LOW TEMPERATURE SPECIFIC HEAT OF HETEROCYCLIC POLYMER NETWORKS: EFFECT OF NETWORK DENSITY

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LOW TEMPERATURE SPECIFIC HEAT OF HETEROCYCLIC POLYMER NETWORKS: EFFECT OF NETWORK DENSITY

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Measurements of low frequency Raman scattering and low temperature specific heat between 2 and 20 K have been performed in two glassy, heterocyclic polymer networks. The effective network densities of heterocyclic polymer networks are varied by changing the ratio of bi- and mono-functional isocyanate monomers leaving the overall chemical structure essentially unchanged. A boson peak at about 20 cm^{-1} characterizes the Raman spectra at room temperature of both the samples. Below 10 K, the specific heats deviate from a cubic temperature dependence, as predicted by the Debye theory, and reveal an excess specific heat having the shape of a well-defined peak in a C_p/T^3 plot with a maximum at about 5 K. The increase of the effective network density is accompanied by a slight decrease of the excess specific heat. These observations have been explained in terms of additional low-energy vibrations associated to the monomers building up the polymer networks.

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1. Introduction

The low-energy vibrational dynamics of amorphous polymers appears to be regulated by the morphology. Linear polymers show an excess specific heat over that predicted by the Debye theory which is markedly depressed by the introduction of cross-links establishing covalent bonds between the polymeric chains [1]. The comparison between the behaviours of the low temperature specific heats of linear and reticulated polymers permits to establish that the presence of cross-links leads to a significant suppression of the low-energy vibrational states which are the main source for the low temperature specific heat capacity. To extend the range of observations which suggest the existence of a correlation between the low-energy vibrational dynamics of amorphous polymers and their low temperature thermal properties, measurements of low frequency Raman scattering and specific heat capacity between 2 K and 20 K have been carried out in two amorphous heterocyclic polymer networks (HPN). The linear chains characterizing the structure of a heterocyclic polymer have been cross-linked in order to obtain a network having a controlled degree of cross-linking density. The network density of two HPNs prepared by simultaneous trimerization of a bi-functional (1,6-hexamethylene diisocyanate, HDI) and a monofunctional (hexyl isocyanate, HI) monomers has been varied by changing the HDI/HI ratio in the reaction mixture [2,3], whereas their overall chemical structure remained essentially unchanged.

The present analysis reveals that variation of HPN morphology by addition of cross-links between the main linear chains leaves almost unchanged the density of additional low-energy vibrations which are the source of the excess low temperature specific heat.

2. Experimental details.

Heterocyclic polymer networks were obtained by simultaneous trimerization reaction of 1,6-hexamethylene diisocyanate (HDI), hexyl isocyanate (HI) and hexabutyl distannum oxide (HBDSO, catalyst) purchased from Aldrich Co. and used as received. The method of the HPN synthesis described elsewhere [2,3] produced a regularly cross-linked copolymer with controlled molar fractions of three-arm (cross-linked) and two-arm (linear) segments, as shown in Fig. 1. Tab. 1 reports some structural parameters concerning HPNs: L/N refers to relative ratio between linear and network structure, $<M_R>$ is the molecular weight of the monomer unit, $<M_c>$ the apparent mean molar mass of chain strands between network junctions. The specific heats of all the polymers were measured in the 2-20 K range using an automated relaxation calorimeter. Temperatures were measured by calibrated commercial germanium thermometers. The random error is apparent from the figures and any systematic errors are believed to be less than 4-5 %.

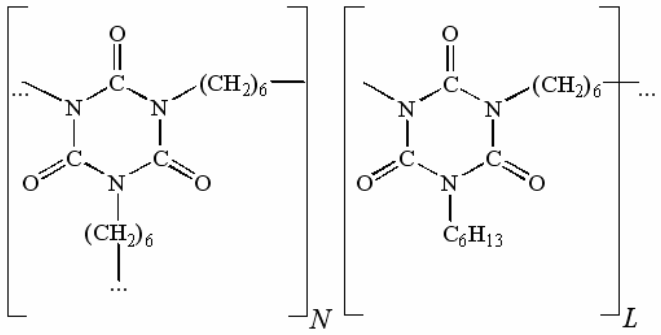

Fig. 1. Generalized chemical scheme of heterocyclic polymer networks (HPN).

