

UV and Raman study of thermochromic phase transition in poly(di-*n*-hexylgermane)

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Dedicated to Professor Dr Oleg Nefedov on the occasion of his 70th birthday

Abstract

The thermochromic phase transition of poly(di-*n*-hexylgermane) (**1**) was reinvestigated using low-molecular-weight (*lmw*) and high-molecular-weight (*hmw*) polymer samples. The equilibrium phase transition temperature T_c of **1**, determined by variable temperature Raman and UV spectroscopy as well as by DSC, was found to lie not in the interval from +15 to –10°C, as was reported previously, but in the region 45–55 °C, that is, very close to T_c of the Si and Sn analogues. Thus, the phase behaviour of the polymetallanes $[\text{Hex}_2\text{M}]_n$, M = Si, Ge, Sn is governed not by the nature of the main chain but by intermolecular interactions of the substituent groups. The nature of the order–disorder phase transition of **1** depends on the polymer molecular weight and the sample thermal history. Above T_c , *lmw* polymer **1** exists as hexagonal columnar mesophase while *hmw* **1** is in amorphous state, both with disordered backbone. On cooling to room temperature, *lmw* polymer transforms to a crystalline modification with an all-*anti* conformation of the backbone and ordered hexyl groups, whereas the process of ordering of the main chain for *hmw* sample is more complicated. © 2001 Elsevier Science B.V. All rights reserved.

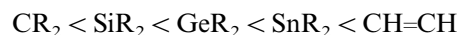
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1. Introduction

Chemistry and physical chemistry of polydiorganylmetallanes, whose macromolecules contain catenated homoatomic chains of Group 14 elements—silicon, germanium, and tin, are rapidly and dynamically developing areas of modern organometallic chemistry. In this paper, it is pertinent to emphasise a fundamental contribution to this field made by pioneering papers of Nefedov and his co-workers in the early 1960s on the synthesis and properties of polysilanes and first polygermanes [1,2].

In 1964, Gilman et al. [3] reported the family of permethylated straight-chain polysilanes $\text{Me}(\text{SiMe}_2)_n\text{-Me}$ with $n = 2\text{--}8$ along with their UV spectra. Surprisingly, the position of the absorption band, λ_{max} , and the

molar absorptivity were found to increase regularly with increasing chain length, in a manner typical for π -conjugated systems. In 1966 Shorygin, Nefedov et al. [4] published analogous UV data for linear homoatomic chains consisting of SiR_2 , GeR_2 and SnR_2 units. They also observed a remarkable red shift of the lowest-energy absorption band with the chain lengthening, the transition energy for a given chain length decreasing in the order Si, Ge, Sn. Moreover, these authors made an important suggestion that there is no principal difference between interaction of σ -bonds in these chain compounds and of π -bonds in linear conjugated polyenes, the degree of interaction between the chain units just increasing in the series



These first findings, along with some others published later (see, e.g. [5,6]), laid the foundation for the concept of σ – σ conjugation, first reviewed by Pitt [7]. Corre-

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sponding theoretical bases can be found in the Dewar's comprehensive paper [8]. The 'σ-delocalization' is now commonly viewed as an intrinsic property of catenated chains of σ-bonded Group 14 heavy atoms [9]. Moreover, Adams and Dräger [10] came up with an idea that the red shift of the UV absorption band with increasing chain length observed for oligomeric polystannanes could be interpreted as the onset of formation of a metal-like electronic band. On this basis they proposed for such compounds the term 'molecular metals'.

Later high-molecular-weight σ–σ conjugated polydi-alkylmetallanes $[R_2M]_n$, M = Si, Ge, Sn, became available [11–16]. Electronic structure of these polymers of a novel type is discussed in the reviews [11], as well as in Refs. [17a,18]. Delocalization of σ electrons along the chain of M atoms results in unique optoelectronic and electrophysical properties of polymetallanes, which are therefore of great interest as potential photodiodes, photoresists, low band-gap one-dimensional semiconductors, and materials for non-linear optics [17].

