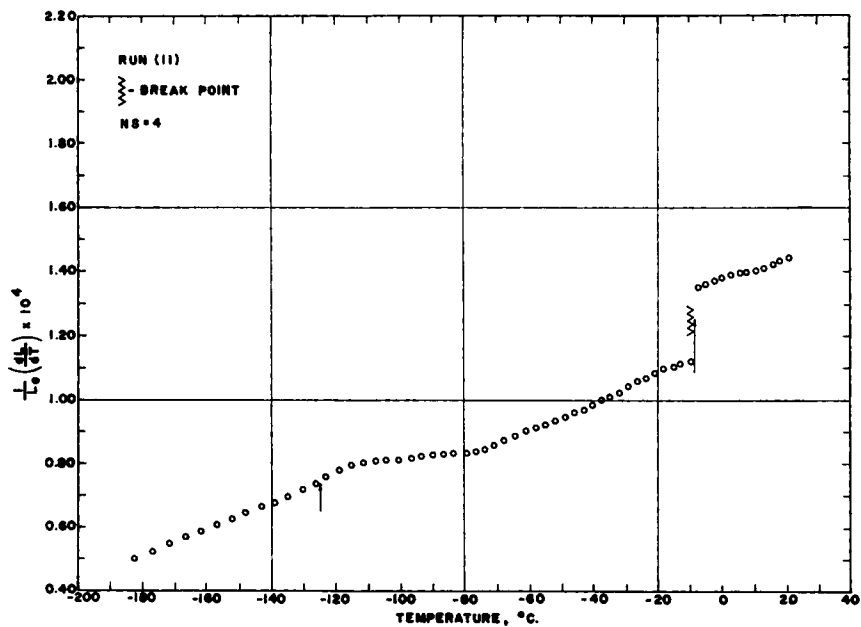


Fig. 7. Linear expansion coefficient as a function of temperature for a polyethylene (88 mole-%)-polypropylene blend, sample I, run 11 (see Tables I and II).

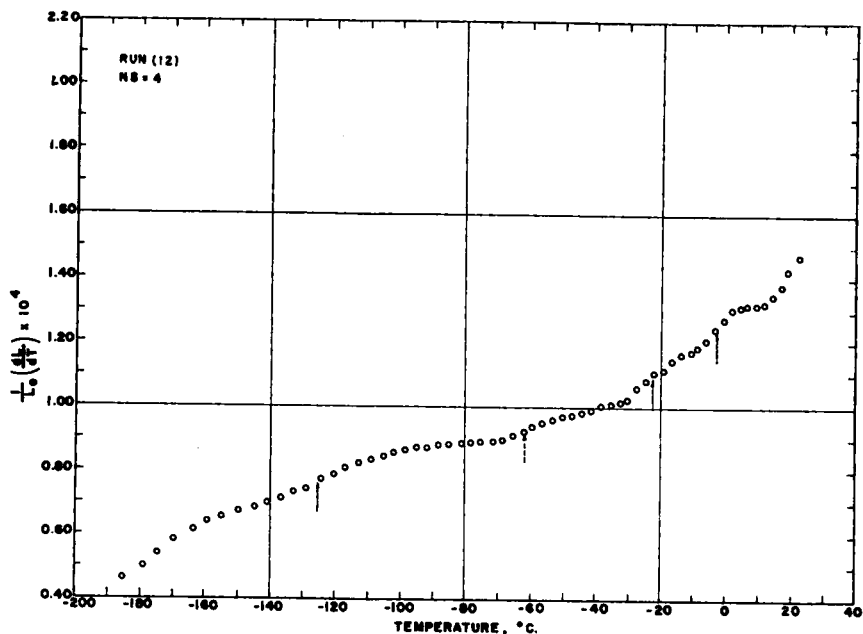


Fig. 8. Linear expansion coefficient as a function of temperature for polyethylene, sample J, run 12 (see Tables I and II).

