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Rounding effects on doped sulfur's living polymerization: The case of As and Se

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The role of "impurities" or doping on the living polymerization of sulfur has been put under focus by means of a temperature dependent Raman study of the As_xS_{100-x} and Se_yS_{100-y} ($x=0.5,2,5$ and $y=2,5$) systems. Reduced isotropic Raman spectra have been analyzed properly to yield the temperature dependence of the extent of polymerization, $\phi(T)$, in each case. The general trend is that the presence of either As or Se facilitates the monomer→polymer transition of sulfur giving rise to three major effects: (i) A reduction of the transition temperature T_{tr} from neat sulfur's $T_\lambda \approx 159\ ^\circ C$ to an extent which depends on the doping level and the type of the impurity, i.e., As or Se. (ii) The presence of As atoms engenders severe "rounding" on the sharpness of neat sulfur's λ-shaped transition as evidenced from both the less abrupt increase of $\phi(T)$ function and the wider and more symmetrical shape of the calculated heat capacity peak. In contrast, in Se-doped mixtures, the characteristics of a second order phase transition seem to be retained. (iii) The As-doped mixtures exhibit appreciable polymer content at temperatures below T_{tr}, whereas in Se doping the low temperature behavior of $\phi(T)$ resembles that of neat S. Thermodynamic parameters concerning the propagation step of sulfur's polymerization reaction have been also calculated demonstrating the apparent reduction of the associated enthalpy with increasing the doping level of As and its approximate invariance with respect to Se doping level. Finally, an examination of the depolarization ratio of the scattered light for the mixtures studied in this paper demonstrated subtle but systematic changes, when crossing the transition temperature, originating from local structural changes associated with the polymerization process.

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I. INTRODUCTION

There has recently been strong renewed interest on aggregation phenomena in condensed matter physics[1–3] and in particular on the issue of living polymerization concerning inorganic, organic, and biological substances.[4–6] Many-body effects in the condensed state become increasingly important under particular circumstances forcing the constituent particles (atoms and/or molecules) to cooperate in the formation of aggregates. Living polymerization is a particular type of aggregation for which an increased tendency of chemical bond formation (between atoms) under certain physicochemical conditions exists. Generally, polymerization is a combined process involving three hierarchical stages: the initiation, the propagation, and the termination. If the last stage, i.e., termination, is avoided then the chainlike structure formed is called a "living polymer." The simplest and most typical kinds of aggregation taking place in living polymerization are the ones involving chainlike configuration of the aggregated molecules. Elemental sulfur is a characteristic paradigm of inorganic substances that exhibit a thermoreversible polymerization with increasing temperature. In particular, above the transition temperature $T_\lambda \approx 159\ ^\circ C$ the opening of S_8 rings leads to an abrupt polymer formation, a process that strongly influences various important physicochemical properties of the system, such as the viscosity and the heat capacity, the values of which exhibit substantial changes; the former shows an increase of almost four orders of magnitude and the latter displays a λ-shaped discontinuity.[4–6]

Recent experimental achievements in living polymerization (see Refs. 4–6) of organic and biological molecules have triggered new theoretical approaches.[1–3,7,8] Specifically, Dudowicz, Freed, and Douglas (DFD) (Ref. 1–3) have worked out a mean field lattice model (Flory-Huggins-type lattice model) for nonzero initiator concentration ($r \neq 0$), emphasizing the role of the latter on the "rounding" of the polymerization transition. Parenthetically, "rounding" is used to express the smearing of the sharp changes observed in the temperature dependence of various physical properties around a second-order-type transition point. Even for small r the polymerization transition does not exhibit the singular variations describing second-order phase transitions. On the contrary, a moderately sharp clustering transition exists. The elimination of singular property variations (typically associated with second-order phase transitions) results in new features that are associated with the analytic property variations of the closely related "rounded" transitions. It should be noted that "rounding" effects are not necessarily caused by some initiator molecules; they are expected to be a general property of dynamical particle clustering transitions, appearing also in the case when the size of the polymeric clusters is limited by some processes.

The key parameter in a polymerization transition is the polymer content ϕ and in particular its temperature dependence. ϕ is defined as the fraction of S atoms participating in polymeric species. External stimuli can severely affect many properties of polymerization transitions, especially the magnitude of ϕ and its temperature dependence. First, temperature plays the major role and in fact acts as the initiator in the case of neat sulfur's polymerization transition.[9,10] The driving force for polymerization is the decrease in system's enthalpy when bond-formation processes reverts monomers to polymers. Moreover, polymerization processes can also occur under condition of increasing enthalpy, especially when the entropy gain compensates the potential energy disadvantage of the polymer phase. Then, polymerization takes place above a minimum temperature usually called the *floor temperature*; this is the case of liquid sulfur. A detailed Raman spectroscopic study of neat sulfur's polymerization transition can be found elsewhere.[11] Secondly, confining a liquid in a porous glass with small pore diameters is a process causing "rounding" as a result of limited growth of polymeric species; this is the result of the appreciable delay of the polymerization transition and the concomitant shift of the corresponding transition temperature to higher values. Details of "rounding" effects under geometrical confinement have been presented in Ref. 12. Thirdly, the presence of initiators (molecules usually incorporated into the monomeric phase to commence and facilitate polymerization) has profound influence on the features of the transition. However, as it will become clear in the next sections, for the cases studied in the present work the initiators or better "impurity" atoms or "dopants" have also an active role in the final molecular conformation of the polymerized phase. In this sense, the term initiator is not the most appropriate. It is however justified because they are responsible for the onset of the polymerization below the T_λ of neat liquid sulfur. We have to stress that in the DFD theory the concentration of polymer chains depends on the concentration of initiators obeying Eq. (4) in Ref. 1. In our case this does not apply since, as mentioned above, temperature is essential for the initiation of the polymerization. Therefore, dopants have a somewhat different role and hence only on a qualitative level the comparison can be made as will become clear in the following sections. The initiators used in this work are the twofold and threefold coordinated atoms, Se and As. The constraints these initiators impose on the clustering dynamics of sulfur's polymerization reflect the corresponding changes in the details of the transition and the rounding effects that are clearly evident for the case of As doping. In contrast, the transition in Se-doped sulfur melts seems to retain its sharp second order-type phase transition.

This paper is structured as follows: Section II contains the experimental details concerning sample preparation and the light scattering apparatus. Section III presents the obtained results and advances the relevant discussion in the framework of recent polymerization theories as well as previously reported related results. It is divided into four subsections for clarity. Specifically, Sec. III A provides some basic spectroscopic features along with the most important steps followed in the analysis of Raman data, which are needed to reliably estimate the extent of sulfur polymerization. Section III B deals with the particular changes brought about in the temperature dependence of the polymerization curves presenting the evaluation of the results obtained for As- and Se-doped sulfur melts. Few important thermodynamic parameters of the clustering transitions are extracted from the obtained temperature dependent polymer content data presented in Sec. III C. An attempt to understand the observed changes in clustering dynamics of doped sulfur melts in terms of structural confirmations is presented in Sec. III D. Finally, the most important conclusions drawn from this study are summarized in Sec. IV.

II. EXPERIMENT

S and Se used in the present work were of 99.999% purity (Alfa Chemical Co.) while the purity of As was 99.9999% (Alfa Chemical Co.). Sulfur was further purified by double distillation into evacuated silica tubes. Before being mixed with sulfur, As and Se were heated under vacuum in order to remove the more volatile oxides that could possibly be formed on their surfaces. Appropriate amounts of neat sulfur obtained by distillation were loaded into five carefully cleaned (with a dilute hydrofluoric acid solution and rinsed many times with triple distilled water) silica tubes with dimensions 6 mm o.d.−4 mm i.d. Additional quantities of As (0.5%, 2%, and 5% in atomic percent) and Se (2% and 5%) were separately inserted in each of the five, sulfur containing, silica tubes, which were subsequently evacuated and flame sealed. Chemicals handling took place in an inert-gas-filled glove box. Homogenization of the mixtures was achieved by heating the samples to high temperatures, up to 250 °C and 500 °C for Se- and As-doped melts, for at least 24 h. While being at high temperatures the samples were frequently mechanically shaken so as to ensure their homogeneity. We have to add that attempts to prepare samples of sulfur doped with Ge resulted in mixtures that suffered from phase separation, even at concentrations of Ge as low as 0.5%, a fact that prohibited their apparent study.

