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Low-temperature excess specific heat and fragility in semicrystalline polymers

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The specific heats of polyethylene oxide (PEO) polymers with two different degrees of crystallinity and of a PEO-NaSCN polymeric complex have been measured between 1.5 and 25 K. The behavior of specific heat with decreasing crystallinity is consistent with the universal feature expected for a solid in which the topological disorder introduces an excess of low-energy vibrational modes: the peak in C_p/T^3, as compared to that revealed in the most crystalline PEO, is enhanced. The specific heat has been interpreted in terms of the contributions from both the crystalline and the amorphous phases characterizing the polymer. The excess specific heat over that provided from the Debye theory has been described by an empirical phonon-fracton density of vibrational states. A density of fracton states with a dimensionality equal to 1 appears to well account for the additional localized vibrations in a polymeric network without sidebonds, such as pure PEO. A comparison between the parameter of ''fragility'' obtained from modeling the mechanical α_a relaxation of the amorphous fraction of the polymers and the excess specific heat has been tried. Within the range of fragilities explored, no definite correlation between the fragility and the density of soft vibrations has been found. [S0163-1829(96)03342-5]

I. INTRODUCTION

Anomalies in the specific heat at low temperatures due to the existence of additional vibrational states besides the acoustic phonons are a dominant feature of polymers. The enhanced low-energy vibrational dynamics producing a broad maximum in the density of vibrational states[1,2] and the excess specific heat in the region between 1 and 20 K (Refs. 3–5) is believed to arise from the amorphous regions of polymeric structures. By low-temperature measurements of specific heat in a simple linear polymer, such as pure polyethylene (PE), Reese and Tucker[3] proved that the characteristic hump in C_p/T^3 decreases with increasing crystallinity degree. They assumed that the specific heat of PE samples with different crystallinity degrees is the result of a linear overlap of the contributions from the crystalline and amorphous fractions. Using this linearity, extrapolation to completely crystalline polyethylene has been tried obtaining a T^3 dependence for temperatures up to about 9 K. This finding appears to be in partial agreement with the theoretical predictions for the vibrational spectrum of a wholly crystalline polymer by Genensky and Newell.[6] This model determines the vibrational density of states (DOS) of a crystalline polymer by considering a semplified set of inter- and intrachain force constants, obtaining frequency regions governed by different power laws ω^{α}. In the framework of this model the specific heat below 25 K is mainly determined by the regions where α is equal to 2 (near ω=0) and 1.5 (for a slightly larger ω). These frequency behaviors of the DOS should correspond to T^3 and $T^{2.5}$ dependences for the specific heat. This statement has been criticized by Tucker and Reese who found in crystalline PE a cubic behavior in the specific heat over a temperature region more extended than might be expected.

Concerning the excess specific heat over that predicted by the Debye theory, it has been clearly proved that it arises from the amorphous regions of the polymer.[3,4] It has been the focus of several theoretical work and can be explained by a sharp increase in the DOS, due to a large number of localized vibrational modes. A phenomenological approach is to consider these modes as independent Einstein oscillators, whose thermal capacity is described by the Einstein function. This interpretation well accounts for the bump in the specific heat, but it is difficult to find for it a convincing microscopic explanation.[3–5,7,8] An elegant theory for the specific heat of amorphous polymers relates its low-temperature behavior to their fractal structure.[9] This model uses the fractal dimension $\bar{d}$ to set the mass scaling (where $\bar{d}<d$, d being the Euclidean dimensionality) and the fracton dimension $\tilde{d}$ to define the vibrations in a fractal structure. The fracton dimension $\tilde{d}$ is related to a characteristic length l in the system. For scale length smaller than l the system shows a fractal character, while it results Euclidean ($d=3$) for distances larger than l. To this characteristic length it corresponds a crossover frequency $\omega_{c0}=(l_0/l)\omega_D$ in the vibrational density of states $g(\omega)$ from Debye like to fracton excitations, where l_0 is an atomic distance setting the shortest length scale in the system and ω_D is the Debye frequency. In the frequency region above ω_{c0}, $g(\omega)$ results proportional to $\omega^{\tilde{d}-1}$, where $\tilde{d}=\bar{d}/a$, a being related to the diffusion constant scaling exponent θ by the relation $a=1+\theta/2$. The exponent θ and consequently a can be evaluated in the limits of low ($a=\bar{d}$) and high ($a=1$) conductivity. The former situation corresponds to vibration propagation just along the polymer chain and gives $\tilde{d}=1$, any deviation from this value ($\tilde{d}>1$) corresponding to the existence of some kind of chain interactions. Following the change in the dimensionality of the polymer, the specific heat will be proportional T^3 ($\omega<\omega_{c0}$) and to $T^{\tilde{d}}$ ($\omega>\omega_{c0}$).