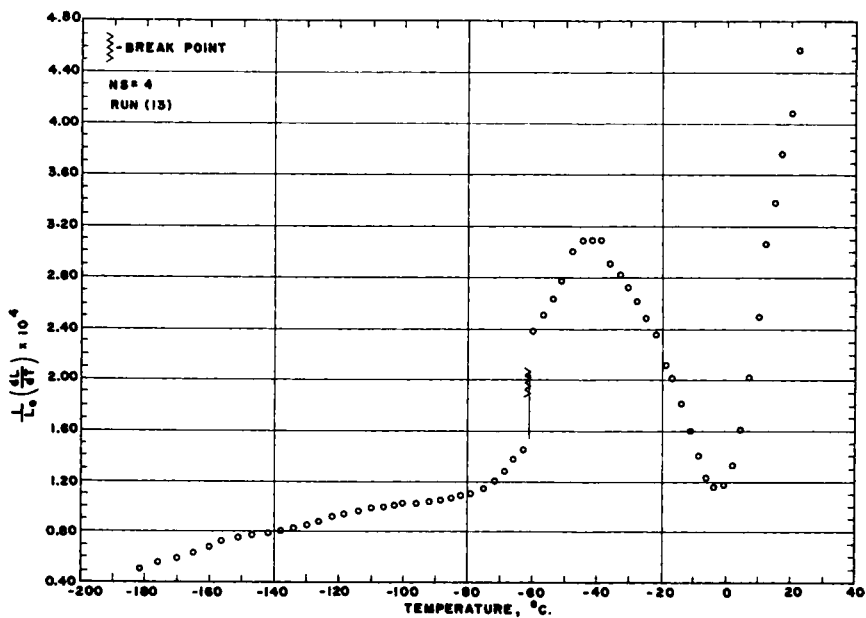


Fig. 9. Linear expansion coefficient as a function of temperature for polyethylene (50 mole-%)-polypropylene copolymer, sample K, run 13 (see Tables I and II).

Results using this procedure on the data for runs 3-15 are shown in Figures 1-10, where $(1/L_0) (dL/dT) = \alpha'$ is plotted against temperature. Tangents to the curves were drawn on both sides of discontinuous sections which appear to be transitions. The point of maximum slope was determined by graphical methods and taken as the transition temperature. The difference in the height of the two tangents at that temperature was taken as the change in α' or $\Delta\alpha'$. Vertical arrows in each figure indicate apparent transitions.

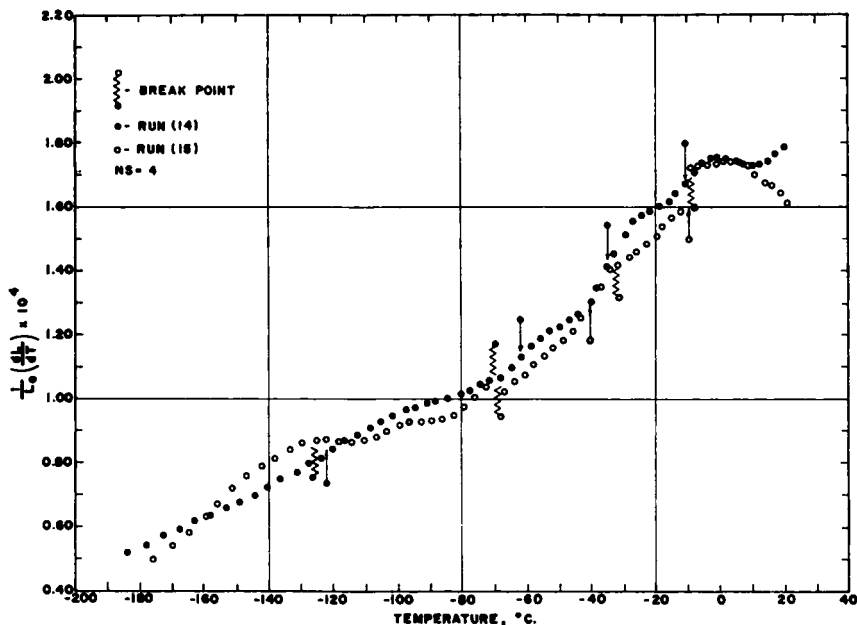


Fig. 10. Linear expansion coefficient as a function of temperature for polyethylene samples L and M, runs 14 and 15 (see Table I).