Polymetallanes can exist in amorphous, mesomorphic and crystalline states, whereas the chain of M atoms can adopt different conformations. The chain can be disordered and can also form helices with a set of dihedral angles ω in the M–M–M–M fragment, the extreme case of a helix with $\omega = 180^\circ$ being a planar zigzag structure. The latter was designated all-*trans* until recently, when a new nomenclature for linear chain conformations has been proposed and new symbols are recommended [11a,11b,19]. For instance, the term all-*anti* (all-*A*) is now used instead of all-*trans*, 7/3 helical conformation with $\omega = 154^\circ$ is named all-*deviant* (all-*D*) and also chain units with $\omega = 165^\circ$ (*transoid*, *T*) are considered among others.

According to quantum chemistry calculations, the degree of σ–σ conjugation depends on the chain conformation, the all-*A* structure favouring to maximum interaction of the σ-orbitals of the adjacent M–M bonds (see reviews [11] and references therein). Conformational transformations of polymetallane chains show themselves as spectacular phase transitions (PTs) of the first order and of order–disorder type; they are accompanied by substantial changes in optical and electrophysical polymer properties [11,13b,16b,20,21].

Thermochromic PTs have been widely studied on examples of numerous polysilanes [11]. The most investigated is poly(di-*n*-hexylsilane) whose PT with equilibrium PT temperature T_c in the interval 40–50 °C has been thoroughly explored by the whole armamentarium of physical methods. It is of fundamental interest to compare the behaviour of analogous polymers $[^n\text{Hex}_2\text{M}]_n$ in the series M = Si, Ge and Sn. Recently the first representatives of high-molecular-weight poly(di-*n*-alkylstannanes) were synthesized and studied [16], including poly(di-*n*-hexylstannane). Variable temperature UV–vis [16b] and Raman [20] as well as DSC [16b]

data obtained for the latter polymer have demonstrated that it undergoes a thermochromic PT at T_c ca. 50 °C, that is, at the temperature close to that for the silicon congener. At the same time, an analogous PT of poly(di-*n*-hexylgermane) (**1**), which was synthesized and investigated by Miller et al. [13], was reported [13b] to take place on cooling, between +15 and –10°C, though the nature of this PT appeared absolutely the same as for the corresponding polysilane [13b,14]. Such an irregular behaviour of T_c for the polymers $[^n\text{Hex}_2\text{M}]_n$ in the series M = Si, Ge, Sn seems unlikely.

Later **1** was synthesized and studied also by Mochida et al. [15]. It is notable that the room-temperature UV data reported for **1** by the two groups of investigators (Refs. [13,15]) are different. The solid *lmw* ($M_w = 950000$) sample [13b] exhibited a broad UV band at 332 nm, which was assigned to hexagonal columnar mesophase (*hcm*) on the basis of the WAXD data [14]. The *lmw* ($M_w = 9000$) polymer film reported in [15] exhibited a complicated contour consisting of two overlapping UV bands: a broad one with λ_{max} at 317 and a narrow one with λ_{max} at 339 nm, which were assigned as helical (all-*D*) and *trans* (all-*A*) conformations of the Ge backbone, respectively. Thus, neither the UV data, nor their interpretations given by the two groups agree. The difference in the UV patterns reported could be due to the difference in the polymer molecular weights, as it was observed for polysilanes (see, e.g. [22]).

With this in mind, we decided to reinvestigate the PT of two sets of samples of $[^n\text{Hex}_2\text{Ge}]_n$, those with *lmw* and *hmv*, by variable temperature UV–vis and Raman spectroscopy and by DSC. Our aim was to check the PT temperature and to clarify the effect of molecular weight. Besides, comparison of the data obtained for three polymers $[^n\text{Hex}_2\text{M}]_n$ in the series M = Si, Ge, Sn will allow us to elucidate the effect of the element M and of the substituents on the phase behaviour of these polymetallanes.