Raman scattering measurements were performed over the range between 80 K and room temperature using an Ar-ion laser (λ=514.5 nm) with a power of 100mW and a double monocromator Yobin Yvon U-1000. The low frequency Raman spectra were observed in a 90° scattering geometry from the laser beam. The resolution of the experimental set-up was 1 cm^{-1}.
In order to estimate longitudinal and transverse sound velocity, we measured Brillouin light scattering (BLS) spectra using a Sandercock tandem Fabri-Perrot interferometer. The spectra were measured at 90 degree scattering in symmetric geometry. This geometry provides estimate of the sound velocity v from the BLS frequency ν without knowledge of the refractive index: $v_i=\lambda\nu_i/[2\mathrm{Sin}(\Theta/2)]$ (λ=514.5 nm is the laser wavelength, the index i corresponds to TA or LA modes, $\Theta=90^o$ is the scattering angle). The BLS spectra were measured in the temperature range between 80 and 295 K.

Table 1. Parameters of the studied HPNs having a relative ratio L/N of linear to network content: $<M_c>$ represents the average molecular weight between cross-links, $<M_R>$ the molecular weight of monomers, T_g the glass transition temperature and ***m*** the fragility. The values of the density ρ at room temperature and of the longitudinal (V_l) and shear (V_t) sound velocities at 0 K (see text) are also included.

L/N	**ρ (k gm^{-3})**	**T_g (K)**	**$<M_c>_{theor}$ (g mol^{-1})**	**$<M_R>$ (g mol^{-1})**	**V_l (m s^{-1})**	**V_t (m s^{-1})**	**V_D (m s^{-1})**	***m***
100/0	1148	291	∞	295	2975	1405	1581	**47**
60/40	1188	313	695	278	3012	1460	1641	**63**

3. Results and Discussion

3.1. Low frequency Raman scattering.

The low frequency Raman spectra measured at temperatures ranging between 80 K and 295 K for HPNs, having the ratios L/N=100/0 and L/N=60/40, are reported in Fig. 2. A boson peak (BP) at about 20 cm^{-1} is clearly visible at room temperature, while the BP for both polymers is masked by luminescence in the spectra measured at lower temperatures (Figs. 2a and 2b). The BP is mainly due to the excess density of low-energy vibrational modes, which also gives a low temperature excess specific heat [4]. At even lower frequencies (<20 cm^{-1}), the light scattering excess (LSE), a further characteristic feature of amorphous solids, is observed: it is usually attributed to relaxation mechanisms because its contribution appears centred at zero frequency and its magnitude increases with increasing temperature faster than the Bose population factor [5]. Unfortunately an unavoidable luminescence that increases markedly at lower temperatures (see Figs. 2a and 2b) prevents any quantitative evaluation of LSE.

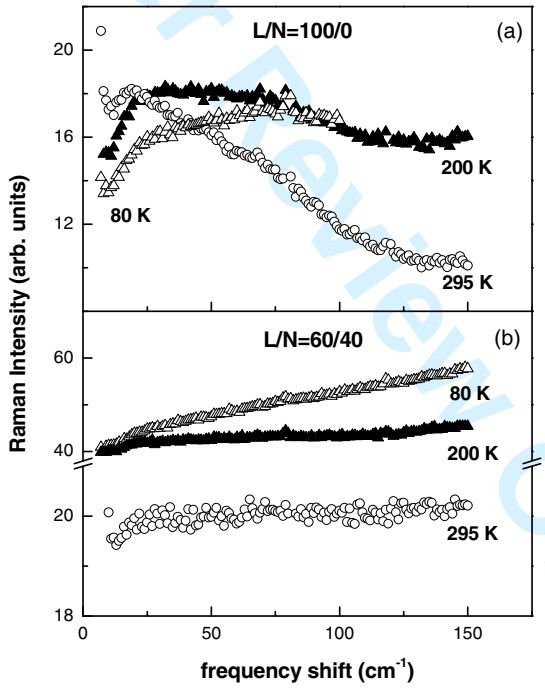

Fig. 2. Low frequency Raman scattering at three different temperatures between 80 K and room temperature 295 K for samples (a) HPN with L/N=100/0 and (b) HPN with L/N=60/40.