After trial procedures,⁶ seven-point parabolas were chosen for calculation of the derivatives of the raw output data. The equation for the slope of the midpoint of a least-squares parabola through seven equispaced points with ordinates y_n is:^{4,6}

$$m_4 = [1/(28\Delta x)] (3\Delta y_1 + 5\Delta y_2 + 6\Delta y_3 + 6\Delta y_4 + 5\Delta y_5 + 3\Delta y_6) \quad (1)$$

where $\Delta y_n = y_{n+1} - y_n$ and $\Delta x = x_{n+1} - x_n = \text{constant}$ for $1 \leq n \leq 6$. Estimates of the slopes of the last three points at the end of the curves are obtained from eq. (2):

$$m_i = [1/(28\Delta x)] (a\Delta y_1 + b\Delta y_2 + c\Delta y_3 + d\Delta y_4 + e\Delta y_5 + f\Delta y_6) \quad (2)$$

where m_i is the slope at the i th point, and the coefficients a , b , c , d , e , and f are listed in Table III.⁴

TABLE III
Coefficients of Equation (2) for Seven-Point Parabola

Point number <i>i</i> at which slope is evaluated	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>e</i>	<i>f</i>
1	39	45	30	6	-15	-21
2	29	35	26	10	-5	-11
3	19	25	22	14	5	-1
5	-1	5	14	22	25	19
6	-11	-5	10	26	35	29
7	-21	-15	6	30	45	39

The further the point from the center of the arc, the less reliable is the estimate of the slope at that point. Where the data are broken (see below) and, of course, at the upper and lower ends of the range, eq. (2) was used.

The raw data are output voltages of the LVDT, indicating length, versus thermocouple voltages, indicating temperature. Changes in LVDT voltage are directly proportional to changes in the sample length. It was found to be convenient in computations to use the product of this derivative and that of the thermocouple output voltage-temperature function. The relation between thermocouple output voltage and temperature is non-linear, and the derivatives were computed by using a five-point moving arc parabola method. From these derivatives the modified linear expansion coefficient α' can be computed:

$$\begin{aligned}\alpha' &= (1/L_0) (dL/dT) \\ &= \frac{C}{L_0} \frac{dE_{LVDT}}{dE_{Thermocouple}} \frac{dE_{Thermocouple}}{dT}\end{aligned}\quad (3)$$

where L is sample length, L_0 is initial sample length at room temperature (in most cases above T_g), C is a proportionality factor between the change in emf output of the LVDT and the change in sample length, and T is temperature (Centigrade).

If the true linear expansion coefficient is assumed equal to one-third the volume expansion coefficient α , then the modified coefficient α' , is nearly equal to $\alpha/3$. It differs from $\alpha/3$ only in that L_0 was not corrected for the decrease in sample length at low temperatures. Thus $\alpha' = \alpha/3$ at room temperature but may be as much as 2% lower than $\alpha/3$ at the lowest temperature (-185°C).

Although data are available in thermocouple output increments of 0.050 mv., the use of alternate points (0.100-mv. increments) smooths the output slopes, and this increment was used in all calculations.⁶

The initial computations were performed on a desk calculator. Later the procedure was programmed in Fortran II, and an IBM 1620 Model 2

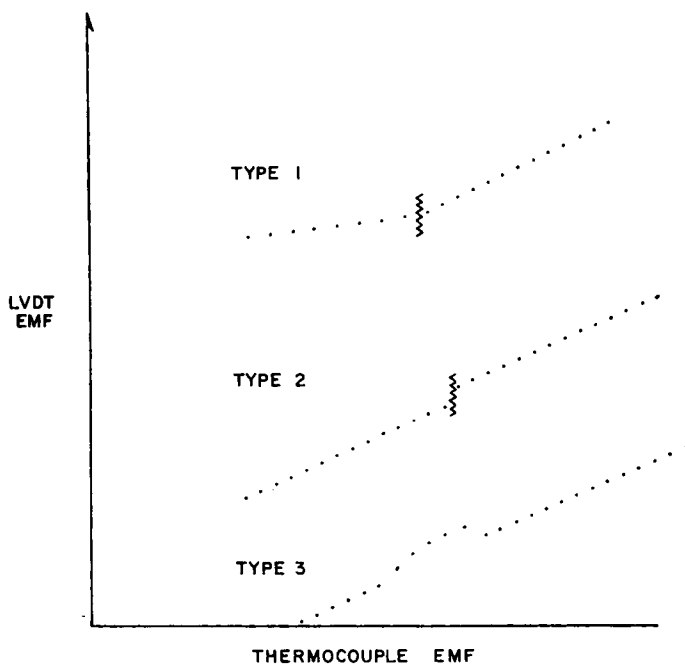


Fig. 11. Schematic representation of discontinuities in data.

computer was used. The program (CNZ001), including several sub-routines, is on file at the University of Missouri at Rolla.⁶

An examination of the plots of the raw data showed discontinuities in several runs. These were of three types and are shown in Figure 11: (1) the initial point in a new slope section of the curve indicative of a transition; (2) a series of new points parallel to the original section of the curve, the point of discontinuity indicating either a human or an instrument error; (3) a series of new points shifted from the original section of the curve which drift back several points later to rejoin the original section of the curve.

