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LOW TEMPERATURE HEAT CAPACITY OF HETEROCYCLIC POLYMER NETWORKS

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Abstract

The predicted crossover to a fractal-like vibrational regime above 8–10 K was apparently proved by precise measurements of heat capacity of a series of cross-linked heterocyclic polymers.

Keywords: heat capacity, heterocyclic polymers, polymers

Introduction

Recent theories of disordered solids [1–4] predict the crossover in the density of vibrational states, $D(\omega) \approx \omega^{d-1}$ (where ω is the frequency of vibrations), in the acoustical limit (i.e., in the temperature interval far below the relevant Debye temperature, $T << \theta$) manifesting itself by a change of the exponent from $d = 2$ (at low frequencies, hence, temperatures) to $d = 5/3$ (at higher temperatures above the crossover point). One possibility to check this prediction may be provided by measurements of the heat capacity which scales as $C_p \approx T^d$ in this temperature interval [1–4]. In the present communication we will briefly report on the experimental evidence apparently supporting the above theoretical predictions which was obtained from precise heat capacity measurements for a series of cross-linked heterocyclic polymers. A more detailed discussion of the experimental data will be the subject of a separate paper.

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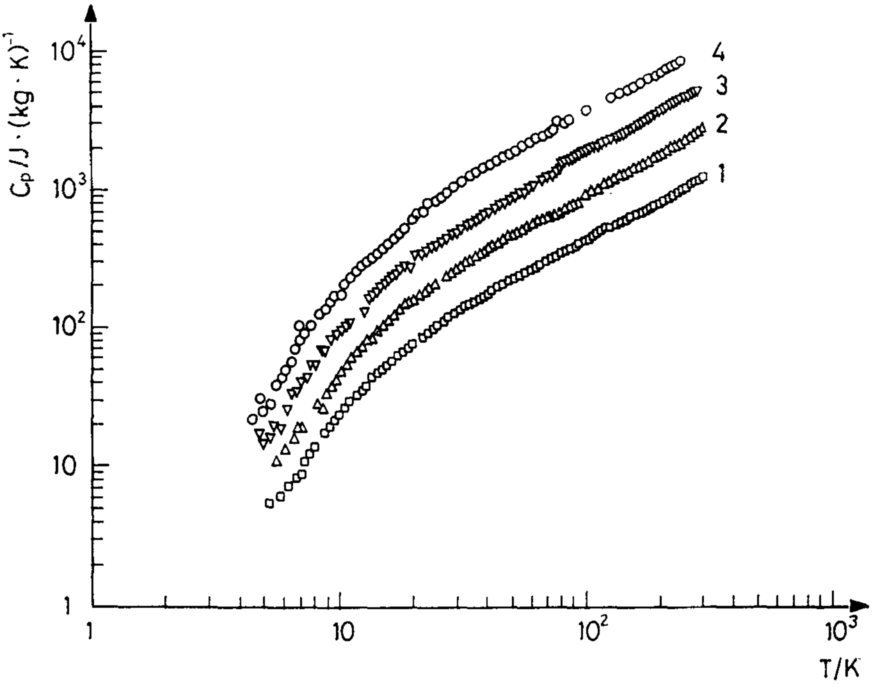

Fig. 1 Lg-lg plot of the heat capacity *vs.* temperature for samples HMDI/ER = 30/70 (1), HMDI/ER = 50/50 (2), HMDI/ER = 60/40 (3) and HMDI/ER = 80/20 (4). Starting from curve 2, each next curve is shifted upwards by lg 2 with respect to the previous curve

Experimental

The samples of the present study were prepared by a catalytic copolymerization of the base epoxy resin (ER) with hexamethylene diisocyanate (HMDI) in the presence of 1% (by weight) of triethylene amine (catalyst) at 393 K during 2 h. Values of the room-temperature density ρ, glass transition temperature T_g and the network mesh size $<M_c>$ (more precisely, mean molecular weight of chain fragments between network junctions) [5–8] are collected in Table 1.

Heat capacity C_p was measured with the aid of an automated adiabatic calorimeter [9] in the temperature interval 4.2–300 K. The data were taken in steps of 0.2–0.6 deg (in the interval 4.2–50 K), 0.6–1.5 deg (in the interval 50–150 K) and 1.5–5 deg (at higher temperatures); the estimated mean errors in the temperature intervals indicated were 2%, 1% and 0.5%, respectively.

Table 1 Selected physical properties of the studied samples

Property	HMDI/ER molar ratio			
	80/20	60/40	50/50	30/70
ρ / g·cm^{-3}	1.2330	1.2293	1.2271	1.1998
T_g / K	390	375	343	331
$<M_c>$	250	520	720	2100
T^* / K	310	305	305	220
ω^* / cm^{-1}	157	153	153	212
m* / mol	105	100	100	95

Results and discussion

The values of the heat capacity of all studied samples are roughly similar both in magnitude and in the patterns of temperature dependence (Fig. 1). In a limited temperature interval (below 30 K for HMDI/ER = 30/70 and up to 40 K for other samples) these data could be reasonably well fitted to the Stockmayer-Hecht model [10] with the values of characteristic parameters (temperature T^*, frequency ω^* and effective mass of a vibrating unit m^*) also shown in

