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HEAT CAPACITY OF CRYSTALLINE
POLYMERS AT LOW TEMPERATURES

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HEAT CAPACITY OF CRYSTALLINE POLYMERS
AT LOW TEMPERATURES

Prepared by:
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ABSTRACT: Published heat capacity data on atactic and isotactic polypropylene, polyethylene and polytrifluoroethylene have been analyzed by the method of Starkweather. The results of this analysis indicate that the model proposed by Stockmayer and Hecht for the thermal motions of crystalline polymers at low temperatures can yield information indicative of the structure of the polymer.

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HEAT CAPACITY OF CRYSTALLINE POLYMERS AT LOW TEMPERATURES

This report contains the results of an analysis of heat capacity data on various crystalline polymers. The data have been analyzed by the procedure of Starkweather to test the Stockmayer-Hecht model for the heat capacity of a polymer. This study was carried out under Project N10-a-1-56 as part of a general polymer investigation and is of importance in furthering basic knowledge of polymer characteristics.

R. E. ODENING
Captain, USN
Commander

Albert Lightbody
ALBERT LIGHTBODY
By direction

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INTRODUCTION

1. There has recently been a revival of interest in the heat capacities of crystalline and amorphous polymers. From heat capacity, C_v , data Wunderlich, (ref. (a)), has calculated the vibrational spectrum of a completely crystalline polyethylene (PE) and found that the models of Stockmayer and Hecht (ref. (b)), and of Tarassov (ref. (c)), are useful in understanding the thermal motions of linear polymers at low temperatures. We have also employed both Stockmayer-Hecht (refs. (d) and (e)), and Tarassov (ref. (f)) models in calculating the C_v of linear polymers at low temperatures and for calculating structural parameters. Recently Isaacs and Garland (ref. (g)), have measured the heat capacity of highly crystalline PE from 1.8° to 5.3°K and have interpreted their results in terms of the Stockmayer-Hecht model.

2. It is the purpose of this report to extend previous studies (refs. (d) and (e)), and to present the results obtained when the Stockmayer-Hecht model is applied to atactic ($\sim$ 16% crystalline) and isotactic ($\sim$ 40% crystalline) polypropylene (PPE) and to highly crystalline polyethylene and polytrifluoroethylene (PTriFE).

THE STOCKMAYER-HECHT THEORY OF HEAT CAPACITY

3. The model of Stockmayer and Hecht assumes that groups in the polymer chain vibrate as units and that there are strong primary bonds between the units and weak interactions between adjacent chains. Temperature dependence of heat capacity at low temperatures can then be expressed in terms of two ratios, $C_v/3Nk$ and T/T_M , where N is the number of vibrating units per gram; T_M (which is analogous to the Debye θ) equals $h\sqrt{\nu_m}/k$, where h and k are the Planck and Boltzmann constants respectively, and ν_m is the maximum frequency of vibration. The analytical procedure of Starkweather (ref. (h)), was employed to evaluate the parameters, T_M , ν_m , and $3Nk$. Details of the calculations have been previously given (ref. (i)).

THE STARKWEATHER METHOD OF ANALYSIS

4. Starkweather (ref. (i)) has developed an analytical procedure for calculating the parameters T_M , ν_m , $3Nk$ and the molecular weight of the repeating unit. Briefly, the procedure is as follows: the experimental heat capacities are plotted logarithmically against the absolute temperature and this plot is placed over a similar logarithmic plot of $C_v/3Nk$ vs. T/T_M : the values of $C_v/3Nk$ and T/T_M being those given by Stockmayer and Hecht (ref. (b)). The upper (C_v vs. T) plot is shifted along the rectangular coordinates of the lower ($C_v/3Nk$ vs. T/T_M) plot until the curves superimpose. Then the experimental temperature corresponding to $T/T_M = 1$, is T_M and the C_p value corresponding to

$C_V/3Nk = 1$, is $3Nk$. It is assumed that at low temperatures $C_p - C_V$ is small. Composite plots of this type are shown in Figures 1, 2 and 3.

5. The experimental data for polyethylene are those recently obtained by Dainton and co-workers (ref. (j)), and the data for polytrifluoroethylene was obtained by Sochava (ref. (k)). Data for the atactic and isotactic polypropylene was obtained by Dainton and co-workers (ref. (l)). Values of the calculated parameters are given in Table 1.

DISCUSSION

6. The calculated value for ν_m of 529 cm^{-1} for PE is very close to the infrared band at 543 cm^{-1} while the calculated value of 226 cm^{-1} for PTrIFE appears reasonable. In the case of atactic and isotactic PPE the calculated values of 325 cm^{-1} and 361 cm^{-1} appear to be associated with the bending motions of the main chain which, according to Liang and Pearson (ref. (m)), should appear near 400 cm^{-1} .