These were treated as follows: whenever the first or second cases occurred, the data points were "broken" at the point of discontinuity. Extrapolations of the preceding and succeeding data were used to estimate the values of α' on both sides of the break. In cases of the first type, the discontinuity was the start of a new level of α' values, and breaking sharpened the transition point. In cases of the second type, reductions in erratic behavior of α' versus T were obtained. All points where breaks were made are shown on the α' versus T graphs with zigzag lines. No breaks were made in cases of the third type of discontinuity in which the data drifted back.

The computer program also included a data-smoothing subroutine which allowed the raw data to be smoothed as many times as desired before sloping.⁶ This was particularly useful for smoothing discontinuities

of the third type described above and also for damping out minor wiggles in the α' versus T curves. The data in Figures 1–10 were smoothed four times and the figures are labelled NS = 4.

Reliability of Results

In virtually all runs, data above about 0°C. are erratic and inconsistent with the adjoining region. This is believed to be due to equipment instabilities which reached equilibrium after the run had progressed. Longer hold times at room temperature were not successful in eliminating the erratic results, and data above 0°C. were generally discounted in drawing conclusions about the results.

One test of the reliability of the results is a comparison of these data with dilatometric results reported earlier. Polystyrene (run 3) has a value of α' at 0°C. of about 0.7×10^{-4} which is close to $(\alpha/3) = 0.6/^\circ\text{C.} \times 10^{-4}$ below T_g , estimated from an equation given by Boyer.¹⁸ The data show the same general shape as those of Martin et al.⁷ A small change in slope occurs at about -140°C. in both sets of results.

Another test is the repeatability of results obtained on the same sample. Two examples of this are shown. Figure 2 shows repeat runs on polypropylene, sample D (runs 4 and 5), and Figure 5 shows repeat runs on sample G, a polypropylene–polyethylene mixture (runs 8 and 9).

Runs 4 and 5 show general parallelism or overlapping throughout most of the range below 0°C. except between -115 to -150°C. , where run 5 shows a hump. This was caused by a discontinuity in the data for this run, and the results for run 4 are more reliable in this region and indicate a transition at -126°C. The location of the major transition, T_g , is virtually identical in the two runs.

Runs 8 and 9 exhibit about the same level of repeatability. Again, the major transition temperature is identical on the two sets of data. Small discrepancies in the values of α' occur at lower temperatures. However, the apparent locations of the lower transition differ by about 15°C.

A third test is the internal consistency of the results. In general it was good, but discrepancies in the form of humps, dips, and discontinuities did appear. The smoothings and breaks in the numerical analysis minimized these effects but did not eliminate all of them as can be seen from the curves. We believe that, for the most part, they were caused by instabilities in the apparatus.

IV. DISCUSSION OF RESULTS

Multiple Transitions in Single-Component Systems

Plots of $(1/L_0) (dL/dT)$ versus temperature are shown in Figures 1, 2, 8, 9, and 10 for runs 3, 4, 5, 12, 13, 14, and 15, the single-component polymer samples. In most cases more than one transition appears to be present in the range of temperatures studied. Tabulations of temperatures of transitions, values of α' above the transitions, $\Delta\alpha'$ and $\Delta\alpha'/\alpha'$ are given

TABLE IV
Summary of Transition Data

Sam- ple no.	Run no.	PE, %	Amorphous, %		$T,$ °C.	$\Delta\alpha'$ $\times 10^4$	$\frac{\alpha'}{\alpha'}$ (higher) $\times 10^4$	$\frac{\Delta\alpha'}{\alpha'}$	$T,$ °C.	$\Delta\alpha'$ $\times 10^4$	$\frac{\alpha'}{\alpha'}$ (higher) $\times 10^4$	$\frac{\Delta\alpha'}{\alpha'}$
			PE	PP								
C	3	—	—	—	—	—	—	—	—	—	—	—
D	4	0	0	82	-14	1.01	1.90	0.53	-126	0.05	0.66	0.07
E	5	0	0	82	-13	1.07	2.00	0.54	Discontinuity near -120°C.			
	6	9	1	75	-12	0.90	1.70	0.53	-132	0.05	0.67	0.08
F	7	32	18	55	-11	0.79	1.70	0.47	-137 ^a	0.02	0.62	0.03
G	8	48	25	40	-13	0.77	1.65	0.45	-110	0.06	0.73	0.08
H	9	48	25	40	-14	0.62	1.50	0.41	-123	0.11	0.72	0.15
	10	64	36	26	-11	0.40	1.40	0.29	-128	0.04	0.70	0.05
I	11	88	46	6	-9	0.23	1.35	0.17	-125	0.05	0.82	0.06
J	12	100	46	0	-2	0.10	1.30	0.08	-62 ^a	0.04	0.98	0.04
	13	50	50	50	-23	0.09	1.10	0.08	-126	0.06	0.83	0.07
L	14	100	—	—	-61	0.08	1.65	0.05	-122	0.05	0.83	0.06
	15	100	—	—	-33	0.22	1.50	0.14	Discontinuity near -137°C.			
M	15	100	—	—	-10	0.13	1.70	0.07	Discontinuity near -67°C.			
	15	100	—	—	-40	0.07	1.30	0.05	Discontinuity near -137°C.			