It is worth to emphasize that the presence of a characteristic length in an amorphous system has been introduced and variously interpreted[7,9,10] in order to justify the sharp onset of localized vibrational excitations involving an intermediate scale length and causing a deviation from the behavior expected for the usual acoustic phonons. This length appears to be a general feature of the topological disorder present in the amorphous systems, although its order of magnitude can depend on the stoichiometry. Many of the commercially available polymers are partially crystalline. The presence of amorphous regions strongly affects the physical properties of the polymer, since a given physical property is now an average of the corresponding values for the amorphous and the crystalline regions. The present concern is to report a study in samples of polyethylene oxide (PEO) with different crystallinity degrees in order to understand as the topological disorder of the amorphous structures can influence the vibrational anomalies of polymers.

By this point of view PEO is an interesting prototypical example of a long chain nonreticulated polymer.[11] It consists of a double helix chain with an interior channel lined by oxygen atoms which has a radius of ~1 Å. In the crystalline state the PEO molecule contains seven chemical units (-CH_2CH_2O-) and turns twice in a periodic length of 19.3 Å. The absence of cross-links or side chains, usually present in many of the polymers studied at low temperatures,[8] eliminates the possibility of anomalies associated with particular details of the structure.

Furthermore the correlation between the ‘‘fragility,’’ determined by an appropriate mechanical study of the primary relaxation, and the excess of low-energy vibrations has been analyzed in polymers of pure PEO and a salt-PEO complex. This paper attempts to explore the range of validity of a recent suggestion which proposes that the complexity of the vibrational characteristics determining the low-temperature anomalies of an amorphous solid could be related to the ‘‘strong’’ or ‘‘fragile’’ character of the corresponding glass-forming liquid.[12]

II. EXPERIMENTAL DETAILS

Commercial samples of polyethylene oxide (M. W. 600 000) obtained from Aldrich were purified by filtration and ion exchange of an aqueous solution passed through appropriate H^+ and OH^- resins. The solvent was removed by drying the polymers under vacuum at 50 °C for 72 h. The samples obtained were stored in a vacuum desiccator. The as-prepared polymers were subjected to two different thermal procedures in order to obtain samples with distinct crystallinity degrees. The quenched polymers (q-PEO) were compression moulded between two disks of Teflon at a temperature of about 373 K, above the melting temperature of PEO, and then rapidly cooled in liquid nitrogen. All procedural steps were carried out under a controlled atmosphere of nitrogen. The quenched samples showed no visible degradation.

The annealed polymers (a-PEO) were obtained by maintaining the as-prepared samples for 72 h at a temperature of about 330 K, just below the melting temperature of PEO. The sample of $(PEO)_{0.78}(NaSCN)_{0.22}$, 0.22 being the proportion between the polymer repeat units (-CH_2CH_2O-) and the salt, has been prepared and stored by using the same procedure described elsewhere.[13]

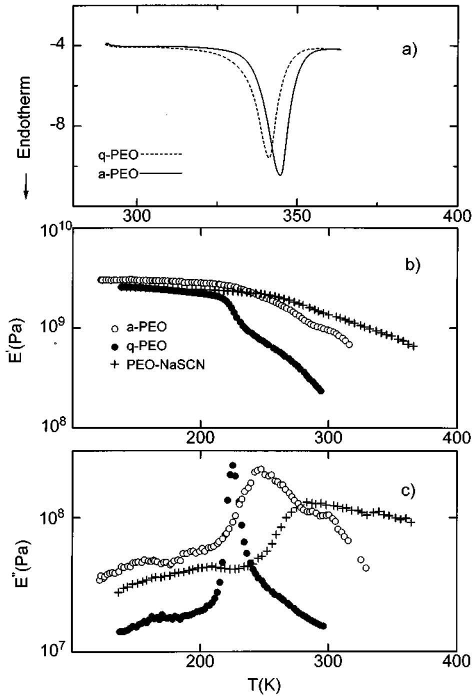

FIG. 1. (a) DSC thermograms in quenched and annealed samples of PEO; temperature dependence of the (b) real and (c) imaginary parts of the complex mechanical modulus in pure PEO and PEO-NaSCN polymers. The mechanical frequency is 30 Hz.

The thermograms of the PEO samples have been determined using a Setaram differential scanning calorimeter (DSC) at heating rate of 5 K/min. The degree of crystallinity has been evaluated by comparing the heats of fusion of q- and a-PEO samples to that of a wholly crystalline PEO ($H_f=205.0$ J/g).[14] DSC traces of q- and a-PEO samples are reported in Fig. 1(a), showing a distinct endothermic peak which is associated with the melting of crystals building up the polymers. It appears clearly that the heat of fusion of a-PEO is larger than that of q-PEO: the corresponding values are $H_f=145.4$ J/g and $H_f=124.4$ J/g. The obtained values of the degree of crystallinity are, respectively, $X=0.71$ and $X=0.61$.

The revealed variation of the degree of crystallinity is also supported by the analysis of the dynamic Young modulus E' in the rubber region, see Fig. 1(b), where the stiffness of semicrystalline polymers is essentially determined from the crystalline fraction. The real and imaginary part of the complex elastic modulus, $E^*=E'+iE''$, have been measured between 120 and 350 K using a dynamic mechanical thermal analyzer driven at a frequency varying in the range between 0.3 and 30 Hz.