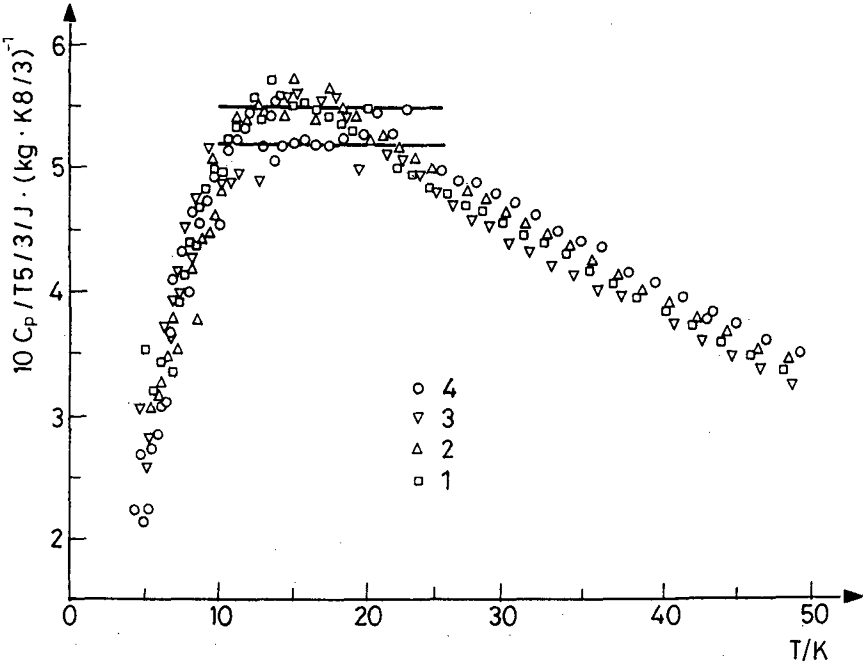

Fig. 2 $C_p/T^{5/3}$ *vs.* T plots

Table 1. Although this model, in a strict sense, was intended to explain the heat capacity behaviour of linear polymers in the ordered (i.e. crystalline) state, its applicability to our data for disordered, cross-linked polymers is no surprise as far as the temperature dependence of C_p is hardly affected by crystallinity in this limited temperature interval [11, 12].

As can be seen from Fig. 2, the predicted proportionality, $C_p \approx T^{5/3}$ holds in a rather narrow temperature range (from the apparent crossover point $T_c \approx 8$–10 K to about 20 K) only for samples HMDI/ER = 80/20 and HMDI/ER = 60/40 with the highest network density (i.e. lowest $<M_c>$, whereas its applicability becomes more doubtful as the HMDI/ER ratio decreases. Moreover, in the temperature interval $T < T_c$ the temperature dependence of C_p proved much more complex than the anticipated simple scaling law, $C_p \approx T^2$ [4]. Partially at least, this discrepancy should be attributed to the occurrence of a low-temperature peak on the C_p/T^3 *vs.* T plots (Fig. 3) which is currently regarded as a universal feature of the heat capacity behaviour of glasses [13–17]. Once again, the resolution of this peak becomes poorer, the looser is the chemical network density.

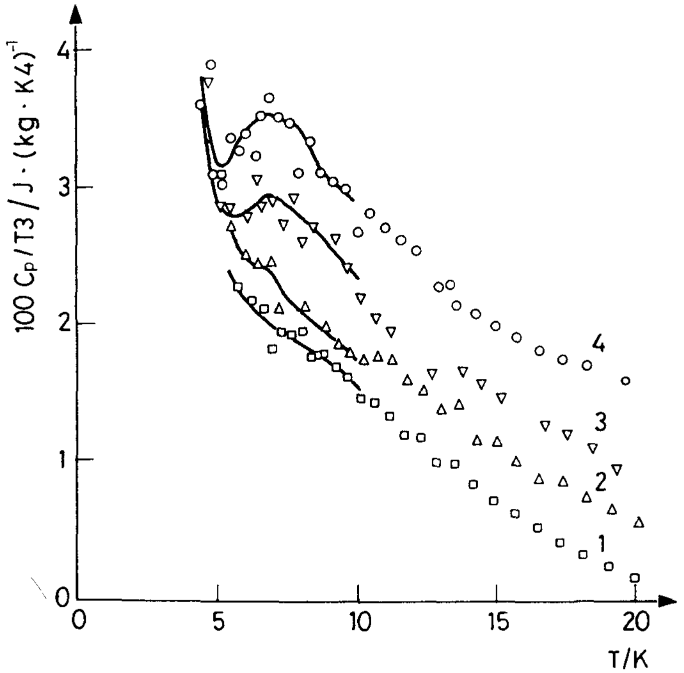

Fig. 3 C_p/T^3 *vs.* T plots. Curve 4 is shifted upwards by 0.5 units, and curves 2 and 1 are shifted downwards by 0.4 and 0.8 units with respect to curve 3. Solid lines are the free-hand best fits to the experimental data

Conclusions

Precise measurements of the heat capacity of a series of cross-linked heterocyclic polymer glasses apparently proved the crossover to a fraction-like regime above 8–10 K (i.e., at the characteristic length scale about 10 nm) for samples with the highest network density. These data are thus qualitatively consistent with the results of low frequency Raman scattering studies [18] in which the upper structural scale for a fractal-like behaviour of these samples at room temperature was estimated as 3.5 nm.

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Zusammenfassung — Durch präzise Messungen der Wärmekapazität einer Reihe von quervernetzten heterocyclischen Polymeren konnte wahrscheinlich die vorausgesagte Querverbindung zu einem fraktionsartigen Schwingungsbereich oberhalb 8–10 K nachgewiesen werden.