^a Questionable transition.

in Table IV. As noted above, erratic fluctuations in the data for many of the runs in the 0–20°C. range are probably due to settling or equilibration of the system at the start of the runs and are not believed to be significant.

The data for polystyrene (sample C, run 3, Fig. 1) do not show a definite transition in this range. However, as noted earlier, there is a drop in the α' values near -140°C ., and a similar change in slope can be observed in the data of Martin et al.⁷ Transitions in this range for atactic polystyrene have been observed with dynamic measurements at about -135°C . at 1 cps by Illers and Jenckel,⁸ at -137°C . at 1 cps by Illers,⁹ at about -85°C . at 10 keps by Baccaredda et al.,¹⁰ and at about -110°C . by Turley and Keskkula.¹¹ The transition was attributed to torsional motions of a number of $-\text{CH}_2-\text{CH}_2-$ units in the backbone where head-to-head coupling occurred.⁸

Polypropylene (sample D, runs 4 and 5, Fig. 2) shows a T_g of -13 or -14°C ., which is in good agreement with the value of -18°C . reported by Reding¹² and by Manaresi and Giannella¹³ and -15°C . reported by Kontos and Slichter¹⁴ and by Beck et al. for their most amorphous atactic sample,¹⁵ all data obtained by using dilatometry. From specific heat measurements, Wilkinson and Dole¹⁶ obtained a value of -12°C . and Passaglia and Kevorkian¹⁷ a value of -14°C . The difference in the linear expansion coefficient α' above and below T_g , is about $1 \times 10^{-4}^\circ\text{C}^{-1}$ for this 82% amorphous polypropylene sample. This compares with a value of $4 \times 10^{-4}^\circ\text{C}^{-1}$ for $\Delta\alpha$, the change in volumetric expansion coefficient, reported by Manaresi and Gianella¹³ for 100% amorphous polypropylene.

The data of run 4 also suggest another transition at about -126°C . A discontinuity in the data for run 5 on the same sample at about -120°C . gives a hump in the α' values in this region and the transition can not be verified. Boyer^{1b} suggests a value of -70°C . for this transition in polypropylene samples based on dynamic measurements of Flocke at 4.6 cps.¹⁸

The three polyethylene samples tested (samples J, L, and M, runs 12, 14, and 15, Figs. 8 and 10) appear to have two transitions in the range of 0 to -40°C . To some extent the separation of these two transitions is arbitrary and a single larger transition in this range may also be postulated. However, the persistence of the apparent double hump in several runs on different samples strongly suggests that polyethylene has two transitions in this range. The data for sample J (Fig. 8) also indicate a transition at -126°C . and possibly another at -62°C . (shown as a dotted arrow). Sample L (run 14) appears to have transitions at -62 and -122°C . The data for sample M (run 15), which was cast from the same polymer sample as L, have discontinuities near -67 and -137°C ., and no conclusions can be drawn about lower temperature transitions in this sample.

Extrapolations of dilatometric data of Kontos and Slichter and of Manaresi and Gianella by Boyer^{1a} on ethylene-propylene copolymers to 100% ethylene give glass transition temperatures of -87 and -83°C ..

respectively. Boyer^{1d} also shows that free volume concepts lead to an estimate of -93°C . for T_g . Finally, at temperatures below -160°C . all three samples show a fairly rapid drop in α' values suggesting another transition.