A rough information on the shape of the low-energy vibrational density of states g(ω) (VDS) in amorphous solids can be obtained from the first order Raman scattering at low frequency (<150 cm^{-1}). The Raman intensity is related to g(ω) through the light-to-vibration coupling function, C(ω) [6]:

$$I^{expt}(\omega,T) \propto \frac{C(\omega)g(\omega)[n(\omega,T)+1]}{\omega} \quad (1)$$

where n(ω,T) is the Bose-Einstein population factor and 1/ω is the harmonic propagator. Both C(ω) and g(ω) are affected by the complex vibrational properties of a disordered topology and it has been shown that, in the low frequency region, $g(\omega)/\omega^2$ has a maximum in a number of glasses [7], while C(ω) exhibits almost a linear frequency dependence [8]. The BP is commonly observed in the low energy region of inelastic neutron and light scattering spectra of glassy polymers [9,10] and is ascribed to an excess density of vibrational states (DVS) associated with the presence of a characteristic length in an amorphous system. The connection between the boson peak frequency ω_0 and the characteristic length scale (e.g. scale of the intermediate range order) varies for different models [10-12]. According to [10], the relevant length scale ξ_b can be estimated as:

$$\xi_b = S\, v_D/c\, \omega_0 \quad (2)$$

where c is the velocity of light and S (=0.65) is a mean shape factor of the structural domain with a relevant size ξ_b. Substituting the value of ω_0=20 cm^{-1}into eq. (2), one obtains ξ_b = *1.2 nm*. The obtained value of ξ_b is quite close to the average size of the monomer, the two-arm isocyanurate heterocycle building up the linear HPN (Fig. 1). By assuming a spherical volume for the monomer, a rough evaluation has been performed obtaining an average diameter of about *1 nm.* This finding can be used to explain the excess C_p observed in HPNs and discussed in the following section: the heat capacity is an integral-type technique (and, consequently, insensitive to the fine detail of phonon spectrum), but at low temperatures it is mainly determined by additional vibrations which are localized within regions having about *1.2 nm* as a relevant size.

3.2. Low temperature specific heat.

The experimental data of C_p, obtained between 2 K and 20 K and plotted as $C_p(T)/T^3$, for HPNs having the ratios L/N=100/0 and L/N=60/40 are compared in Fig. 3. All the samples exhibit an excess low temperature specific heat capacity (LTSH) over the Debye contribution C_D/T^3 (dotted lines in Fig. 3), having the characteristic shape (for a glass) of a broad peak. The Debye contributions have been evaluated using the classical relation

$$\left(\frac{C_D}{T^3}\right) = \frac{2\pi^2 k_B^4}{5\hbar^3\rho}\left[\frac{1}{3}\left(\frac{1}{v_l^3}+\frac{2}{v_t^3}\right)\right]$$