In Fig. 1(b) the temperature behaviors of E' are shown for all the samples. It appears clearly that above the glass transition temperature T_g, which is marked by the drop in the modulus associated to the glass-rubber transition, the magnitude of E' in a-PEO is appreciably larger than in q-PEO.

Furthermore the highest value of the rubber modulus (1.33 GPa) in $(PEO)_{0.78}(NaSCN)_{0.22}$, as compared to those of q-PEO (0.22 GPa) and a-PEO (0.89 GPa), can be correlated with a largest degree of crystallinity introduced by the salt addition (values taken at $T=295$ K and $f=3$ Hz).[13] In fact it has been proved that, at high salt concentrations (mol. fract.~0.2), the polarizing power of the alkaline salt molecules, which are coordinated to the neighboring oxygens of the main chain, enhances the intermolecular forces favoring the formation of a stoichiometric salt-polymer crystalline phase.[13,15] To better illustrate the effects of the annealing and the salt addition on the degree of crystallinity of these polymers, the experimental results for the temperature dependence of E'' of 30 Hz mechanical waves for the same samples are compared in Fig. 1(c). As the temperature is increased from 120 K to about 200 K, E'' increases exhibiting the γ-relaxation peak due to local segmental motions within the main chain.[13] Above this region E'' increases with a small slope up to about 210 K and, for higher temperatures, shows the broad peak typical of the glass to rubber transition (the α_a relaxation). The maximum shifts to higher temperatures as the mechanical driving frequency is increased. It can be seen that the α_a peaks are strongly affected from the increased degree of crystallinity introduced by the annealing and the salt addition: the strengths decrease showing the largest reduction in the polymeric complex and the maximum shifts to higher temperatures, pointing to a corresponding elevation of the glass transition.

The specific heat was measured in the range between 1.5 and 25 K using an automated calorimeter which operated by the thermal relaxation method. A surface mounting device resistor as the temperature sensor and a constantan strain gauge as the heater element were attached to the opposite faces of the samples using a cyanoacrilate resin. The experimental error in the measured specific heat has been evaluated as about 2%. The density was measured at room temperature by weighing the samples in air and in decane.

III. RESULTS AND DISCUSSION

A. Crystallinity and low-temperature specific heat excess of PEO

The experimental results obtained for the specific heat C_p of q-PEO polymer between 1.5 and 25 K are plotted in Fig. 2(a). The specific heats of a-PEO and $(PEO)_{0.78}(NaSCN)_{0.22}$ polymers show a similar behavior. These specific-heat results, when plotted as C_p/T^3, show behaviors very different from the Debye prediction, see Fig. 2(b). As the temperature is reduced the specific heat of all the polymers deviates markedly from a cubic temperature dependence showing an excess specific heat having the shape of a well-defined peak in a C_p/T^3 plot. It appears that the crystallinity influences appreciably the specific heats of pure PEO samples in the temperature region below 14 K, the heat capacities of both the polymers becoming equal slightly above 14 K. The excess specific heat is strongly decreased in the PEO-NaSCN complex which, as discussed in the previous section, is the most crystalline system. These peculiarities give evidence of the fact that the source of the anomalous specific heat lies in additional localized vibrational states whose density decreases with increasing degree of crystallinity.

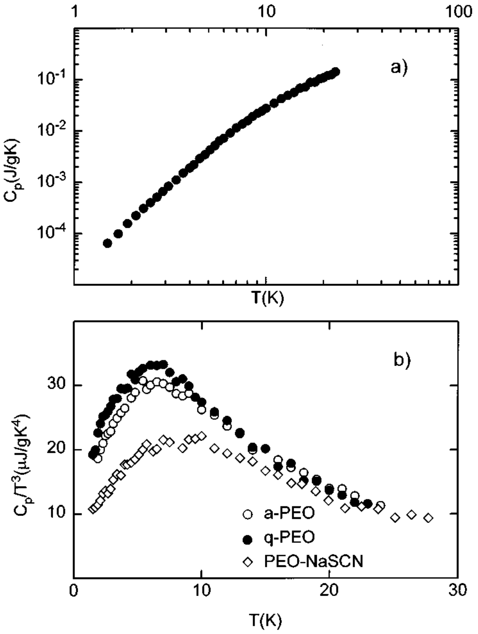

FIG. 2. (a) The specific heat of q-PEO sample measured between 1.5 and 25 K; (b) The temperature dependence of C_p/T^3 in pure PEO and PEO-NaSCN polymers.

The present concern is to report a study of the variation of the specific heat with the crystallinity and, as a matter of the fact, we analyze the behavior of C_p in the temperature region where the PEO polymers show different heat capacity ($T<14$ K). The PEO-NaSCN polymer is not considered in the following analysis as a consequence of its structural complexity which makes difficult the correlations between vibrational modes and structure. Further considerations on the specific heat of this sample are made in the next section, where the connection between the fragility and the excess of low-energy vibrations of amorphous systems is discussed.