Transitions in the 0 to -40°C . range in polyethylene have been ascribed to branching^{1c} and those in the -122 to -126°C . range to subgroup motion.^{1c,19} Bohn¹⁹ has found that the transition temperature in polyethylene around 0°C . is lowered as branching increases (crystallinity decreases). Similar results were obtained by Tanaka²⁰ and Kline et al.²¹

The lower transition temperature found in this range for samples L and M compared with J suggests that they are more branched and presumably less crystalline than J (54% crystalline). Furthermore, at temperatures above -140°C ., α' values for J are considerably lower than those for L and M, as expected for a more crystalline sample.

Because of discontinuities in the data for run 15 near -67 and -137°C ., a comparison of the effect of heat treatment (run 15 was cast, while run 14 was machined to form the test samples) can only be made in the high and low ranges. The differences between samples L and M in the high and low temperature regions are not large enough to permit meaningful conclusions to be drawn about the effect of heat treatment on crystallinity, but the lower level of α' for the cast sample throughout most of the temperature range could mean that crystallinity is increased by casting.

The 50:50 propylene-ethylene copolymer (sample K, run 13, Fig. 9) gives erratic results above -40°C . but shows a major transition at -61°C . Kontos and Slichter,¹⁴ using dilatometry, reported a T_g value of -58°C . for this composition, and Manaresi and Giannella's results on other copolymer compositions¹³ predict a value of -53°C . Below -120°C ., α' values drop again, but the change is small and it is questionable whether this represents a transition. However, it should be noted that Turley and Keskkula,¹¹ using dynamic measurements observed a transition in copolymers near this composition at about -130°C . A further drop in α' begins at about -150°C . The erratic results obtained here above -40°C . may be due to trapped stresses in the sample. Similar fluctuating results were obtained in this temperature range on several other runs using a less sensitive LVDT.²²

Multiple Transitions in Physical Mixtures of Polyethylene and Polypropylene

Figures 3-8 show the linear expansivities α' for runs 4-12 for a series of mixtures of polypropylene and polyethylene designated D, E, F, G, H, I, and J (described in Tables I and II). Tabulations of temperatures of transitions, values of α' above the transitions, $\Delta\alpha'$, and $\Delta\alpha'/\alpha'$ are given in Table IV.

In all of the samples except J which is 100% polyethylene, a major transition occurs in the range of -9 to -14°C ., and the magnitude of the change in the linear expansion coefficient $\Delta\alpha'$ at this transition decreases

with increasing polyethylene content. However, the ratio of $\Delta\alpha'/\alpha'$ diminishes more slowly since α' , the linear expansion coefficient just above the transition, also decreases with increasing polyethylene content.

It should also be noted from comparison of Figures 7 and 8 that data for sample I (88% PE) are similar in shape to those of sample J (100% PE), suggesting the possibility of transitions near -30 and -60°C . However, the apparent transitions are so small that they are not shown in Table IV.

TABLE V
Estimation of $\Delta\alpha'$ for 100% Amorphous Polypropylene

Sample	Run no.	Amorphous, %		$\Delta\alpha'$ $\times 10^4$, $^\circ\text{C}^{-1a}$	$\Delta\alpha''$ $\times 10^4$, $^\circ\text{C}^{-1b}$	Estimated $\Delta\alpha' \times 10^4$ 100% PP
		PE	PP			
D	4	0	82	1.01	1.01	1.23
	5	0	82	1.07	1.07	1.30
E	6	1	75	0.90	0.90	1.20
F	7	18	55	0.79	0.75	1.36
G	8	25	40	0.77	0.72	1.80
	9	25	40	0.62	0.57	1.42
H	10	36	26	0.40	0.32	1.23
I	11	46	6	0.23	0.13	2.17
J	12	46	0	0.10	—	—

^a Transition in range 0 to -15°C .

^b $\Delta\alpha'$ is reduced by the contribution of amorphous PE in this same temperature range. Correction is based on data for sample J: Correction = $\{(\% \text{ amorphous PE})/46\} (0.10) \times 10^{-4} = (0.00217 \times 10^{-4})(\% \text{ amorphous PE})$.

Estimates of the value of $\Delta\alpha'$ for 100% amorphous polypropylene in the temperature range of 0 to -15°C . were made from the results on each sample containing polypropylene, and the calculations are summarized in Table V. The contributions by amorphous polyethylene and amorphous polypropylene present in each sample were assumed to be additive, and the measured value of $\Delta\alpha'$ was reduced by the former. The estimated value of $\Delta\alpha'$ for 100% amorphous polypropylene was then obtained by dividing the adjusted $\Delta\alpha'$ (called $\Delta\alpha''$) for each sample by the fraction of amorphous polypropylene present.