2. Results and discussion

2.1. UV and DSC data

Freshly prepared films of the *lmw* polymer samples exhibit at room temperature different UV patterns, depending on the conditions of the film preparation. If the films are obtained from a diluted solution in hexane, then the temperature evolution of the UV spectrum, reflecting the thermochromic phase transition (Fig. 1), is quite similar to that reported by Miller et al. [13]: a broad band at ca. 335 nm (with a half-width $\Delta\nu_{1/2}$ of about 3500–4000 cm^{-1}) is gradually replaced by a sharp band at ca. 380 nm ($\Delta\nu_{1/2}$ about 1500 cm^{-1}). According to [14], the former band corresponds to *hcm*, while the latter to a crystalline phase with an

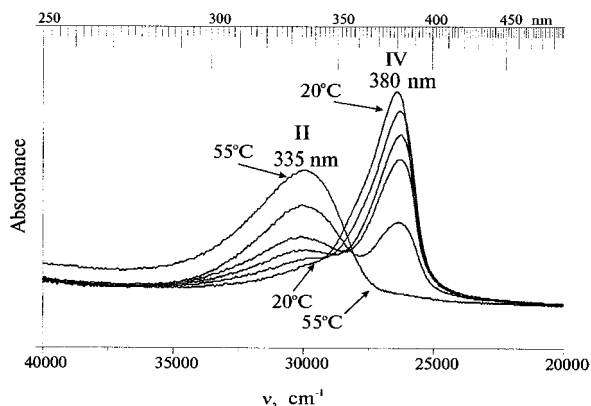


Fig. 1. Temperature evolution of the UV spectrum of the *hmw* sample of $[\text{Hex}_2\text{Ge}]_n$ (prepared as a thin film cast from a diluted solution in hexane), reflecting its thermochromic phase transition with participation of bands II and IV.

all-*trans* (all-*A*) backbone conformation. However, there is a striking difference between our results and those reported in Ref. [13]: we have observed this PT not on cooling but on heating to ca. 50 °C. Thus, the process described above and shown in Fig. 1 takes place when the sample heated to 55 °C is then cooled to room temperature.

The films of *hmw* **1**, prepared under other conditions, could exhibit in the UV spectrum at room temperature complicated contours, like that given in Fig. 2, which are, according to computer curve-fitting analysis, the results of an overlap of the above mentioned bands at ca. 380 and ca. 335 nm, and also of a band at ca. 350

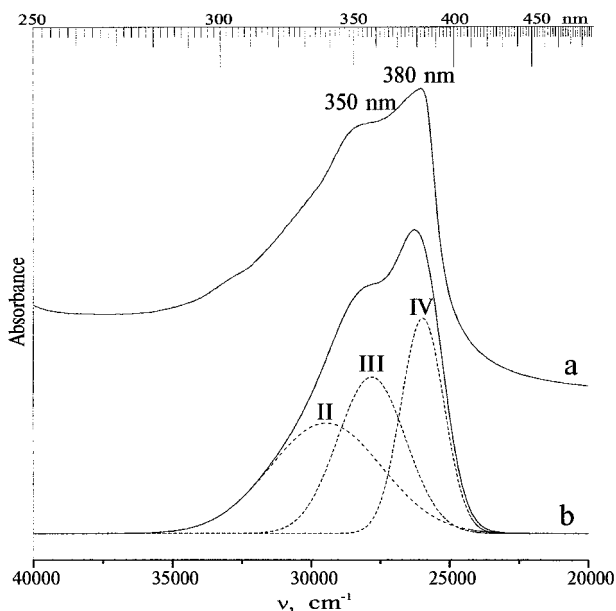


Fig. 2. A room temperature UV spectrum of another thin film of the *hmw* sample (prepared under different conditions) with a distinct band III at ca. 350 nm (a) and the results of the curve-fitting analysis after base line subtraction (b).

nm ($\Delta\nu_{1/2}$ about 2500 cm^{-1}), present in various ratios. The latter band was mentioned in [13b] as an intermediate, it disappeared after thermal treatment. Actually, in our experiments the band at ca. 350 nm, if present, disappears on heating first, before that at ca. 380 nm, and only the band at ca. 335 nm persists above T_c .

The PT of the *lmw* samples also takes place on heating to ca. 50 °C, but the overall UV pattern, reflecting this PT, differs from that of the *hmw* samples. At room temperature, the UV spectra of freshly prepared films of the *lmw* polymer show themselves as complicated absorptions of various shapes, in which the curve-fitting analysis reveals the same three bands (at ca. 335, ca. 350 and ca. 380 nm), which were observed for *hmw* samples, but in different proportions. However, when the *lmw* samples are heated to 50 °C and above, all these bands disappear and only a very broad band with λ_{max} at ca. 320 nm ($\Delta\nu_{1/2}$ about 5000 cm^{-1}) is observed. When the *lmw* film is gradually cooled from T_c to room temperature (an example of such PT process is given in Fig. 3), the initial UV spectrum does not restore, but a complicated pattern is formed with the band at ca. 350 nm predominant.