7. The calculated molecular weights of each of the vibrating units are in good agreement with the expected values, particularly in the case of PE. In the case of the two forms of PPE it would appear that the pendent $-\text{CH}_3$ group does not make a large contribution to the heat capacity.

8. It is of interest to note that Isaacs and Garland (ref. (g)) considered the heat capacity of highly crystalline polyethylene in terms of the Stockmayer-Hecht model and were able to fit their experimental data and obtain a value of 885°K for T_M . This value can be compared with the value of 760°K given in Table 1.

9. Both Wunderlich (ref. (a)), and Isaacs and Garland (ref. (g)) have pointed out that the Stockmayer-Hecht model does not apply exactly to polyethylene (or to any other crystalline polymer). What is needed is a new and more exact model which takes into account the form of the crystal lattice of the polymer and the zig-zag chain structure. However, the degree of fit which has been obtained using the Stockmayer-Hecht model with simple linear polymers has been encouraging.

CONCLUSION

10. It can be concluded that the model of Stockmayer and Hecht is useful in understanding the thermal motions of crystalline polymers at low temperatures.

RECOMMENDATIONS

11. It is recommended that calorimetric measurements be made of heat capacity over a broad temperature range for a number of polymers. This data would be useful in testing the validity of the Stockmayer-Hecht model. Data of this type would also permit the calculation of the thermodynamic parameters, entropy, enthalpy, and free energy of the polymers considered.

TABLE 1

CALCULATED PARAMETERS FOR CRYSTALLINE POLYMERS

Parameter	Polyethylene	Polytrifluoro- ethylene	Atactic Polypropylene	Isotactic Polypropylene
Region of fit, °K	20-120°	23-70°	20-90°	20-95°
T _M , °K	760°K	325°K	466°K	519°K
$\sqrt{m}$, cm ⁻¹	529	226	325	361
3Nk, CAL/ gm.deg.	0.348	0.104	0.242	0.238
Average Molecular Weight of Vibrating Unit, M(gm/mole)	17.1	57.3	24.6	25.2
Vibrating Units/ Repeating Units	0.82	1.43	1.71	1.67