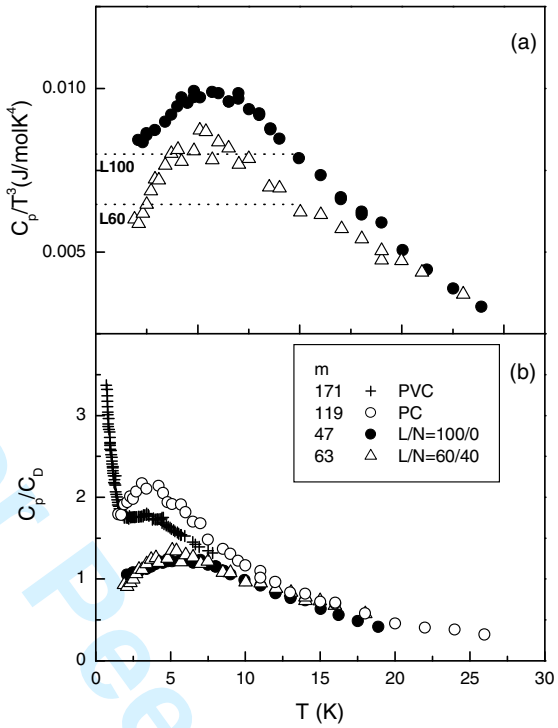

Fig. 3. (a) Temperature dependences of C_p/T^3 for HPNs with L/N=100/0 (●) and L/N=60/40 (Δ). (b) Comparison of the experimental LTSH of HPNs with L/N=100/0 (●) and L/N=60/40 (Δ), plotted as C_p/C_D. The C_p experimental data for BPA-PC are taken from D'Angelo et al [17] and those for wholly amorphous PVC from Duval et al [20].

where the term in parenthesis in the r. h. s. is the inverse of the cubic power of the average Debye sound velocity v_D and the other parameters have their usual meaning. The values of longitudinal (v_l) and transverse (v_t) sound velocities (see Table 1) for both the samples were estimated extrapolating down to 0 K the temperature behaviours of the Brillouin shifts measured over the range between 80 K and 300 K.

The maximum of the hump is located at about 5.5 K in both HPNs and its magnitude decreases by going from the virtually linear polymer to the cross-linked network having a ratio of L/N=60/40. By comparing the LTSH scaled to the Debye contribution C_D of both HPNs (Fig. 3b), it results that the ratios $C_p(T)/C_D$ are very close over the whole temperature range explored. This observation gives evidence of the fact that the source of the excess LTSH in HPNs lies in additional low-energy vibrational states localized within the monomers whose number changes slightly by cross-linking the polymer network (from $2.04*10^{21}$ to $2.17*10^{21}$ monomers per mole by going from L/N=100/0 to L/N=60/40). It is suggested that local vibrational motion within the

monomers building up the polymeric networks of HPNs controls the low-energy vibrational dynamics of these systems resulting in an excess heat capacity above the contribution of the ordinary elastic waves. The revealed features are consistent with the supposed nature of the additional anomalous vibrations, which are ascribed to quasi-local modes in quasiparticles frozen in the amorphous solid whose characteristic length sets the crossover from Debye-like (extended states) to localized excitations in the low-energy DVS [13].

A further consideration concerns the behaviours of $C_p(T)/C_D$ observed in HPNs and the correlation between fragility and excess LTSH over the predictions of the Debye theory [14]. This correlation implies that the dynamics of a glass-forming liquid at the glass transition influences the vibrational aspect of the glass: "strong" as opposed to "fragile" glassformers should have a larger density of low energy or soft vibrations and consequently a higher excess LTSH. "Strong" liquids are systems, which exhibit an Arrhenius dependence of the viscosity over broad ranges of temperature, while "fragile" liquids display pronounced deviations from that behaviour [15]. The dynamic fragility *m* of these HPNs has been determined by dielectric measurements [2] giving the values of *m*=47 for L/N=100/0 and *m*=63 for L/N=60/40 [16]. The experimental data of $C_p(T)/C_D$, reported in Fig. 3b, show that the increase of fragility is not related to a corresponding decrease of the excess LTSH. In the class of linear amorphous polymers, the excess LTSH increases by going from the extremely fragile polyvinylchloride (PVC, *m*=191) to the bisphenol-A-polycarbonate (BPA-PC, *m*=119) [17]. It is worth noting that, in Ref. [17], the average velocity v_D of BPA-PC has been evaluated by linear extrapolation down to 0 K of the sound velocities measured below and above room temperature obtaining a value of C_D/T^3=0.00463 J/molK^4. The value of C_D/T^3=0.00704 J/molK^4, used in the present work, has been more accurately determined by the sound velocity measurements on BPA-PC at temperatures close to 0 K [18].