The dependence of specific heat on crystallinity has been accounted for by considering C_p as given by the overlap of the heat capacities from the crystalline (C_{cr}) and amorphous (C_{am}) regions weighted by the corresponding crystallinity fractions. This interpretation has been successfully applied in the analysis of the low-temperature specific heat of pure PE,[3] and can be represented in terms of the following expression:

$$C_p=XC_{\mathrm{cr}}+(1-X)C_{\mathrm{am}}. \tag{1}$$

Since it has been proved that pure crystalline PE is characterized by a cubic temperature dependence for C_{cr} over the temperature interval up to about 12 K, we assume that C_{cr} for pure PEO can be evaluated by

$$C_{\mathrm{cr}}=\left[9\nu R\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_D/T}\frac{x^4\exp(x)}{[\exp(x)-1]^2}\,dx\right], \tag{2}$$

where θ_D is given by

$$\theta_D=\left(\frac{6\pi^2N_A\rho\nu}{P_M}\right)^{1/3}\frac{\hbar}{k_b}\,\overline{v}.$$

Here N_A is Avogadro's number, ρ is the density, ν is the number of atoms per formula unit, $\overline{v}$ is the average velocity of sound, P_M is the molecular weight, and k_B is the Boltzmann constant. The contribution $C_{\rm am}$ of the amorphous fraction has been analyzed in terms of a simplified phonon-fracton model, as proposed by Avogadro *et al.*[16] In this model the acoustic contribution, which governs the DOS up to the crossover frequency $\omega_{\rm co}$, should produce a cubic dependence for the specific heat. The noncubic dependence of the specific heat arises through a density $D_{\rm fr}(\omega)$ of fracton states which accounts for the excess localized vibrational states and has a frequency dependence $\omega^{\tilde{d}-1}$.

Recent measurements[17] of low-frequency Raman scattering in epoxy resins with a high degree of structural connectivity due to crosslinks between the chains gave a value for $\tilde{d}$ of ~1.7. This finding has been interpreted as the result of the occurrence in the system of relevant interchain interactions.

In the framework of the empirical correlation between $\tilde{d}$ and the intensity of interchain interactions, we think it quite reasonable that pure PEO, which is a linear polymer having weak interchain interactions, can be assumed as a polymeric system characterized by $\tilde{d}=1$. Of course this assumption could appear quite strong, because the value of $\tilde{d}$, also in a linear noncrosslinked polymer as PEO, can be slightly different from 1. A proper determination of $\tilde{d}$ should require the determination of $g(\omega)$ by inelastic neutron experiments, which are not available in PEO. Consequently this choice provides a convenient algorithmic basis for reproducing the behavior of localized vibrational states, keeping in mind that values of $\tilde{d}$ little higher than 1, corresponding to a slightly frequency-dependent $D_{\rm fr}(\omega)$, do not alter appreciably the analysis of the specific-heat data. It is worthwhile to note that, in the context of these assumptions, the present analysis can be compared to an early model of the specific heat in polymers by Tarassov.[18] In his simple continuum model Tarassov associates the low-frequency region of the spectrum to three-dimensional vibrations over the chains and the high-frequency part to one-dimensional vibrations propagating within the polymeric chains. The value of $\tilde{d}=1$ corresponds to presume the limit of low conductivity for fractons, which leads to the following expression for $C_{\rm am}$:

$$C_{\rm am}=\left[9\nu R\left(\frac{T}{\theta_D}\right)^3\int_0^{\theta_{\rm co}/T}\frac{x^4\exp(x)}{[\exp(x)-1]^2}\,dx\right.$$
$$\left.+9\nu R\left(\frac{T}{\theta_D}\right)Q\int_{\theta_{\rm co}/T}^{\theta_M/T}\frac{x^2\exp(x)}{[\exp(x)-1]^2}\,dx\right],\qquad(3)$$

where the high-frequency cutoff ω_M of the spectrum is determined by the normalization condition

$$\int_0^{\omega_M}D(\omega)d\omega=3N_A\nu(1-x)\qquad(4)$$

and Q is a dimensionless constant equal to $D_{\rm fr}(\omega)k_B\theta_D/9N_A\nu$. In principle the present description of the heat capacity of semicrystalline polymers implies the use of different Debye temperatures for the amorphous and crystalline fractions. In fact a wholly crystalline polymer is expected to display a higher θ_D than that characterizing the amorphous form of the same polymer, being the θ_D of samples with decreasing degree of crystallinity an appropriate overlap of the two contributions.[3] This peculiarity, however, would increase the number of fitting parameters and so as to reduce them we introduce the restriction to use only the θ_D describing the average vibrational behavior of the whole polymer.