Right-angle Raman spectra were recorded with the aid of a He−Ne laser operating at a power level of ~10 mW. The scattered light was analyzed by a triple monochromator (Jobin-Yvon T64000) operating at double subtractive mode and was then detected by a CCD cooled at 140 K. Both polarized (VV: vertical polarization of incident laser–vertical analysis of scattered light) and depolarized (VH: vertical polarization of incident laser–horizontal analysis of scattered light) scattering geometries were employed. Accurate polarization conditions were achieved with the aid of a set of Glan and Glan-Thompson polarizers (Hale) with extinction coefficients better that 10^{-6} and 10^{-7}, respectively. The spectral resolution of the recorded spectra was set to 1 cm^{-1} in order to achieve maximum signal quality. Stokes-side Raman spectra were recorded for all mixtures (apart from the one containing 5% As) from 130 °C (a temperature at which all mixtures are in the molten state) up to 200 °C with a temperature step of 5 °C and then up to approximately 300 °C with a step of 10 °C. For the 5% As mixture a temperature increase of 10 °C was applied after each measurement for the whole temperature range. A temperature controller was employed in order to maintain the temperature constant during each measurement with stability better than 0.5 °C. Short accumulation times were sufficient to achieve a high signal to noise ratio in the spectra of all samples. All samples becomes darker as the temperature rises; this resulted to lower signal to noise ratios in the Raman spectra and hence the accumulation time was increased.

In order to ensure that equilibrium was reached before starting Raman spectra collection at each temperature we followed a procedure that has been mentioned elsewhere.[12] In brief, the temperature was gradually increased and the system was let to equilibrate for ~20 min in each step before accumulation of appropriate polarized Raman spectra. It is worth mentioning here that equilibration/relaxation in systems that exhibit the livening polymerization effect in general consists of two steps: the equilibration/relaxation of polymeric fraction, and the equilibration/relaxation of polymer length distribution.[7] Our equilibration procedure described above relates to the first step. Sulfur atoms that participate in polymers do this function in a time scale shorter than the time we mentioned (20 min). The equilibration of the first step is enough for reliably monitoring the polymer content. The second step might have an enormous relaxation time constant and this time could exceed our experimental time scale. However, this effect will not affect our results. The redistribution of the polymer lengths is expected to influence dynamical properties but not the polymer content since the fraction of sulfur atoms participating in polymeric chains will not change.

The maximum temperature reached was the one at which good quality Raman spectra could be recorded. By gradually lowering the temperature and accumulating the corresponding Raman spectra we found no hysterisis effects for the polymerization process details. All Raman spectra recorded at each step of either increasing or decreasing temperature were identical. Lowering the temperature below 130 °C permitted the accumulation of spectra from the supercooled liquids. Thus, all presented experimental data, below melting point, were extracted by manipulation of spectroscopic data obtained by supercooling the respective liquids. More than 300 spectra (VV and VH) were recorded and analyzed in this work.

III. RESULTS AND DISCUSSION

A. Spectra description and data analysis procedure

As has already been mentioned, previous spectroscopic studies of neat sulfur's structure as a function of temperature (both bulk[11] and under confinement[12]) indicated that quantitative results concerning the quantity $\phi(T)$ could be achieved by fitting the vibrational band assigned to the S···S symmetric stretching vibrational mode with two peaks, one attributed to the S_8 species (~472 cm^{-1}) and the second attributed to the polymeric species S_μ(~463 cm^{-1}).

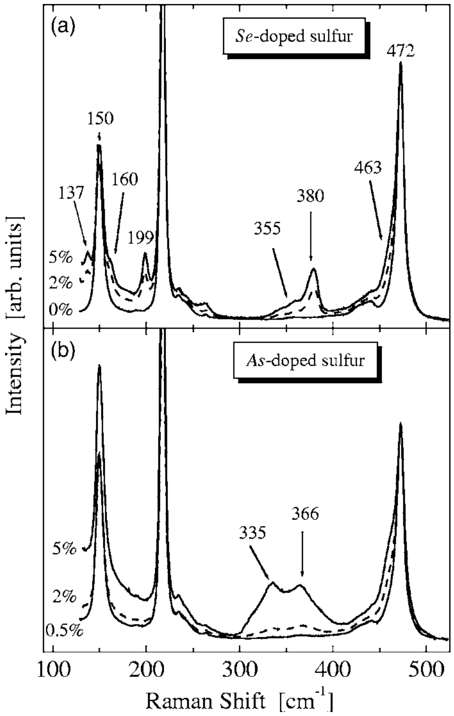

FIG. 1. Polarized Raman spectra recorded at 143 °C of (a) Se-doped sulfur (2% and 5%) and neat sulfur (bottom curve); (b) As-doped sulfur (0.5%, 2%, and 5%). Spectra corresponding to 2% Se and As-doped sulfur are presented with dashed lines.

Representative polarized spectra of pure sulfur, mixtures of sulfur with As (0.5%, 2% and 5%) and mixtures of sulfur with Se (2% and 5%) are presented in Fig. 1. All spectra have been recorded at 143 °C; a temperature above neat sulfur's melting point but also well below its polymerization transition. Among the other distinctive vibrational bands of pure sulfur,[11] the characteristic S···S stretching vibration of the S_8 species is resolved at ~472 cm^{-1}. Besides the vibrational bands of pure sulfur, the spectra of mixtures with As are characterized by additional bands positioned at ~335 cm^{-1} and ~366 cm^{-1} [Fig. 1(b)]. These bands can be attributed to vibrations of pyramid structures of As connected with S atoms.[13–15] As expected from the very low As concentration, no bands are evident in the region of ~190 cm^{-1} that could be attributed to As···As vibrational modes. Correspondingly the spectra of Se mixtures contain bands at ~380 cm^{-1} and ~355 cm^{-1} [Fig. 1(a)] that can be attributed to Se···S stretching vibrations of Se_nS_{8-n} species.[16] Further support for the concept of Se atoms participating in the 8-membered rings of sulfur is given from the respective ring (Se_nS_{8-n}) deformation vibrations that can be distinguished in the spectral region below 220 cm^{-1}, and in particular at 137, 160, and 199 cm^{-1}. The presence of the polymeric species existing in the melts, above the corresponding characteristic transition temperatures T_{tr}, is evident in the S···S stretching vibration spectral region as a low-frequency shoulder of the S_8 vibrational mode.

The analysis of the spectra has not been limited only to the spectral range in question i.e., S···S stretching band. The fitting procedure was applied to the spectral range 300–525 cm^{-1} in order to take into account overlapping effects from vibrational bands at lower frequencies. The raw spectra have been subjected to the *reduced representation* according to Eq. (1). The reduced representation relates the Stokes-side reduced Raman intensity I^{red} to the experimentally measured one ($I^{\exp}$) with the equation:

$$I^{\mathrm{red}}(\tilde{\nu}) = (\tilde{\nu}_0 - \tilde{\nu})^{-4}\tilde{\nu}[n(\tilde{\nu},T) + 1]^{-1}I^{\exp}(\tilde{\nu}), \tag{1}$$

where the term in the fourth power is the usual correction for the wavelength dependence of the scattered intensity; $\tilde{\nu}$ is the Raman shift in cm^{-1}, and $\tilde{\nu}_0$ denotes the wave number of the incident radiation. The factor $n(\tilde{\nu},T)=[\exp(\hbar\tilde{\nu}/k_BT)-1]^{-1}$ describes the mean occupation number of a specific vibration at temperature T in terms of the Bose-Einstein statistical description obeyed by phonons. $\hbar$ and k_B are the Planck and Boltzmann constants, respectively. The use of the reduced representation is particularly important if the spectral changes brought about either by temperature or structural changes (polymerization in our case) are to be disentangled. By applying Eq. (1), we get rid of the former and are thus able to follow more accurately the latter. Details concerning the use of the reduced representation in heat-induced structural changes can be found elsewhere.[17]

The determination of the relative population changes concerning two coexisting chemical species in a liquid can in principle be achieved via the comparison of the scattering intensity, arising from all the Raman active vibrational modes of one of the chemical species, with the corresponding intensity of the other species. This method was partly followed by Ward and Myers[18] in an attempt to determine the polymer content of liquid sulfur using Raman spectroscopy. However, a shortcoming of their approach is that they chose the spectral range 400–500 cm^{-1} and compared the scattering intensities of the S_μ and S_8 species in this region, instead of performing the comparison over the total frequency region of the Raman spectrum. An alternative way, especially in the case of complex forms of Raman spectra, is to perform a comparison between the intensity of a particular mode (usually symmetric bond stretching) of one chemical species with the intensity of the corresponding mode of the second species that is characterized by the same type (symmetry) of vibrational motion. Taking into account that one of the most representative Raman peaks in sulfur is that associated with the symmetric S···S bond stretching vibrational mode we have chosen the modes at ~472 cm^{-1} and 463 cm^{-1} to conduct our analysis. To avoid any further implications of possible different degree in the symmetry of the mode we further proceed to the comparison of the *isotropic* Raman intensity, defined as

$$I^{\mathrm{iso}}(\tilde{\nu}) = I^{\mathrm{VV}}(\tilde{\nu}) - \tfrac{4}{3}I^{\mathrm{VH}}(\tilde{\nu}). \tag{2}$$

The isotropic intensity separates the scattered intensity caused by the diagonal elements of the Raman scattering tensor from the corresponding intensity caused by the off-diagonal elements [*anisotropic* spectrum, $I^{\mathrm{aniso}}(\tilde{\nu})=I^{\mathrm{VH}}(\tilde{\nu})$].