The most reliable estimates are for samples D, E, and F with high amorphous polypropylene and low amorphous polyethylene contents, since the correction term is smallest here and the results are less sensitive to small errors in the analyses of per cent amorphous polypropylene. These values of $\Delta\alpha'$ average about $1.3 \times 10^{-4}^\circ\text{C}^{-1}$, which is a close check on Maresi and Giannella's measured value¹³ of $4 \times 10^{-4}^\circ\text{C}^{-1}$ for $\Delta\alpha$, the change in the volumetric expansion coefficient, which was determined dilatometrically on amorphous polypropylene.

If the correction were to include the $\Delta\alpha'$ value of 0.09 for polyethylene (-23°C . transition), the estimates of $\Delta\alpha'$ for polypropylene from samples

G, H, and I would be lowered, but the effect on the estimates from samples D, E, and F would be small.

In most of the same samples, a much smaller transition appears to be present at -110 to -132°C . The magnitude of the change in the expansion coefficient here ranges from 4-22% of the higher temperature transition. Estimates of transition temperatures in this lower region are subject to larger errors because of the smaller changes in slope.

Run 4 on sample D shows this transition, but the discontinuity in the data for run 5 on the same sample at about -120°C . gives a hump in the

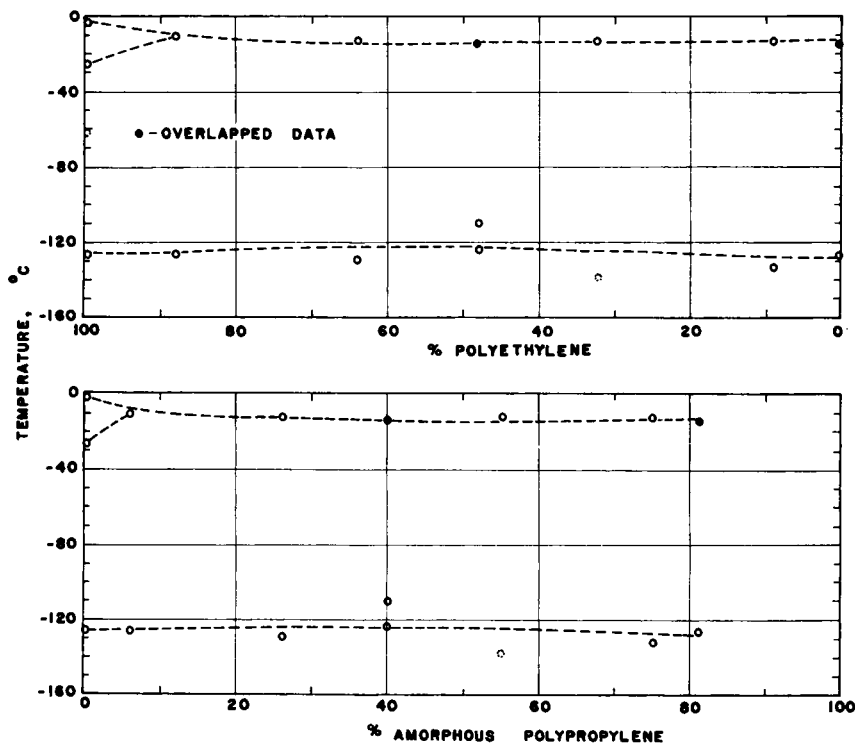


Fig. 12. Transition temperatures as a function of composition for polyethylene-polypropylene blends.

α' values in this region and the transition cannot be verified. The apparent transition in sample F (run 7) is so small that it is questionable whether it is actually present. It is therefore shown as a dashed arrow in Figure 4.

The trend of the data for sample G in run 8 suggests that another transition may be present below -135°C . This is also observed in run 9 on sample G but at a lower temperature (below -150°C .), and on samples H, I, and J which are the high polyethylene content samples, and also in the copolymer sample.

Plots of transition temperatures as a function of polyethylene content and of per cent amorphous polypropylene in the mixture are shown in Figure 12. The higher-temperature transition is quite insensitive to polyethylene content until 100% polyethylene (and the "double" transition) is reached. The low temperature (-110 to $-132^{\circ}\text{C}.$) transition is also fairly insensitive to composition. However, this relative independence of transition temperatures with composition seems to occur because the transitions of the two polymers are so close to each other. There is no evidence of any transitions in the mixtures which are not found in the pure polymers.