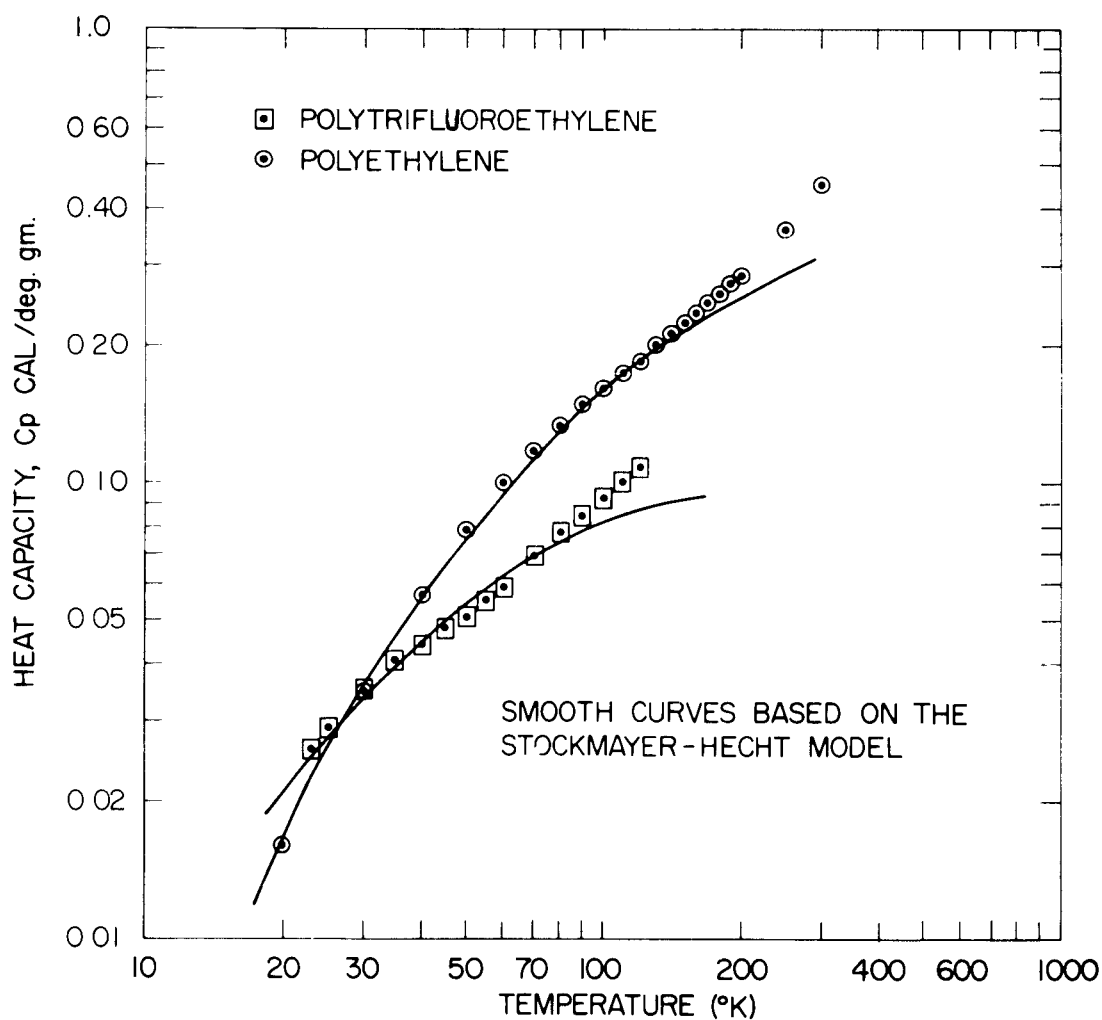


FIG. 1 LOG-LOG PLOT OF HEAT CAPACITY VERSUS TEMPERATURE

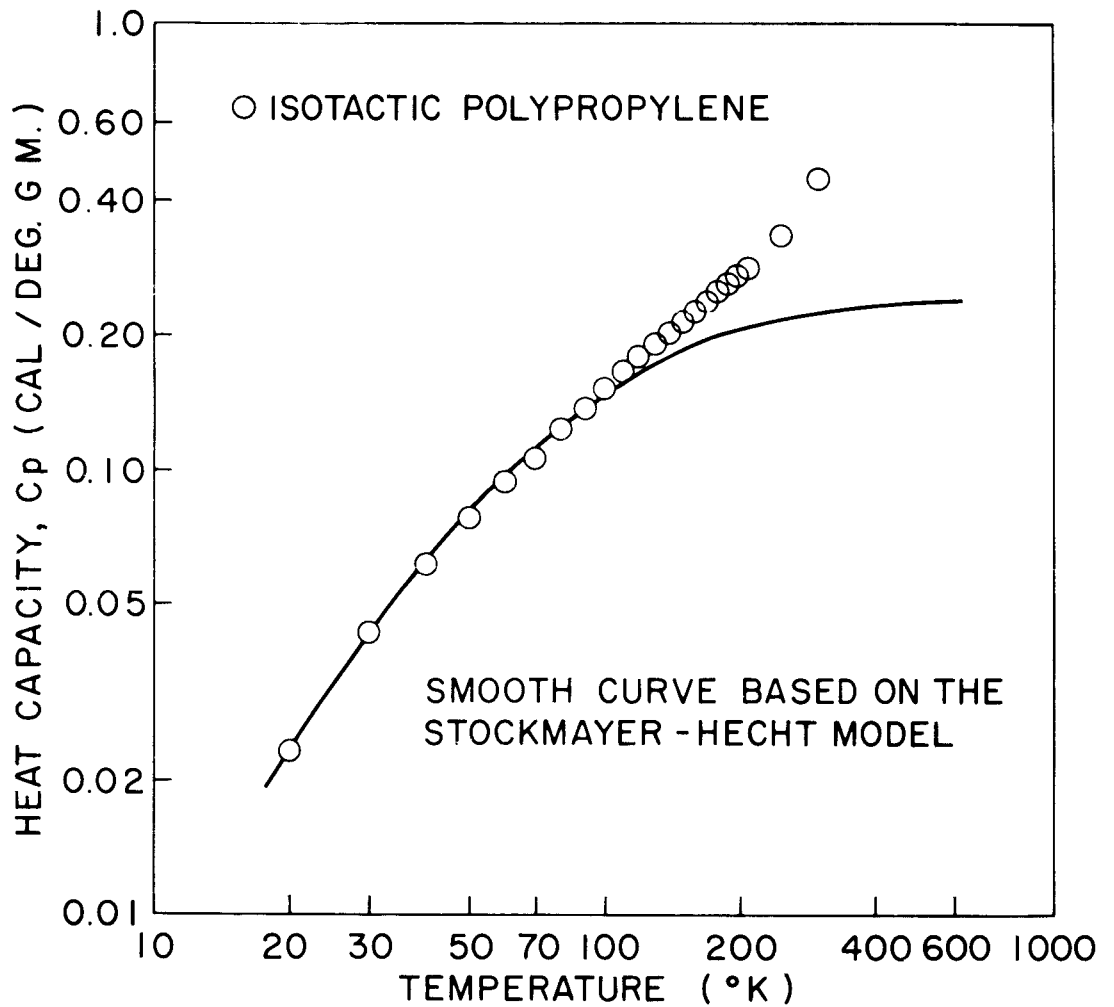


FIG. 2 LOG-LOG PLOT OF HEAT CAPACITY VS TEMPERATURE FOR ISOTACTIC POLYPROPYLENE

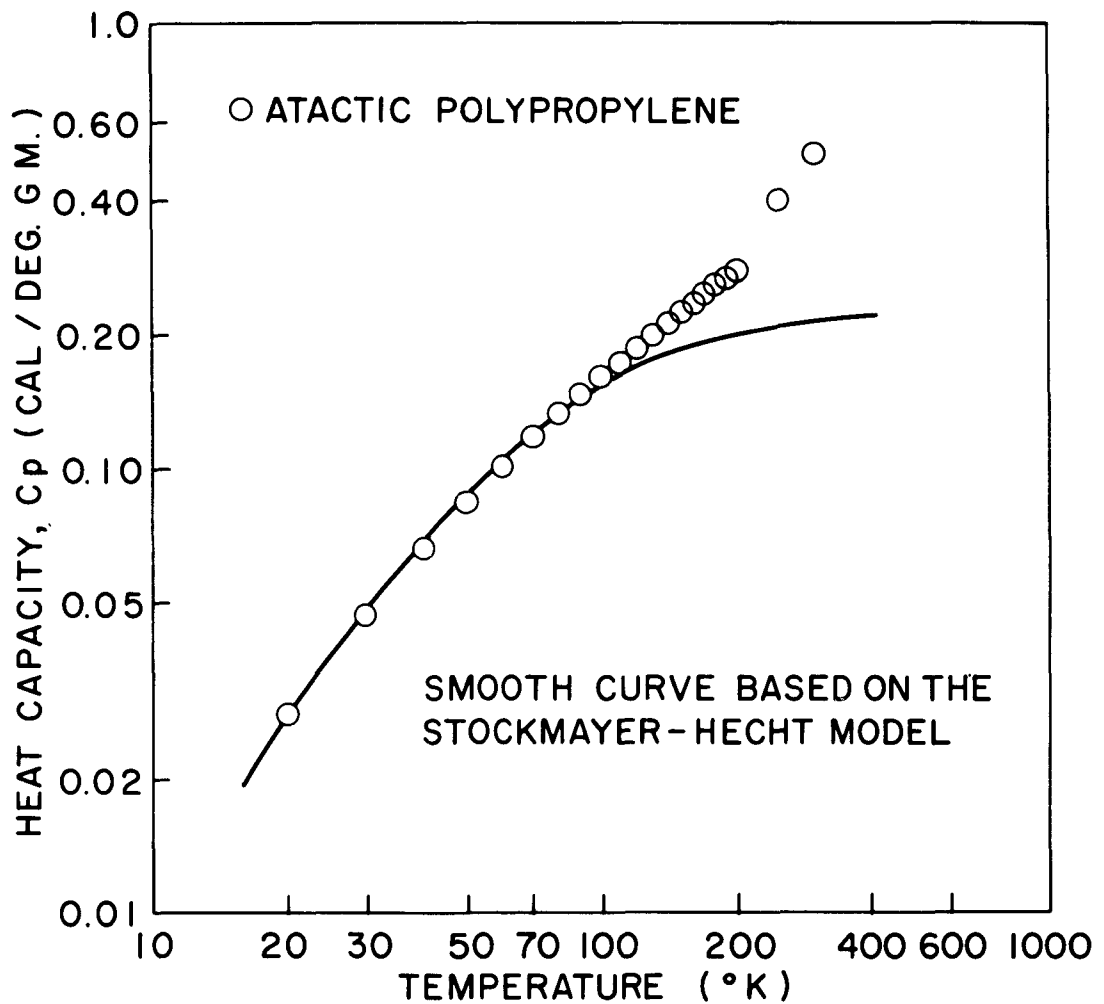


FIG. 3 LOG-LOG PLOT OF HEAT CAPACITY VS TEMPERATURE FOR ATACTIC POLYPROPYLENE

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SUBJECT ANALYSIS OF REPORT				
	DESCRIPTORS	CODES	DESCRIPTORS	CODES
Heat		HEAT	Analysis	ANAL
Capacity		CAPC	Stockmayer-Hecht	STHT
Crystalline		CRYS	Measurement	MEAU
Polymers		POLY	Model	MODE
Low temperature		LOWM	Structure	STRC
Polypropylene		PLVT	Polymers (Characteristics)	POLYC
Polyethylene		POLH	Parameters	PARA
Poly		POYA	Temperature	TEMP
Tri		TRIY	Structure	STRC
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