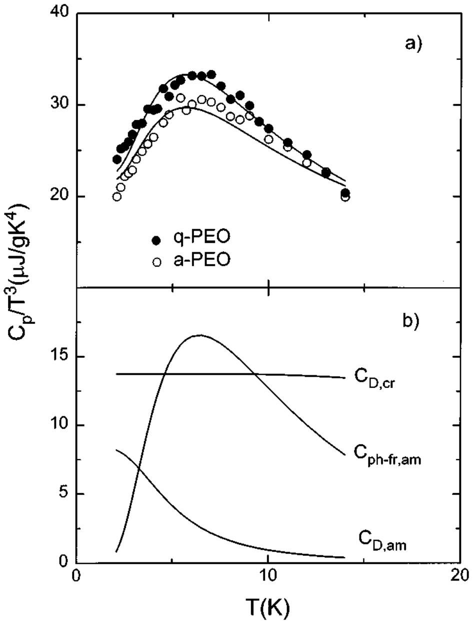

FIG. 3. (a) Theoretical fit by Eq. (1) (see text) of the temperature dependence of C_p/T^3 in samples of q- and a-PEO between 2.0 and 14 K; (b) Debye-like phonon and fracton theoretical contributions from the crystalline ($C_{D,\rm cr}$) and amorphous ($C_{D,\rm am}+C_{\rm fr,am}$) phases of q-PEO, weighted by the crystallinity fraction.

A further contribution to the specific heat can arise from the ‘‘two-level systems.’’ This term, universally observed in amorphous solids[19] and polymers,[4,20] is approximately linear in temperature and becomes dominant below 1 K. It is associated with the tunneling motions of group of atoms (or single atoms) between different positions available in the network. In a plot of C_p/T^3 it should result in an upturn by decreasing temperature below about 1 K. In the present data, which extend only to 1.5 K, there is no evidence for an upturn, so we are unable to evaluate the magnitude of this linear term. However there are evidences in polyethylene terephtalate[4] and in Teflon[21] that this contribution becomes rapidly very small at $T>1$ K. Consequently it is expected that it can be completely neglected for $T\geqslant 2$ K.

The best fit to experimental data obtained by considering the addition of the crystalline and amorphous contributions to the specific heat [Eq. (1)] of q-PEO over the 2–14 K temperature interval is shown in Fig. 3(a). The curves, labeled as $C_{D,\rm cr}$, $C_{D,\rm am}$, and $C_{\rm fr,am}$ in Fig. 3(b), correspond to the Debye and fracton contributions assessed by Eqs. (2) and (3), respectively, for the crystalline and amorphous phases. The values obtained for the parameters are $\theta_D=239.4$ K, $\theta_{\rm co}=22.1$ K, $\theta_m=70$ K, $Q=5.26\times10^{-2}$. It is to be emphasized that the obtained values define a fracton spectral density in the interval between ~1.9 and 6.0 meV. This energy range corresponds quite closely to the region in the inelastic neutron-scattering spectra of amorphous polymers where an excess of low-energy excitations is usually observed.[2,22]

By the calculated values of $\theta_{\rm co}$ and θ_D and by using for l_0 an average value (1.49 Å) between the C-C and C-O distances, a value of 16.3 Å for the characteristic length l has

TABLE I. Values of the fragilities m and of the primary relaxation parameters β, B, T_0, τ_0, Δ, and of anharmonicity coefficient b'. The values of density ρ refer to room temperature.

Samples	ρ (g cm^{-3})	**T**$_g$ (K)	**m**	β	**B** (K)	**T**$_0$ (K)	τ_0 (10^{-13} s)	Δ	**b**$'$ (10^{-3} GPa K^{-1})
q-PEO	1.23	213	165	0.37	1891	155	0.15	4.15	6.47
a-PEO	1.29	228	110	0.13	2806	155	6.87	1.96	2.10
$(PEO)_{0.78}(NaSCN)_{0.22}$	1.31	251	79	0.16	3192	168	1.27	0.86	2.78

been obtained. In order to check the validity of this theoretical approach the parameters obtained by the fit of C_p for q-PEO, except the Debye temperature θ_D, have been used to reproduce the specific heat of the a-PEO sample, which is characterized by a crystallinity fraction $X=0.71$. θ_D has been varied to account for its dependence on the crystallinity degree, as revealed by calorimetric[3] and ultrasonic[23] measurements in low- and high-density pure PE.

In the absence of a complete set of acoustic data on longitudinal and transverse sound velocities in pure PEO at low temperatures, we used an alternative procedure described in the following. It allows us to obtain a rough evaluation of $\theta_{D,a}$ for a-PEO by the knowledge of $\theta_{D,q}$ for q-PEO and of the low-temperature values of the Young modulus for both the samples.

The expression of the Young modulus in terms of the longitudinal (v_l) and transverse (v_t) sound velocities is

$$E' = \rho v_t^2\left(3 - \frac{v_t^2}{v_l^2 - v_t^2}\right). \tag{5}$$

For a given material and at a given temperature $v_l = \gamma v_t$, where γ ranges between 2 and 3.5 for a relevant number of different polymers near room temperature.[23] Consequently, it is also possible to write Eq. (5) in the form