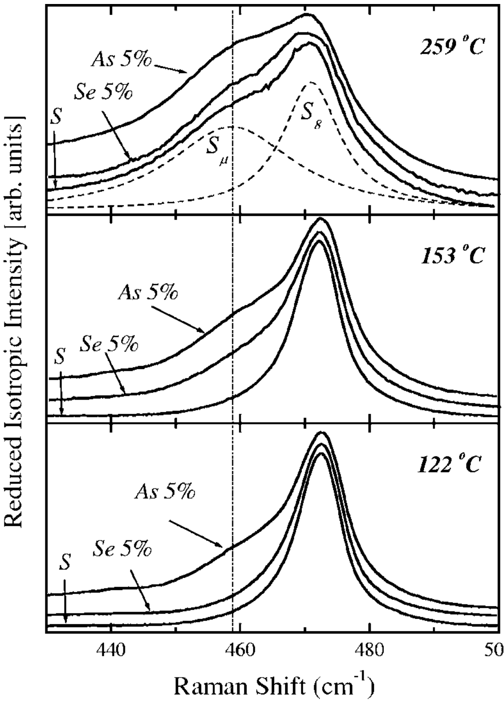

FIG. 2. Reduced isotropic Raman spectra (S···S stretching spectral region) recorded at 122 °C, 153 °C, and 259 °C of (i) pure bulk sulfur, (ii) sulfur mixed with 5% Se, (iii) sulfur mixed with 5% As. Dashed lines give an example of S_8 and S_μ peaks that contribute to the S···S band.

Representative Stokes-side reduced, isotropic spectra of sulfur and the mixtures containing 5% As and 5% Se, respectively at three distinct temperatures are presented in a comparative way in Fig. 2.

B. Calculation and analysis of $\phi(T)$: Determination of T_{tr} and $C_p(T)$

To facilitate the subsequent discussion it would be useful to briefly mention here the mechanism of sulfur's polymerization. The quest for a correct description of sulfur's polymerization counts more than six decades and has eventually been initiated after the seminal work of Bacon and Fanelli[19] who published the first accurate data for sulfur's viscosity across the polymerization transition. A successful unified theory has been worked out by Tobolsky and Eisenberg (TE).[20,21] The key outcome of their theory is its validity both above and below T_λ; thus predicting actually the transition temperature. The TE theory was based on the following chemical reactions:

$$\mathrm{S}_8 \rightleftarrows \mathrm{S}_8^* \quad [\mathrm{S}_8^*] = K_{\mathrm{init}}[\mathrm{S}_8], \tag{3a}$$

$$\mathrm{S}_8 + (\mathrm{S}_8^*)_{n-1} \rightleftarrows (\mathrm{S}_8^*)_n \quad [(\mathrm{S}_8^*)_n] = K_{\mathrm{prop}}[\mathrm{S}_8][(\mathrm{S}_8^*)_{n-1}]. \tag{3b}$$

Equations (3a) and (3b) describe the initiation (opening of the S_8 to S_8^* diradicals) and the propagation of the polymerization process, respectively. The above reactions are characterized by the equilibrium constants K_{init} and K_{prop}. The monomer↔polymer transition is mathematically sharp only in the limit $K_{\text{init}} \rightarrow 0$.[8] This is the case for neat sulfur where the extremely small magnitude of the initiation equilibrium constant ($K_{\text{init}} \approx 10^{-12}$) accounts for the experimentally detected sharpness of the temperature dependence of quantities such as the viscosity, the heat capacity etc., around T_λ.

Before presenting and discussing the results for $\phi(T)$ it would be helpful to briefly survey on different methods employed up to now for its determination. The main method used up to now to determine the polymer content is the so-called *quench-and-dissolution* (QD) method. This is an *ex situ* method aimed at isolating the polymer fraction from other molecular species. The method employs the fast cooling of the melt to low temperatures. Supposing that the cooling is efficient enough to preserve the polymer content, the quenched product is dissolved in CS_2 in order to dilute S_8 rings as well as other bigger molecules, while long chains remain intact. The elution and weighting step is repeated until there is no more reduction in the insoluble product. Since the quench-and-dissolution method requires quite laborious procedures the experimental works using this method in order to determine $\phi(T)$ are sporadic throughout the literature. The latest available reliable set of experimental data is that provided by Koh and Klement (KK),[22] where $\phi(T)$ was estimated by rapidly quenching very small quantities of liquid sulfur to increase the possibility of preserving the melt composition.[23] KK noticed several shortcomings of this complex procedure. The most serious among them are: (i) The reversing of the polymer content back to monomers during the quenching procedure; (ii) the existence of a systematic error in the temperature measurement due to the injection of cold gas in order to eject the melt onto the substrate; and (iii) the fact that repeated weightings and dissolutions in CS_2 have to take place at ambient conditions where humidity can readily affect (reduce) the polymer content. All these shortcomings unavoidably lead to an underestimation of the magnitude of ϕ and hence the QD data can be considered as a lower bound of the correct values. Almost all QD experiments show two features: (a) absence of reproducibility, i.e., the magnitude of ϕ differs by almost 100% among various works, and (b) ϕ reaches a plateau above ≈ 250 °C. On the other side, *in situ* determination of ϕ has been achieved by high temperature static susceptibility,[24(a)] electron paramagnetic resonance measurements,[24(b),24(c)] and Raman spectroscopy.[11,18] All *in situ* methods show that ϕ *increases monotonically* with temperature reaching a magnitude of $\sim 0.67 \pm 0.05$ at about 300 °C. Although the behavior of ϕ at high temperatures has not been experimentally demonstrated, *in situ* measurements of neat sulfur polymerization support the fact that at least up to 300 °C ϕ does not reach a plateau. More details about the weaknesses associated with the QD method can be found elsewhere.[25]

After this short parenthesis we can turn to the analysis of the data using the method described above. We illustrate in the upper panel of Fig. 2 a representative example of the fitting procedure followed in order to separate the monomeric from polymeric species. In Fig. 3 we present representative series of reduced isotropic spectra of all the studied systems at various temperatures from much below, to well above, the T_λ of pure sulfur, focusing on the S···S stretching spectral region.

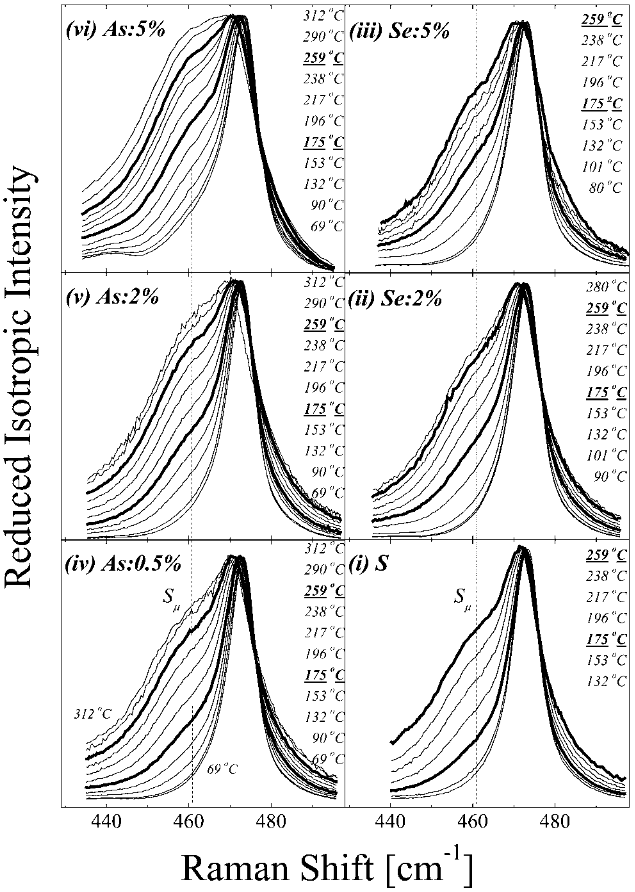

FIG. 3. Sequence of reduced isotropic Raman spectra (S···S stretching spectral region) recorded at progressively increasing temperatures for each system studied: (i) neat S, (ii) Se 2%, (iii) Se 5%, (iv) As 0.5%, (v) As 2%, and (vi) As 5%. Thicker lines (representing spectra obtained at 175 °C and 259 °C) are used in order to render separation of spectra corresponding to the various temperatures easier.