These results are consistent with the proposed correlation [14], in which a growing excess of soft vibrations causing the anomalous LTSH is expected to characterize increasingly stronger systems. A different scenario appears when the class of HPNs is considered: the comparison between $C_p(T)/C_D$ for BPA-PC, PVC and HPNs (see Fig. 3b) shows clearly that the strongest HPNs exhibit an excess LTSH which is smaller than that of the most fragile PVC. Consequently the class HPN contrasts with the above correlation, widely recognized in inorganic glasses and linear amorphous polymers, which relates the "fragile" or "strong" character of glass-formers to a smaller or larger excess of low energy vibrations, respectively. In agreement with the conclusions of a study mainly concerning the contrasting trends exhibited by the dynamic and thermodynamic (measured by

$\frac{C_{p,l}}{C_{p,g}}$, the ratio of the liquid to glassy heat capacities at T_g) fragility in polymeric glass-formers [19], we believe that the concept of fragility and the related correlations need to be more deeply explored in polymers.

4. CONCLUSIONS

Low temperature specific heat capacities of two heterocyclic polymer networks having a different effective network density reveal an excess specific heat having the shape of a well-defined peak in a C_p/T^3 plot with a maximum at about 5 K. The increase of the effective network density gives rise to a slight decrease of the excess LTSH. When scaled by the Debye contribution, the LTSHs of both HPNs result to be very close giving strong evidence that the source of the excess LTSH could be additional low-energy vibrations associated to the monomers building up the polymer network. The comparison between the behaviours of the fragility and the excess LTSH leads us to establish that HPNs do not comply with the trend usually observed in glasses and amorphous linear polymers, where a larger excess of additional low-energy vibrations is found to characterize a stronger system.

Acknowledgements

We wish to dedicate this paper to the memory of Prof. Valery P. Privalko, who inspired this work and provided the samples for the present study. It was a honour and a privilege for us to have known a man of such important achievement and personality, who was always innovative and enthusiastic, open to new ideas and always willing to share his thoughts with colleagues. We also thank Prof. Alexei Sokolov for helpful discussions and assistance with Brillouin measurements.

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L/N	ρ (kg m^{-3})	T_g (K)	$<M_c>_{theor}$ (g mol^{-1})	$<M_R>$ (g mol^{-1})	V_l (m s^{-1})	V_t (m s^{-1})	V_D (m s^{-1})	***m***
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Figure Captions.