$$E' = \rho v_t^2\left(3 - \frac{1}{\gamma^2 - 1}\right). \tag{6}$$

The room-temperature values of the density of q-PEO and a-PEO are quite different (see Table I). However it is expected that, by crossing the glass transition region, this difference should become negligible as a consequence of a larger volume contraction shown from the most amorphous polymer. So assuming that the surely slight changes of the density ρ and of γ due to the small increase of the crystallinity from q-PEO to a-PEO can be neglected, a simple relation is obtained between the ratio of Young moduli and the ratio of transverse sound velocities for both the polymers: $E'_a/E'_q = v_{t,a}^2/v_{t,q}^2$. The proportionality between v_t and v_l also allows us to obtain the relation $v_{t,a}/v_{t,q} = \theta_{D,a}/\theta_{D,q}$, which leads to $\theta_{D,a}/\theta_{D,q} = (E'_a/E'_q)^{1/2}$. By extrapolating down to 0 K the linear behaviors of E' in both the polymers [see Fig. 1(b)], we get a value of 1.026 for E'_a/E'_q and of 1.013 for $\theta_{D,a}/\theta_{D,q}$, which corresponds to a value of 242.4 K for $\theta_{D,a}$. By inserting this value and the parameters derived for q-PEO in Eq. (1), the curve, shown in Fig. 3(a) as a solid line over the experimental specific heat of a-PEO, has been obtained. It results that the same theoretical parameters obtained from the fit of the experimental data of q-PEO permit us to reproduce quite closely the shape and the magnitude of the specific heat of a-PEO. This finding seems to prove the validity of the approach used to evaluate the low-temperature specific heat in these semicrystalline polymers.

There is a quite close correspondence between the characteristic length l and the length of the structural repeat unit which characterizes the PEO in the crystalline state. This finding, also observed in a semicrystalline sample of poly(vinylchloride),[24] could be interpreted as an evidence of fracton localization in fractal clusters within amorphous regions of the polymer where distorted structural units, similar in size to those characterizing the crystalline phase, are preserved.

Despite the ability of the fracton model in reproducing the excess specific heat of semicrystalline PEO, we remark that it has been used in a general context as a theory of localization and, most importantly, in consequence of the fractal character of polymers. The latter circumstance implies that the randomly coiled chains must be self-similar in a range of dimensions lower than the characteristic length l.

Good fits below 14 K were also obtained by the addition of a Debye term, which evaluates the contribution of the acoustic phonons in the system, and two Einstein functions of the form $C_E/R = nE(\theta_E/T)$. In the fits it was allowed that both the characteristic temperature θ_E and the coefficient n to vary. The obtained values of the parameters for both the polymers are: q-PEO, $\theta_{E1}=13.6$ K, $\theta_{E2}=34.2$ K, $n_1 = 7.33\times10^{-3}$, $n_2=15.83\times10^{-2}$; a-PEO, $\theta_{E1}=13.6$ K, $\theta_{E2}=34.2$ K, $n_1=5.28\times10^{-3}$, $n_2=15.22\times10^{-2}$.

Since the number of the chain-end groups is of the order of $\sim10^{18}$ cm^{-3}, the values found for n exclude them as possible microscopic origin for the Einstein contributions. Furthermore it is difficult to associate the frequencies corresponding to the characteristic temperatures θ_E to particular units in a polymer without side groups, such as PEO. Nevertheless the validity of the Einstein terms in accounting for the excess specific-heat confirms, once again, the localized nature of the additional vibrational modes.

B. Fragility and excess of low-energy vibrations in semicrystalline polymers

Recently a possible correlation between the dynamics of a glass-forming liquid at the glass transition and the low-temperature anomalies has been proposed.[12] In this scheme the ratio between the density of relaxations and the excess of low-energy vibrations arising from the disordered topology of an amorphous structure is regulated by the ''strong or fragile character'' of the corresponding glass-forming liquid.[25] ''Strong'' liquids should be characterized by a larger number of soft vibrations than ''fragile'' liquids where the relaxations are the dominant feature. The memory of this scenario should be preserved in the glassy state determining the magnitude of the linear and ''excess'' (the bump) specific heat, respectively, below and above 1 K.

To evaluate the degree of fragility of these polymers, a study of the primary relaxation has been performed by analyzing the temperature dependence of the complex mechanical modulus $E^* = E' + iE''$. The behavior of E' has been used to determine the parameter β which accounts for the nonexponentiality of the α_a relaxation; then, by the values of β the product $(\omega\tau)_M$ between the angular frequency ω and the relaxation time τ, at the temperature at which E'' has its maximum value, has been estimated correctly[26] [it is to be noted that $(\omega\tau)_M = 1$ only for a Debye or single relaxation time process]. Considering the curves of $E''(T)$ at different frequencies, the behavior of the relaxation time in a temperature range above T_g is derived and the fragility m or the correlated strength parameter D can be calculated.[27] The relations defining m and D are

$$m = \frac{d \log\tau}{d(T_g/T)_{T=T_g}} \quad \text{and} \quad m \approx 16 + \frac{590}{D}. \tag{7}$$