1. Polymerization features in As-doped sulfur melts

Following the fitting method described above we determined the polymeric fraction $\phi(T)$ as a function of temperature for all mixtures. The results for the case of As-doped sulfur melts are presented in Fig. 4. To allow for a direct comparison we included the corresponding data of neat sulfur.[26] From this figure we can reveal the quantitative effect on the polymerization of sulfur brought about by the presence of As atoms. In particular, the following important observations can be mentioned:

(i) A shift of the $\phi(T)$ curve, and hence shift of the corresponding $T_{\text{tr}}^{\text{As}}$, towards lower temperatures occurs. The magnitude of the shift proceeds systematically with the amount of As doping.

(ii) The sharpness of the upturn of the $\phi(T)$ curve occurring above the corresponding $T_{\text{tr}}^{\text{As}}$ is appreciably moderated in a manner almost proportional to the percentage of As doping.

(iii) The contribution of sulfur polymer content at low temperatures, i.e., below the obvious upturn of each $\phi(T)$ curve, a finite polymer contribution becomes progressively

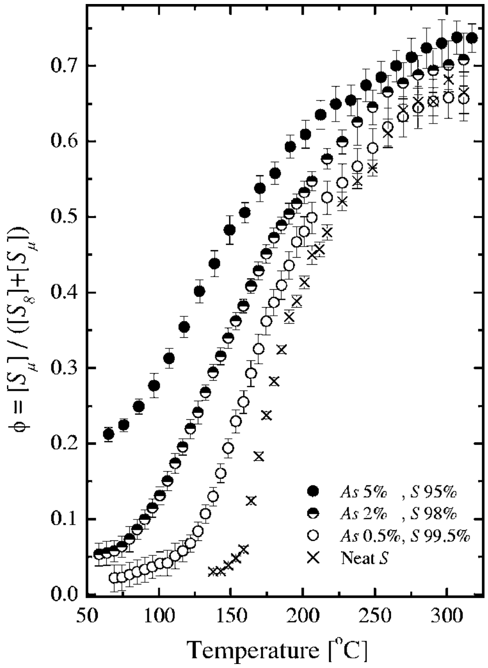

FIG. 4. Plot of calculated $\phi(T)$ for the mixtures of sulfur containing As impurities. The corresponding calculated data for the case of neat sulfur (obtained from Ref. 11) are given for comparison.

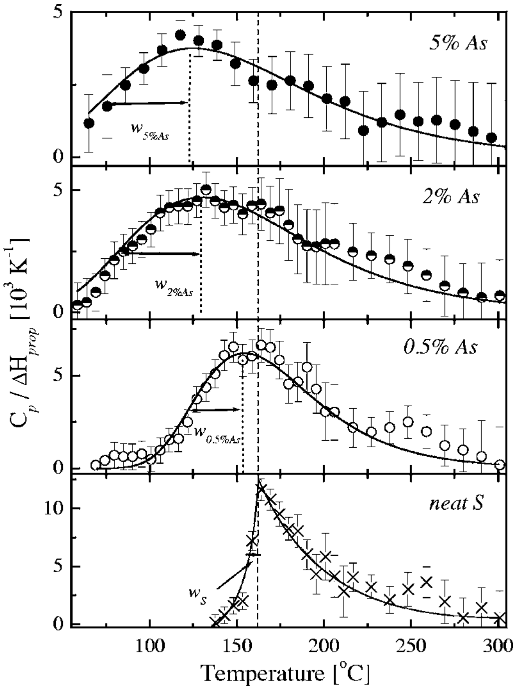

FIG. 5. Calculated values of $d\phi(T)/dT$ [Eq. (4)] for the mixtures of S with As. Lines resulted by fitting the data with a function of an asymmetric peak and have been used in order to obtain a rough approximation of the temperature T_{tr} and the corresponding width w^{C_p} and height h^{C_p}.

measurable with increasing the doping concentration of As atoms.

(iv) The high temperature values of $\phi(T)$ curves presented by the more heavily doped melts (i.e., the 2% and 5%) seem to comprise a plateaulike region with values somewhat higher compared to the corresponding ones of neat sulfur.

The four major effects mentioned above result from the two main functions of As atoms, namely initiation and participation in the melt structure. Specifically, observation (i) mentioned above, namely the shift of the corresponding $T_{\mathrm{tr}}^{\mathrm{As}}$, is a manifestation of the initiating role of As atoms. It is reasonable to assume that the presence of As atoms affect the equilibrium K_{init} of neat sulfur's initiation step [reaction (3a)]. The weakening of the S···S bond strength due to the proximity of arsenic's electric density near this bond facilitates its disruption at temperatures lower than neat sulfur's T_λ and hence might be the cause of this effect. Further, we cannot exclude the possibility that the rate constant of the forward reaction of the propagation step (3b) could also be affected (enhanced) by the presence of the dopants.

As regards effect (ii), gradual loss of the sharpness of the $\phi(T)$ curve, we can attribute this to the second function of As atoms; its participation to the structure and the concomitant stabilization of the latter. In fact, "rounding" is a common effect in living polymerization transitions when specific interparticle interactions occur;[3] for details, see Sec. III D 1.

More quantitative arguments concerning these two effects can be given by determining the temperature dependence of the constant-pressure heat capacity $C_p(T)$. The latter is a system-specific physical property that is sensitive to the changes of the sharpness of the living polymerization transition. A very useful relation has been shown to exist between the polymer content ϕ and the specific heat, which reads as[8,27]

$$C_p(T) \approx \Delta H_{\mathrm{prop}}\left[\frac{d\phi(T)}{dT}\right], \tag{4}$$

where ΔH_{prop} denotes the enthalpy of the polymerization reaction, Eq. (3b). Dudowicz *et al.*[1] have verified that this approximation holds accurately in their calculations. We have previously applied Eq. (4) for the determination of neat and nano-confined sulfur's heat capacity C_p.[12] The obtained $C_p(T)$ curve, at least for the case of neat S, was found to exhibit the characteristic singular behavior of second order phase transitions, pointing to the validity of Eq. (4) as well as the accuracy of the $\phi(T)$ data obtained by Raman spectroscopy. It is thus plausible to apply this procedure for the $\phi(T)$ data shown in Fig. 4. Indeed, Fig. 5 presents the $C_p(T)$ curves for the As-doped sulfur melts together with a comparison with the corresponding data for neat sulfur. It is evident that even at concentrations of As as low as 0.5% there is a significant rounding of the second order-type phase transition describing sulfur's polymerization. Rounding becomes more prominent when the doping concentration increases.