This investigation was supported by the National Aeronautics and Space Administration under grant NSG-343 to the University of Southern California.

It is a pleasure to acknowledge discussions with Dr. J. M. Zimmerman.

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Résumé

Des mesures de longueur-température ont été effectuées sur une série de mélanges de polymère sur un gamme entière de composition variant depuis le polyéthylène pur au polypropylène pur de même qu'une série de déterminations a été effectuée sur un copolymère 50:50 et du polystyrène. La cristallinité totale des échantillons ne dépassait point 54%. Les procédés expérimentaux utilisaient un transformateur linéaire différentiel variable sans utiliser de fluide de contact et la température variait de $+20$ à $-180^{\circ}\text{C}.$ Un procédé de différentiation numérique des moindres carrés, basée sur des arcs mobiles, est appliqué pour fournir directement des coefficients d'expansion thermique en fonction de la température. Les techniques de transformation linéaire différentielle de

voltage (LVDT) permet de détecter les transitions dans lesquelles les coefficients d'expansion étaient inférieurs à $10^{-5}^{\circ}\text{C}^{-1}$. Pour le polypropylène aussi bien que pour les mélanges, la transition vitreuse principale apparaît clairement dans le domaine observé par les autres auteurs, à savoir à environ -9 à -14°C . Sa localisation varie uniquement légèrement avec la composition, c.a.d. la teneur en polyéthylène lorsque celle-ci est inférieure à 88% mole. Pour le polyéthylène la région de transition s'est élargie notablement. Les résultats suggèrent deux transitions pour $0 > T > -40^{\circ}\text{C}$. Une seconde transition est observée pour chacun des composants pur aux environs de -126°C . Sa localisation varie quelque peu avec la composition. Toutefois, nos résultats n'indiquent pas une région de transition additionnelle caractéristique du mélange. Le copolymère montre une transition principale à -61°C en bon accord avec les auteurs précédents. L'expansion thermique décroît à nouveau vers -150°C . En général nos observations concernant les transitions en-dessous de T_g sont en accord avec les résultats dynamiques.

Zusammenfassung

Messungen der Länge in Abhängigkeit von der Temperatur an einer Reihe von Polymischungen über den gesamten Zusammensetzungsbereich von reinem Polyäthylen, bis zu reinem Polypropylen sowie eine Bestimmungsreihe eines 50:50-Copolymeren und von Polystyrol werden ausgewertet. Die Gesamtkristallinität der Probe überschritt 54% nicht. Bei der experimentellen Ausführung wurde ein variabler linearer Differentialumwandler ohne eine begrenzende Flüssigkeit verwendet, die Temperatur variierte von etwa $+20^{\circ}\text{C}$ bis -180°C . Ein auf Bogenbewegung beruhendes numerisches Differentiationsverfahren der kleinsten Quadrate wird zur direkten Gewinnung der Wärmeausdehnungskoeffizienten als Funktion der Temperatur angewendet. Mit Hilfe des LVDT-Verfahrens können Umwandlungen mit einem Unterschied im Wärmeausdehnungskoeffizienten von weniger als $10^{-5}^{\circ}\text{C}^{-1}$ aufgezeigt werden. Sowohl bei Polypropylen als auch bei den Mischungen kann die Hauptglasumwandlung in dem von anderen Autoren angegebenen Bereich, nämlich von etwa -9°C bis -14°C beobachtet werden. Bei einem Polyäthylengehalt von weniger als 88 Mol% variiert ihre Lage nur schwach mit der Zusammensetzung. Bei Polyäthylen verbreitert sich der Umwandlungsbereich wesentlich. Die Ergebnisse lassen im Bereich $0 > T > -40^{\circ}\text{C}$ zwei Umwandlungen erkennen. Um 126°C wird für jede reine Komponente ein zweiter Umwandlungsbereich beobachtet. Seine Lage schwankt etwas mit der Zusammensetzung. Unsere Ergebnisse lassen jedoch einen zusätzlichen für die Mischung charakteristischen Umwandlungsbereich erkennen. Das Copolymere zeigt in guter Übereinstimmung mit früheren Arbeiten einen Hauptumwandlung bei -61°C . Die Wärmeausdehnung nimmt bei etwa -150°C wieder ab. Im allgemeinen stimmen unsere Beobachtungen in bezug auf Umwandlungen unterhalb T_g mit dynamischen Ergebnissen überein.

Received April 7, 1966

Prod. No. 1379