The ''fragility'' has been introduced by Angell[25] to classify the glass-former liquids in terms of the nature of bonds present in the system. High values of D (~ 100) set covalently bonded liquids and low values (<10) the weak molecular and simple liquids. Now it has been shown[28] that, in PEO-salt solid blends, the behavior of E' in the region of the α_a relaxation can be described by the overlap of the anharmonic interactions of vibrational modes in both the amorphous and crystalline fractions of the polymer and of the dispersion due to the cooperative relaxation in the amorphous phase only. In the framework of this approach the modulus $E'(T)$ can be written as

$$E' = E'_{\text{anh}}(T) + E'_{\text{rel}}(T). \tag{8}$$

The first term in the right-hand side of Eq. (8) accounts for the temperature dependence of the elastic modulus due to the vibrational anharmonicity. In the high-temperature region, where all the vibrational modes are excited, it approaches the linearity and can be expressed by

$$E'_{\text{anh}}(T) = E_0 - b'(T - T'_0), \tag{9}$$

where E_0 is the value of E' at the lowest temperature T'_0 in the experiment. The parameter b' is mainly determined by the Grüneisen coefficients which account for the anharmonic interactions between the vibrational modes.[29]

The relaxation term in Eq. (8) can be evaluated by the Fourier transform in the frequency domain of the stress relaxation function $E'(t)$ (Ref. 30)

$$E'(t) = E'_0 + (E'_\infty - E'_0)\phi(t), \tag{10}$$

where E'_∞ and E'_0 are the high- and low-frequency limits for the modulus, respectively, and the relaxation function $\phi(t)$ represents the change of the stress with the time following a perturbation. In order to account for the marked nonexponentiality characterizing the α_a relaxation in polymers, the ''stretched-exponential function'' $\phi(t)$ of Kolrausch-Williams-Watt has been used[31]

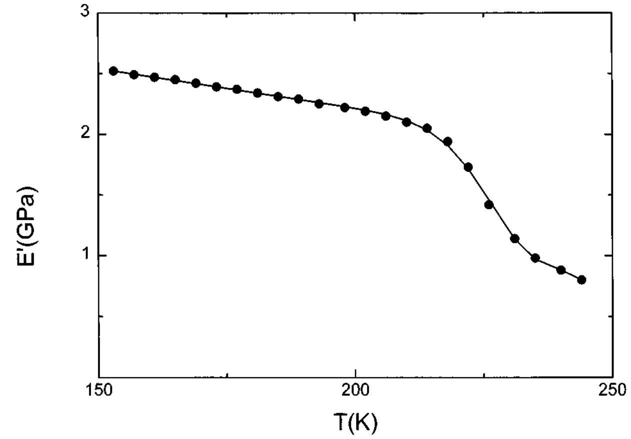

FIG. 4. Theoretical fit (solid line) by Eq. (8) of the temperature behavior of the elastic modulus below and in the region of the α_a relaxation for pure q-PEO. The mechanical frequency is 30 Hz.

$$\phi(t) = \exp\left[-\left(\frac{t}{\tau}\right)^\beta\right], \tag{11}$$

τ being the relaxation time and β is a parameter ranging in the interval $0<\beta<1$. Above T_g polymers behave as non-Arrhenian liquids[32,33] and the temperature dependence of their structural relaxation time can be well described by the Vogel-Tamman-Fulcher relation

$$\tau = \tau_0 \exp\left(\frac{B}{T - T_0}\right), \tag{12}$$

where τ_0, B, and T_0 are empirical constants. This relation expresses the temperature dependence of the structural relaxation time τ, by using the ideal glass-transition temperature T_0 (closely correlated to T_g).

The experimental data have been analyzed by combining the contributions of the anharmonic effects and of the relaxation process, as given by the Eqs. (9) and (10) and using the same procedure elsewhere described.[28,34] The anharmonic parameter has been directly evaluated through the slope of $E'(T)$ in the glassy region, because, in these polymers, the dispersion due to the low-temperature γ relaxation does not affect the linear trend of the modulus. The relaxational drop in the modulus, derived by subtracting the anharmonic contribution from the experimental data,[34] has been analyzed by the Fourier transform of $E'(t)$, as given by Eq. (10), in a least-squares fit using a minimum search program with $(E_\infty - E'_0)$, β, B, T_0, and τ_0 as free parameters. The relaxation strength, as given by $\Delta = (E'_\infty - E'_0)/E'_0$, and the other parameters, resulting from this analysis, are given in Table I together with the values of the anharmonicity coefficient b'. A typical fit of relaxational modulus is shown by a solid line in Fig. 4. The good fit to the shape of the experimental results and the finding that the theoretical parameters obtained from the fits to the experimental data at different frequencies

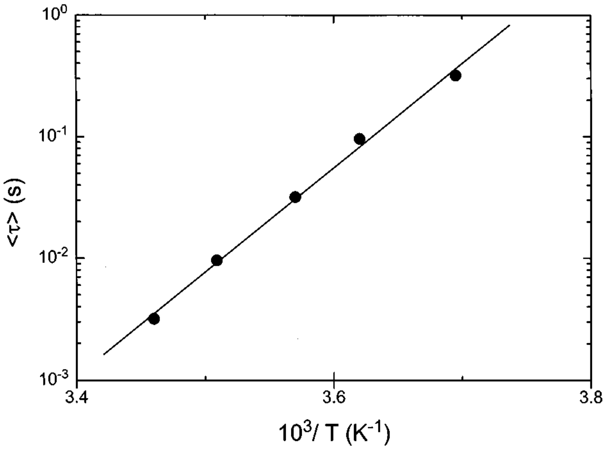

FIG. 5. Logarithm of the average α_a-relaxation time $\langle\tau\rangle$ vs the inverse temperature.

are the same within a few percent prove the validity of this theoretical approach.