The rounding, or alternatively, the loss of the sharp features, can be qualitatively characterized by the decrease of the specific heat maximum, h^{C_p} (more precisely the maximum of the quantity $C_p^{\max}/\Delta H_{\mathrm{prop}}$) and the increase of the width w^{C_p} of the $C_p(T)$ peak. In addition, it is also accompanied by a noticeable shift of the maximum towards lower

TABLE I. Characteristic parameters of the polymerization transition for the doped sulfur melts studied in this work

Doping level	Polymerization temperature (°C)[a]	ΔH_{prop} (kcal/mol)	Strength of the transition $h^{C_p^i}/h^{C_p^S}$[b]	Breadth of the transition $2w^{C_p^i}$[b]	ϕ ($T \ll T_\lambda$)	$\phi_{\max}$
neat S	163±2 (153±13)	4.80±0.11	1	14±1	~0.012	~0.67
As 0.5%	153±3 (126±8)	3.36±0.08	0.70±0.033	60±3	~0.017	~0.66
As 2%	131±4 (97±7)	2.61±0.04	0.54±0.021	94±3	~0.048	~0.70
As 5%	120±5 (64±9)	2.23±0.05	0.46±0.021	102±3	~0.160	~0.74
Se 2%	144±2 (127±14)	3.89±0.15	0.81±0.05	26±1	~0.020	~0.67
Se 5%	131±2 (117±36)	5.05±0.36	1.05±0.099	14±1	~0.020	~0.67

[a] T_{tr} values calculated from Eq. (6) together with the respective uncertainties are given in parentheses.
[b] i=S, As or Se.

temperatures. Analogous trends have already been found in the lattice model of living polymerization where the terms "strength" and "breadth" of the transition have been coined to account for the magnitudes of h^{C_p} and w^{C_p}, respectively.[1] The position of the maxima obtained from the $C_p(T)$ curves cannot be easily defined with high accuracy. However, with the aid of an interpolation, a rather good approximation yields the values tabulated in Table I. The corresponding "breadths" of the transitions shown in Fig. 5 have been determined using the low temperature half part of the curve multiplied by two, in order to avoid unpredictable errors emerging from the long high temperature tail. The results obtained in this way are summarized in Table I and plotted in Fig. 6. Figure 6(a) shows the r-dependence of the clustering transition temperature, whereas Fig. 6(b) shows the dependence of strength and breadth of the transitions as a function of doping level or initiator concentration. We observe that the increase in the transition breadth is accompanied by a corresponding decrease in transition strength. The r-dependence (r denoting the mole fraction of the dopants) of these parameters bears a close resemblance with the theoretical results.[3]

The third observation (iii), namely the appearance of polymeric species even at temperatures below the polymerization transition of each mixture, is also a characteristic effect accounted for by the presence of an initiator. It is remarkable that in the case of 5% As concentration, appreciable polymer content exists even at 100 °C below neat sulfur's T_λ as is evident from Fig. 4. This observation recalls the theoretical predictions of living polymerization theories for the case of clustering transitions that evolve with decreasing temperature[1]

$$\phi(T \ll T_{\mathrm{tr}}^{\mathrm{As}}) = r, \tag{5}$$

i.e., the polymer content at temperatures much below the transition temperature is proportional to the concentration of the initiator molecules. This equation is expected to be valid, although not strictly, in our case if the dopant concentration is considered proportional to r. Indeed, despite the fact that Eq. (5) is not accurate for the As mixtures, it provides a systematic trend. The As concentration sets a finite (nonzero) limit for the low temperature values of $\phi(T)$ that increases as the doping level increases. The ability of As atoms to be chemically bonded with three sulfur atoms reduces the possibility of the latter in participating in S_8 ring formation. The structures formed can be considered as centers initiating the polymerization process. The actual higher measured values of the limiting low temperature $\phi(T)$ values with respect to the theoretical ones dictated by Eq. (5), indicate that As atoms act not only as initiators of sulfur's polymerization but contribute in the melt structure as well, by participating in a

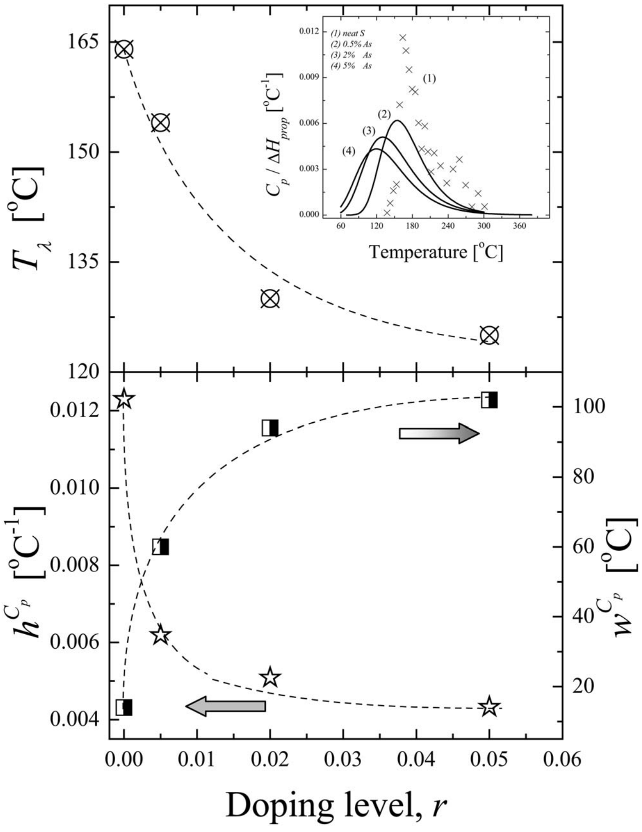

FIG. 6. Upper panel: Transition temperatures T_{tr} vs. As concentration. Characteristic curves of C_p for the various concentrations of As are plotted in the inset. Lower panel: Strength and breadth of the transition vs. As concentration.

locally threefold-coordinated crosslinking network of sulfur chains.

As for the fourth (iv) observation mentioned above, the dependence of the $\phi(T)$ values at the high temperature region of our experiment on the concentration of As is much less prominent than the corresponding $\phi(T)$ values at the low temperature region of our measurements. However, sulfur melts doped with 2% and 5% As atoms exhibit slightly higher values compared to the corresponding ones of neat sulfur, a fact that might indicate a higher extent of polymerization in these melts. This can alternatively be explained by the observation that the $\phi(T)$ curves of these mixtures present a considerable shift towards lower temperatures compared to the $\phi(T)$ curve of neat sulfur. The calculated values of $\phi(T)$ for the high temperature limit reached by the aforementioned mixtures could probably collate to the same values of $\phi(T)$ reached by neat sulfur at higher temperatures [how much higher could be determined by the corresponding shift of $\phi(T)$ curve i.e., ~28 °C for 2% As mixture and 43 °C for 5% As mixture]. Of course such data, i.e., $\phi(T)$ values of neat sulfur at temperatures above 300 °C have not yet been accumulated. Nevertheless, recent data on the polymerization of neat sulfur at high temperatures (300–450 °C) by utilization of a near-IR laser source (used in order to avoid absorption effects),[28] indicate that the polymer content of neat sulfur does indeed increase monotonically up to the limit of 450 °C.

2. Polymerization features in Se-doped sulfur melts

Having discussed in detail the changes brought about in the Raman spectra and the extracted temperature dependent polymer content curves, the explanation of selenium's effect on sulfur's polymerization becomes straightforward. Inspecting Fig. 7, which illustrates the temperature dependence of the extent of polymerization in Se-doped sulfur melts, it becomes obvious that observation (i) holds also in the case of Se doping. Polymerization curves shift to lower temperatures in a proportional way with the doping level. As regards observation (ii) it is obvious that it does not apply in the Se case. Actually, the sharpness of the transition does not seem to deteriorate at all with the addition of Se atoms contrary to what happens in the case of As. In addition, the effect summarized in observation (iii) is not as prominent as in the case of As doping. Obviously, the concentration of polymers at temperatures below the respective transition temperatures of the Se-doped melts is higher than that in neat molten sulfur but much lower than the corresponding doping levels of As atoms. Finally, as regards observation (iv), this also does not apply in this case since the high temperature limit of $\phi(T)$ is practically independent of the doping level and almost the same as that of neat sulfur.

The aforementioned noteworthy dissimilarity in the particular features of the polymerization transitions between As- and Se-doped sulfur melts arises from a profound difference between the As and the Se atoms, namely the different bonding configurations that these two atoms exhibit, threefold and twofold, respectively. Specifically, both atoms act partly as initiators and partly as constituents of the final polymer melt structure. However, the action of Se remains more silent due to its twofold coordination nature, which is the same as that of S.

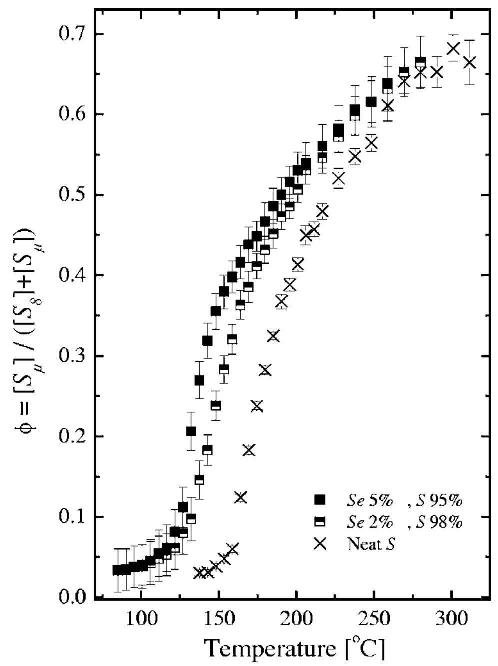

FIG. 7. Plot of calculated $\varphi(T)$ for the mixtures containing Se impurities. The corresponding calculated data for the case of neat sulfur are given for comparison.