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Fig. 1

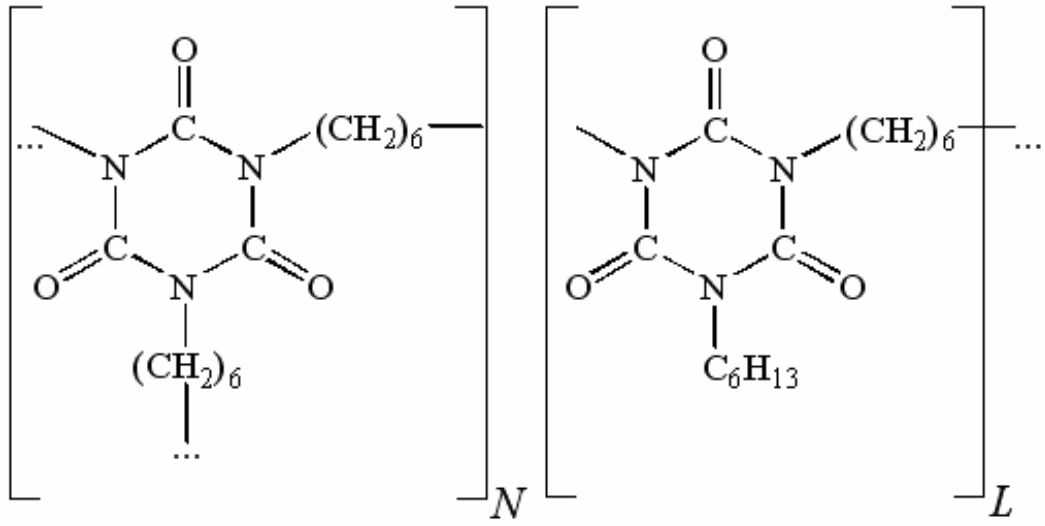

Fig. 2

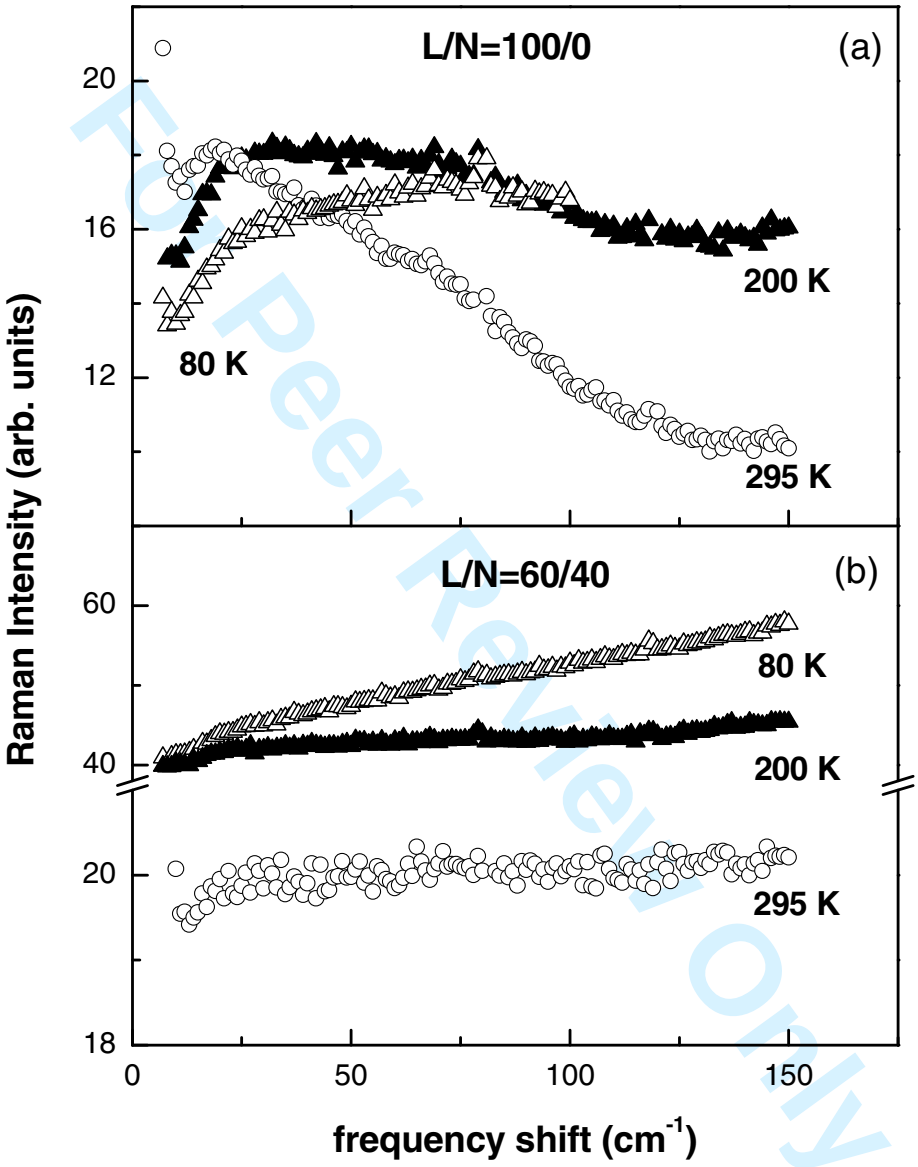

Fig. 3