An interesting feature is that anharmonicity parameter b' and the nonexponentiality parameter β decrease with increasing crystallinity in the system. Such a peculiarity, already observed in a wide range of semicrystalline polymers,[28,34] can be correlated to the reduction of the free volume present in the system and of the constraints imposed by the crystalline regions on the long-range segmental motions of the chains in the amorphous phase.

As discussed, the temperatures of α_a peaks at different frequencies combined with the values of β permit an accurate evaluation of the average relaxation time over the frequency range explored. As a consequence of the restricted temperature range above T_g the relaxation time τ follows an Arrhenius behavior, see Fig. 5 where the logarithm of τ vs the inverse temperature in one of the polymer studied is reported as typical. In this case, as suggested by Böhmer *et al.*,[27] the fragility can be calculated by the relation $m = E_A/(RT_g \ln 10)$, E_A being interpreted as an apparent activation energy of the process only. A typical fit by the Arrhenius law to the data of τ deduced by the mechanical experiments is shown as a solid line in Fig. 5. The values obtained for the fragility parameter m are inserted in Table I. In the calculations the glass transition temperature T_g has been taken as the temperature at which τ has a characteristic value, $\tau(T_g) = 100$ s,[35] because mainly in the most crystalline polymers the glass transition range is broadened, making the calorimetric effect unobservable. The values of m place the amorphous phase of these systems in the ''fragile'' range, except the PEO-salt complex which appears to be intermediate between fragile and strong glass formers. The behavior of m is strictly correlated to the growing degree of crystallinity and supports the reduction of the average segmental mobility of the amorphous polymeric chains. The growing amount of crystalline regions, introduced in pure PEO by annealing or salt addition reduces the long-range movements of the chain and the fragility of the system.

Now the decrease of the fragility is not related to a corresponding increase of the excess specific heat in these semicrystalline polymers, the strongest polymer (PEO-NaSCN) showing the lowest excess C_p, see Fig. 2(b). The result of subtracting the Debye contribution $C_{D,\mathrm{am}}$ from the total heat capacity ascribed to the amorphous phase C_{am} [the experimental excess heat capacity normalized to the amorphous fraction $(1-X)$] reveals excess contributions which are close for q- and a-PEO. The amount of amorphous phase and the values of $C_{D,\mathrm{cr}}$ and $C_{D,\mathrm{am}}$ are not known in PEO-NaSCN, but this polymer shows an α_a-relaxation strength which is only little lower than that of a a-PEO and a Young modulus which, at low temperatures, appears to become quite close to those of q-PEO and a-PEO [see Figs. 1(b) and 1(c)]. Consequently it is not expected that the amount of amorphous phase (as related to the α_a-relaxation strength) and the Debye temperature can be so different from that of pure PEO to balance a difference in the excess C_p, which is about 10 μJ/g K^4 in the region of the maximum. It can be concluded that the connection between fragility and excess of specific heat, arising from additional low-energy vibrations, is rather obscure in these semicrystalline polymers. Even if a wider range of polymers needs to be explored to get more conclusive insights, no clear correlation between the excess density of soft vibrations and the fragility appears to result in PEO-based semicrystalline polymers.

IV. CONCLUSIONS

The specific heat C_p in samples of semicrystalline PEO with two different crystallinity degrees and of a PEO-NaSCN polymeric complex has been measured in the temperature range 1.5–25 K. It has been found that the main effect of increasing the crystallinity degree is the decrease of C_p below 14 K, as a consequence of the corresponding reduction of the excess specific heat due to the amorphous fraction. In the range of crystallinity explored for pure PEO polymers the specific heat can be given by a linear overlap of the contributions from the crystalline and amorphous phases of the samples, weighted by the parameter which expresses the crystallinity fraction. The contribution from the crystalline phase has been evaluated by the usual Debye theory and that from the amorphous phase by an empirical phonon-fracton DOS which accounts for a fractal-like behavior of the polymeric backbone for a length scale lower than a characteristic length l. A power-law dependence, $\omega^{\tilde{d}-1}$, has been used for the fracton density of states assuming a fracton dimensionality $\tilde{d} = 1$. Such a value corresponds to one-dimensional vibrations which are localized within the polymer chain. This low conductivity limit for the vibrations is suggested to be consistent with the molecular structure of PEO which is characterized by quite weak interchain interactions as compared to the intrachain ones. This theoretical approach permits us to account for the variation of the specific heat following the increase of the degree of crystallinity of the polymer and demonstrates that the source of the excess specific heat lies in additional localized vibrational states arising from the amorphous phase. Finally it has been shown that the decrease of the ''fragility'' of the amorphous fraction of pure PEO, obtained by annealing or by the addition of an alkaline-metal salt, does not correspond to a clear indication for an increase of the density of soft vibrations which cause the excess specific heat at low temperatures.

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