We proceed now to a more quantitative discussion of the features of the polymerization transitions in Se-doped melts. As mentioned above, $\phi(T)$ curves shift systematically to lower temperatures with increasing Se concentration. Values of $\phi(T)$ at temperatures lower than the melting point of neat sulfur were calculated from spectra of supercooled liquids. The absence of a smoothing (rounding) in the upturn of the $\phi(T)$ curves becomes more evident after the calculation of $C_p(T)$ curves with the aid of Eq. (4). Indeed, Fig. 8 demonstrates that there is no evident rounding of the polymerization transition. On the contrary, the transition retains its second order-type nature and furthermore seems to be even sharper for the 5% Se mixture, indicting a higher strength of the polymerization process. This last statement, however, should not be taken for granted since the level of the experimental uncertainties does not permit definite conclusions. The above results lead to the unexpected conclusion that *although the addition of Se causes aggregation at temperatures below neat sulfur's transition point, the features of the transition do not exhibit rounding effects as expected in the case of finite initiator concentration*. An estimation of the parameters of the polymerization transition of Se-doped sulfur melts—$T_{\mathrm{tr}}^{\mathrm{Se}}$, strength and breadth—has resulted to the values tabulated in Table I.

Rounding effects on liquid sulfur's sharp polymerization transition have also been observed in heat capacity experiments of halogen doped sulfur melts.[29] Forced by these data, Kennedy and Wheeler[27] extended and applied their nonclassical scaling theory of the polymerization transition in liquid sulfur based on the $n=0$ limit of the n vector model of mag-

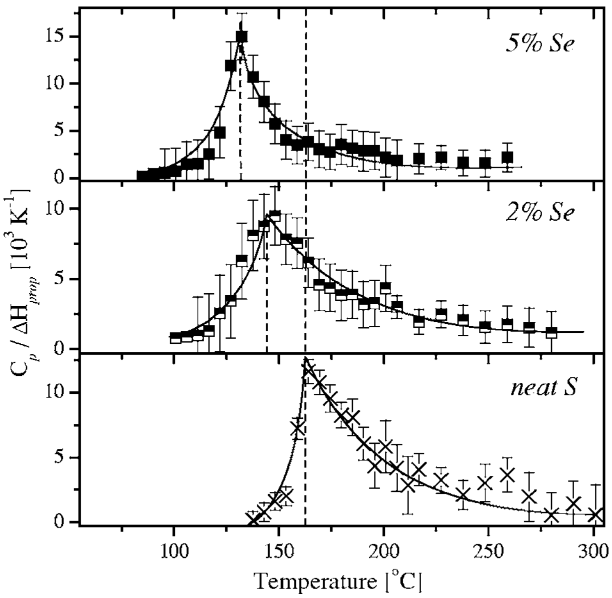

FIG. 8. Calculated values of $d\varphi(T)/dT$ [Eq. (3)] for the mixtures of S with Se. Transition temperatures can be defined easier than the respective ones of As mixtures as in both Se concentrations the C_p curves resemble the sharp curves of second order phase transitions. Calculation of w^{C_p} results in values of the order of 10 °C, close to the values presented by neat S.

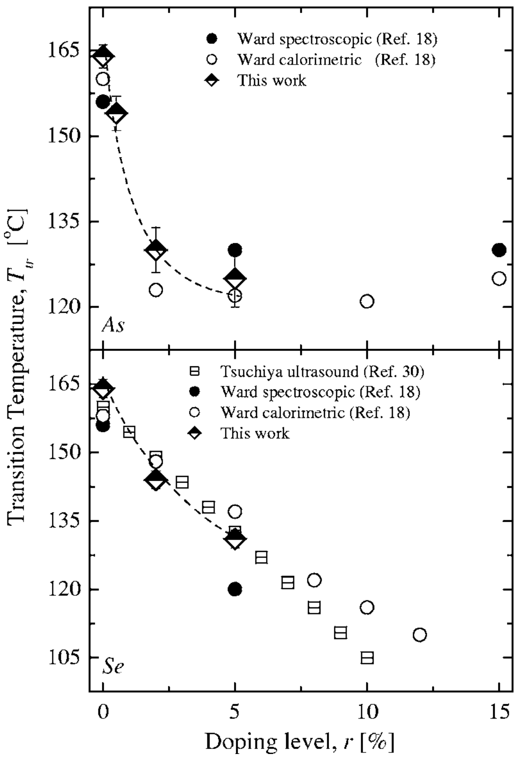

FIG. 9. Comparison of transition temperatures calculated in this work with the ones previously reported by application of Raman spectroscopy, dynamic scanning calorimetry, and ultrasound experiments.

netism to the polymerization of sulfur in the presence of a reactive dopant. They found that their extended theory describes the rounding effects of heat capacity better than the previous mean field theories by Tobolsky and Eisenberg.[20,21] It is worth mentioning that the case of halogen doping is qualitatively different from the doping employed in the present study. Halogens tend to reduce the viscosity of the melt by reacting with the free ends of the diradical chains, thus preventing further polymer growth. On the other hand, the role of As and Se atoms is different as described below.

3. Comparison with previous works

As has already been mentioned in Sec. III A, an attempt to investigate neat and doped sulfur polymerization transitions has been carried out in the work of Ward and Myers.[18] These authors were primarily concerned about the determination of the transition temperatures with the aid of Raman spectroscopy and calorimetric methods. The values of the transition temperatures $T_{\mathrm{tr}}^{\mathrm{As}}$ that arose from manipulation of the spectroscopic data as well as calorimetric data of that work[18] are plotted in Fig. 9 together with the corresponding values extracted in the present work. The main conclusion of Ward and Myers,[18] namely, a considerable decrease of $T_{\mathrm{tr}}^{\mathrm{As}}$ with even small amounts of As and subsequently its near invariance with further addition of As up to 15%, seems also to be verified from the data of the present work. Nonetheless, $\phi(T)$ does not seem to just shift to lower temperatures by the addition of As, thus maintaining its second order phase transition characteristics, as evidenced by the results of Ward and Myers Raman studies. On the contrary there seems to be a rounding on the sharp increase of $\phi(T)$ followed by the appearance of a tail in the low temperature limit. Of course, in their experiments Ward and Myers[18] did not supercool the liquid, thus they were unable to record the behavior of the binary mixtures below the corresponding melting temperatures. In addition, the main disadvantage of their analysis is the fact that they used a procedure that involves a comparison of absolute Raman peak intensities from different spectra; hence introducing great uncertainties.

As far as the Se-doped sulfur melts are concerned, apart from the data of Ward and Myers,[18] an extra set of transition temperatures as a function of the doping concentration is available from ultrasonic sound velocity measurements.[30] The transition temperatures obtained from the ultrasonics studies, for several doping concentrations, are plotted in Fig. 9(b). For comparison the corresponding transition temperatures from the present work are also included.

Ward and Myers have applied Raman spectroscopy in order to study the monomer concentration of sulfur melts containing low doping levels of Se. They presented only one data set of Raman measurements related to the $\phi(T)$ curve (5% in Se) which gave evidence of a more abrupt polymerization with respect to the one presented by neat sulfur a result that seems to agree with the result derived from our calculations. Furthermore the spectroscopic results gave evidence of a decrease in the transition temperature of neat sulfur in Se-doped melts. The systematic calorimetric data reported in the same work (also included in the graph of Fig. 9) demonstrated a rapid decrease of the transition temperature, $T_{\mathrm{tr}}^{\mathrm{Se}}$, with increasing Se concentration.