Thus, equilibrium PT temperatures T_c for both *hmw* and *lmw* samples of **1** were found to be close in value, lying at about 50 °C (more precisely, in the temperature interval from 45 to 55 °C). This was confirmed by DSC data (Fig. 4). Thus, there is a big difference in the T_c values between that reported in Ref. [13] and our data [23]. The low T_c value reported in [13] seems to be erroneous and could be explained by the presence of impurities, which always result in a decrease in PT temperatures.

Numerous variable-temperature UV experiments have shown that the UV pattern observed at a given temperature below T_c for both *hmw* and *lmw* polymer samples of **1** is not a single-valued function of temperature, but strongly depends on the method of the sample

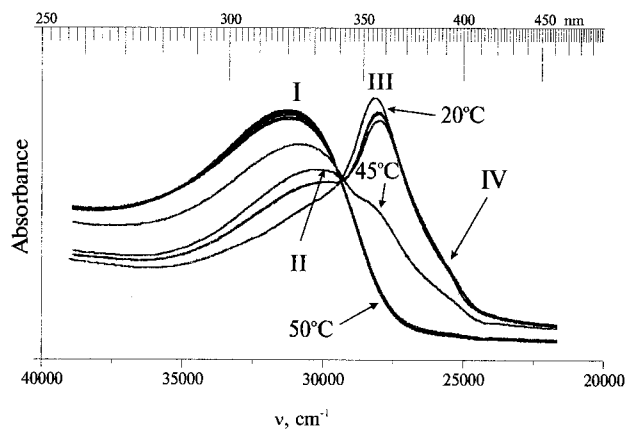


Fig. 3. Temperature evolution on cooling of the UV spectrum of a thin film of the *lmw* sample heated to 50 °C.

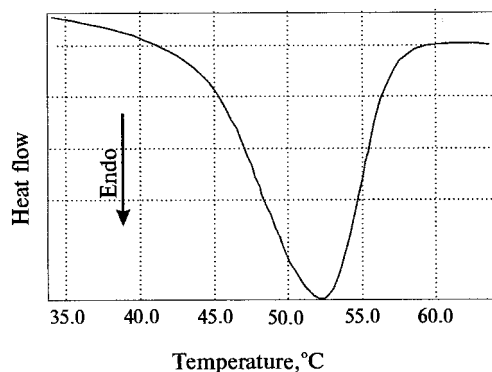


Fig. 4. DSC trace for the *lmw* sample of $[{}^n\text{Hex}_2\text{Ge}]_n$ reflecting a first-order phase transition.

preparation, its thermal history and the rate of cooling. Detailed computer analysis has shown that all complicated patterns can be represented as superpositions of the four main bands, having different λ_{max} and $\Delta\nu_{1/2}$ values (Fig. 5, Table 1), present in variable proportions.

Let us designate the observed UV bands and corresponding modifications of **1** by the figures I (λ_{max} ca. 320 nm), II (λ_{max} ca. 335 nm), III (λ_{max} ca. 350 nm) and IV (λ_{max} ca. 380 nm). It is necessary to emphasise that the exact λ_{max} and $\Delta\nu_{1/2}$ values of each UV band slightly depend on the way of the sample preparation and exhibit slight but regular temperature dependence which is clearly seen in Fig. 1 for the band IV. The same dependence was observed by us for the UV bands of the polysilanes studied previously [24].

Table 1

Absorption bands observed in the UV spectra of poly(di-*n*-hexylgermane) and their assignment

	Band I	Band II	Bands III	Band IV
λ_{max} (nm)	316–320	332–337	345–355	372–385
$\Delta\nu_{1/2}$ (cm^{-1})	4500–5500	3200–4000	1500–2500	1000–1500
Phase state	Amorphous	<i>hcm</i>	Cryst.	Cryst.
Backbone conformation	Disordered	Disordered	all- <i>A</i> or all- <i>T</i>	all- <i>A</i>