The data of Tsuchiya *et al.*[30] on the other hand suggested an almost linear dependence of $T_{\mathrm{tr}}^{\mathrm{Se}}$ with Se concentration,

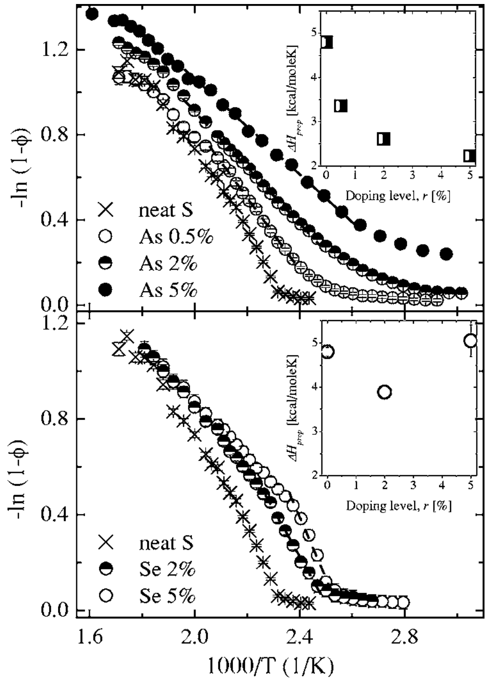

FIG. 10. Plot of the quantity $-\ln[1-\phi(T)]$ vs $1/T$ for all the studied systems. The solid lines represent best fits using Eq. (6). Insets present plots of the calculated enthalpies of propagation of polymerization step (ΔH_{prop}) as a function of doping level.

see Fig. 10(b). Our results seem to follow the same nonlinear trend of the Ward and Myers calorimetric data but lie closer to the values given by sound velocity measurements. The sensitivity of ultrasonics to detect the transition temperature has also been recently verified in a study of neat sulfur.[31] A comparison of the polymer content obtained by Raman spectroscopy and that obtained by ultrasonics has been discussed in detail eslwhere.[11]

C. Thermodynamic properties of Se- and As-doped sulfur melts

A valuable consequence of the $\phi(T)$ temperature dependence knowledge is that various thermodynamic quantities characterizing the clustering transition can be estimated. In brief, the enthalpy of the propagation step ΔH_{prop} [cf. Eq. (3b)] can be estimated with the aid of the following equation:[33]

$$\phi(T) = 1 - \exp\left\{ \frac{\Delta H_{\text{prop}}}{R}\left(\frac{1}{T_{\text{tr}}} - \frac{1}{T} \right) \right\}, \qquad (6)$$

where R is the gas constant. After fitting the experimental data using the above equation the transition temperature T_{tr} can be also estimated, however, the associated uncertainty, especially in As mixtures that present strong rounding of the polymerization transition, renders its calculation rather precarious. Details about this procedure can be found elsewhere.[12,24] In Fig. 10, plots of $-\ln(1-\phi(T))$ vs $1/T$ for all studied mixtures are given, along with linear fittings in the corresponding temperature region presenting linear relation (127–169 °C for the Se-2%, 122–153 °C for the Se-5%, 144–217 °C for the As-0.5%, 127–238 °C for the As-2%, and 110–233 °C for the As-5%). Calculation of the slope and abscissa of each linear fitting enables the extraction of ΔH_{prop} as well as T_{tr}. The extracted ΔH_{prop} values are plotted against doping level in the respective insets of Fig. 10, while both ΔH_{prop} and T_{tr} extracted values are summarized in Table I. The thus obtained T_{tr} values are subjected to major errors and hence the corresponding transition temperatures obtained from the temperatures of the heat capacity maxima are considered as more reliable. Having extracted the corresponding ΔH_{prop} values for all studied melts we plot the heat capacity ratio C_p^i/C_p^{S} (i: S, As or Se) as a function of corresponding doping level (Fig. 11).

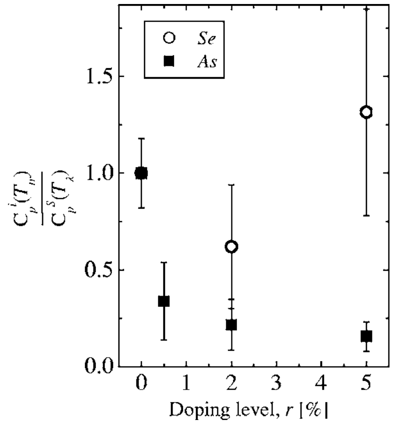

FIG. 11. The ratio of the transition strength $[h^{C_p^i}/h^{C_p^{\text{S}}} = C_p^i(T_\lambda)/C_p^{\text{S}}(T_{\text{tr}})]$ of each of the studied mixtures with respect to the strength of neat sulfur plotted as a function of doping level. As shows a progressive lowering of the calculated ratio with increase of the doping level whereas Se shows no systematic performance.

D. Structural considerations in As- and Se-doped sulfur melts

1. Possible models of As and Se atoms accommodation in sulfur melt structure

In this section we will try to substantiate the results discussed in the preceding sections in terms of possible structural conformations of the melts studied. Sulfur species can accommodate the dopants, As and Se, in specific ways dictated by the coordination properties of these atoms, twofold, and threefold, respectively. The fact that S atoms prefer the same coordination as Se is the cause of the quite different behavior of the polymerization processes between Se and As-doped melts.

A possible sketch of the incorporation of Se into the structure of S is shown in Fig. 12(a). The graphs show a part (in two-dimensional representation) of the melt structure, which is close to the 5% doping level; for simplicity we mark with lines only the S···Se bonds. It is interesting to note that the S···Se bond is weaker than the S···S bond; their energies being 255 kJ mol^{-1} and 280 kJ mol^{-1}, respectively.[32] This fact might be the reason for the shift of the polymerization transition temperature of neat S to lower temperatures with addition of Se. For each Se atom participating in an eight-membered ring two weaker bonds appear. Hence, the melt

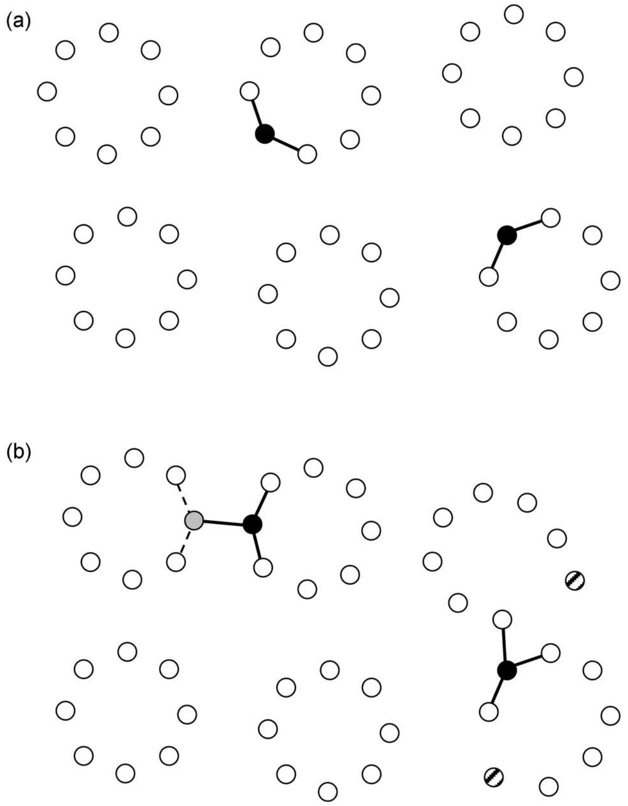

FIG. 12. A representative two-dimensional graphical example of the structure in: (a) Se-doped melts. The sketch is a typical one of ~5% concentration in Se. Open circles denote S atoms participating in eight member rings while filled circles stand for Se atoms. Black lines are drawn in place of Se···S bonds (no lines representing S···S bonds are drawn for simplicity), (b) As-doped melts. An example of ~5% concentration in As is given. S atoms participating in eight member rings are denoted by open circles. Grey circle indicates the position of an overcoordinated S atom, while hatched circles indicate free ends formed soon after ring opening. As atoms are drawn in black circles. Black lines represent As···S bonds, dashed represent the weak S···S bonds of the overcoordinated S atom.

with 5% concentration contains 10% weaker bonds compared to neat S melt. Obviously, the lower energy barrier of the S···Se bond can be overcome easier when thermal energy is provided to the system by increasing the temperature and as a result the rings containing a Se atom will transform to the diradical conformation at temperatures below T_{λ}^{S}. This reasoning explains the initiating role of the Se atoms. Since the sharpness of the neat sulfur λ-transition depends on the smallness of the initiation equilibrium constant K_{init} [cf. Eq. (3a)] it is easily conceived that the Se-doped melts maintain this property due to the presence of the twofold coordinated Se. In the final (or living) polymerized state Se can be considered as being indistinguishable from S atoms with respect to the coordination and hence will have no active structural role.

Two of the various possible ways under which As atoms can be accommodated into the sulfur melt structure are shown in Fig. 12(b). The threefold coordination nature of As atoms offers a much richer variety of local structural conformations, e.g., an As atom can join two rings by participating into one of them. A metastable configuration is thus created where an S atom is overcoordinated. This last structural arrangement is energetically unfavorable and will relax into a new state, possibly after the breakage of one of the bonds denoted by the dashed lines; thus generating diradical species. In another likely configuration the presence of an As atom can engender the opening of two neighboring rings and at the same time join these two rings in a chainlike conformation. This last situation is also able to explain why appreciable polymer content exists at very low temperatures; even in the temperature region below the melting point of neat sulfur. The energy of the As···S bond, 260 kJ mol^{-1},[32] is also smaller than that of the S···S bond thus favoring the formation of free S ends (radicals) which in turn facilitate the commence of polymerization at low temperatures. In contrast with the Se-doped melts, As atoms participate actively in the final melt structure leading to the formation of branched or cross-linked polymeric species. As a result, the melt viscosity increases and the reduced mobility of species with free radical ends is possibly the decisive factor for the strong rounding effects observed in As-doped melts. It is interesting to note that in the theoretical studies of the appearance of rounding effects in polymerizations transitions Dudowicz *et al.* stated:[3] "*Rounding of the clustering transition also occurs generally when the mass of the dynamical cluster is restricted to be finite or has a particular structure dictated by specific interparticle interactions.*" Arsenic atoms do have a definite role in producing particular structures and hence rounding is naturally explained.

2. Modifications in the symmetry nature of vibrational modes as a probe of polymerization transitions

A physical quantity, which derives from the polarized Raman profiles and is interrelated with the local structure, is the depolarization ratio. Defined as the intensity ratio of the depolarized and polarized intensities, $\rho = I^{HV}/I^{VV}$, it provides valuable information concerning the symmetry nature of vibrations.

In Fig. 13 the value of depolarization ratio calculated at the maximum of the S···S stretching vibrational band of the S_8 species (at ~470 cm^{-1}) for all studied mixtures is plotted against temperature. The band is expected to be totally polarized, for isolated S_8 species with no intermolecular interactions. Indeed, at least for the system of neat S as well as for the Se mixtures it possesses very low but finite (nonzero) values, $\rho \approx 0.02$. All the curves exhibit almost the same characteristics: A plateau at the low temperature region followed by a subsequent increase after crossing approximately the corresponding transition temperature. The associated slope is more intense for neat sulfur and in Se mixtures compared with the slope exhibited by As mixtures. This increase, which implies a reduction of the symmetry of the vibrational mode in question, may be explained by either change in the local environment surrounding each S_8 ring and/or contribution in the calculated intensity from the S_μ vibrational band, which possess to some extent different symmetry characteristics. Furthermore, the plateau value for the As mixtures depends on the doping level. The latter can be explained by

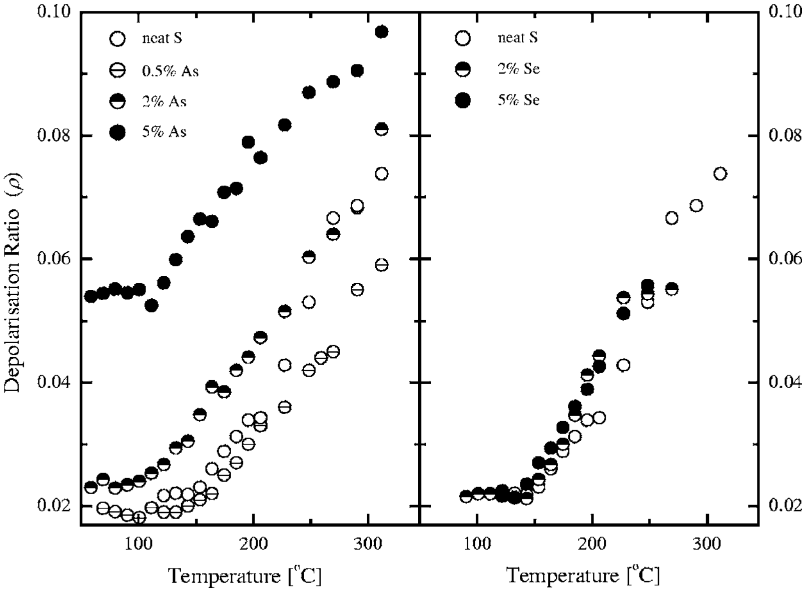

FIG. 13. Plot of the depolarization ratio calculated at the position of the S_8 stretching band maximum. The calculated values seem to be steady with temperature for all systems until approximately the beginning of each transition, where an abrupt increase in the calculated values is noticed. The slop of this roughly linear increase is similar for the mixtures containing the same dopant and seems to be greater for the case of Se. Notice that the low temperature (plateau) values seem to progressively increase with As concentration while they possess the same value for Se mixtures as well as neat S.

the alteration of the symmetry of some of the sulfur rings' vibrations due to the presence of an As atom near an S_8 ring (Fig. 12).

Both sudden increase and plateau region of the depolarization ratio curves presented in Fig. 13 can be compared with the respective $\phi(T)$ curve features linked to the rounding of the transition and the asymptotic polymer concentration at the low temperature limit. It is thus obvious that the depolarization ratio may be used as an alternative method to qualitatively follow sulfur's polymerization. In addition it provides supplementary support to the already mentioned arguments concerning the melt and supercooled structure of the studied sulfur mixtures.

Although the depolarization ratio curves cannot be considered as the most accurate ones, they do indicate transitions temperatures close to the ones given in Table I, i.e., $T_{tr}=154$ °C, 128 °C, 104 °C, respectively, for As mixtures of $r=0.5\%$, 2%, 5% for and $T_{tr}=140$ °C, 137 °C, for Se mixtures of $r=2\%$, 5% whereas $T_\lambda=170$ °C for the case of neat S.

IV. CONCLUDING REMARKS

This paper has been focused on the changes brought about on neat sulfur's living polymerization with the addition, at low doping levels, of "impurity" atoms, utilizing Raman spectroscopy. Divalent Se and trivalent As were employed as impurities atoms, while efforts to check the role of the tetravalent Ge were not successful due to a miscibility gap that the phase diagram of Ge-S exhibits. Based on our previous work where the details of neat sulfur's polymerization transition were discussed, we have been able to unravel modifications related to the shift of the transition temperature, the temperature dependence of the polymer content $\phi(T)$ and rounding effects on heat capacity for the studied mixtures. In particular, the main findings of the present study are summarized as follows: (i) The transition temperature of the doped melts decreases systematically with increasing the doping level. The trivalent As atoms engender a more drastic shift compared to that of Se atoms. (ii) The presence of As atoms causes severe "rounding" on the sharpness of neat sulfur's λ-transition, whilst in contrast, Se-doped sulfur melts retain the characteristics of a second order-type phase transition. (iii) The As-doped mixtures present a characteristic finite polymer content at temperatures below T_{tr}, whereas $\phi(T)$ in Se-doped melts resembles that of neat S. (iv) The plateau of $\phi(T)$ in Se-doped melts is similar to the corresponding one of neat sulfur, while in As-doped melts we observed a measurable increase.

The accurate determination of $\phi(T)$ made it possible to extract useful thermodynamic parameters, such as the constant pressure heat capacity and the enthalpy of the propagation step of polymerization. A detailed study of the temperature dependence of the heat capacity revealed important information concerning the rounding of neat sulfur's λ-transition in the presence of "impurity" atoms. In the case of As-doped melts considerable rounding of the transition was found. This finding is consistent with recent theories of living polymerization, which state that rounding effects might arise when the dynamical cluster has a particular structure dictated by specific interparticle interactions. However, an unexpected outcome of the present paper is that although Se atoms do indeed act as initiators in the melt polymerization process, they intriguingly do not cause rounding effects. The fact that Se doping does indeed facilitate the onset of polymerization while at the same time causes no rounding is an unexpected result which call for new theoretical investigations.

The enthalpies of the propagation step of the living polymerization transition have been determined showing that their corresponding values (compared with the value presented by neat S) drop with increasing As concentration, while remain approximately unaltered with increasing Se doping level.

An attempt has been made in order to account for the above observations in terms of the structural modifications that the doping atoms induce in sulfur's melt structure. The proposed structural configurations describing the accommodation of As and Se atoms in S seems compatible with most of the dynamical and thermodynamic features of the clustering transitions.

Finally, an examination of the temperature dependence of the depolarization ratio of the scattered light demonstrated that this symmetry-sensitive quantity exhibits subtle but systematic changes when crossing the transition temperature and thus can be used as a rough but useful indicator for the onset of the transition. On the basis that the depolarization ratio is susceptible to local structural changes associated with the polymerization process we reconfirm the virtue of Raman spectroscopy in studies of aggregation phenomena.

ACKNOWLEDGMENTS

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