Comparison of the results given above with those obtained for various polydialkylsilanes [11,24] and with the WAXD data for the *lmw* **1** [14] allows one to assign the four UV bands observed to particular polymer modifications. Band II at 335 nm corresponds to *hcm* [14] (like the band at ca. 315 nm for polysilanes). Band I at ca. 320 nm, blue-shifted and more wide compared to II, could be assigned to an amorphous phase of the polymer with a most disordered backbone (its analogue in the spectra of polysilanes is the band at ca. 300 nm). The most red-shifted narrow band IV at ca. 380 nm evidently corresponds to a crystalline all-*A* modification [14]. Basing on the Raman spectra (see below), we assign the band III also to an ordered all-*A* modification, but with a less perfect higher-order structure. As it is seen from the Table 1, the UV bands of disordered modifications of the polygermane **1** are red-shifted

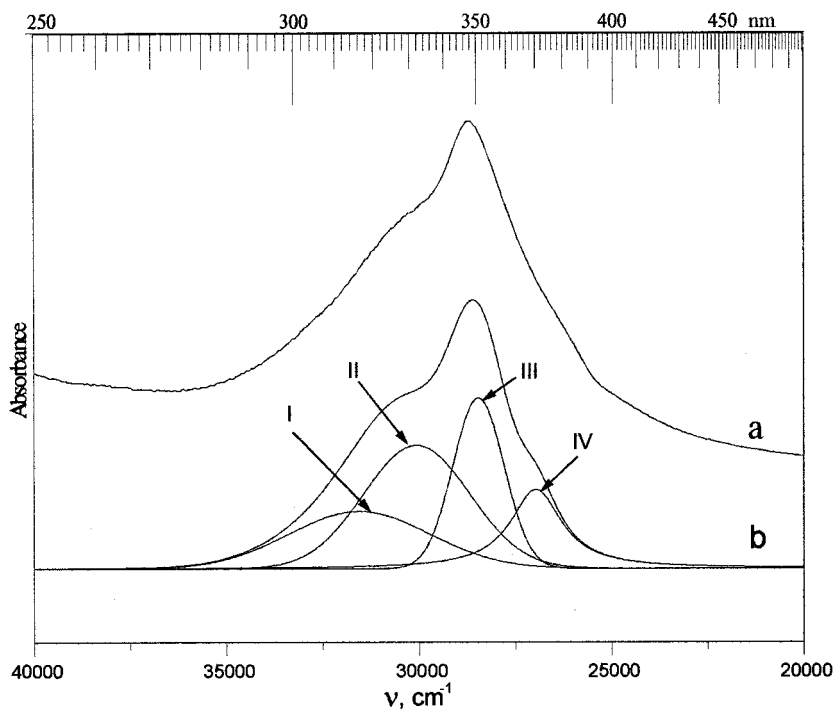


Fig. 5. A UV spectrum observed at room temperature for one of the *lmw* samples (a) and the results of the computer curve-fitting analysis after base line subtraction (b).

compared to those of the corresponding polysilane by ~ 20 nm, while those of all-*A* modifications are not.

Thus, our UV results for **1** comprise the bands reported in Refs. [13,15] and contain additional information, showing that the nature of the thermochromic PT of **1** depends on the molecular weight of the given polymer sample, though all the samples have close T_c values. Above T_c , the *hmw* samples exist as *hcm*, whereas the *lmw* samples are amorphous. The process of PT of the *hmw* samples always involves *hcm* and the most ordered all-*A* modification (UV band IV) and sometimes also a less perfect all-*A* modification (UV band III), whereas in the PT of the *lmw* samples all the four modifications participate.

2.2. Raman data

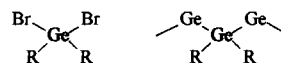
The Raman spectra of *hmw* **1** (at 25, 13 and -50 °C) in the region 50 – 1600 cm^{-1} excited by 488.0 nm line were reported in [13b] together with the FT-Raman spectra in the region 500 – 1700 cm^{-1} . We have studied variable-temperature Raman spectra in the interval from 19 to 100 °C for many samples, both *hmw* and *lmw* (as polymer chunks and thin films cast from solutions in hexane), using an excitation line of 514.5 nm. The main result is that the room-temperature Raman spectra of all our *hmw* and *lmw* samples are absolutely identical (see Fig. 6a) and closely resemble the Raman spectrum reported by Miller et al. [13b] but obtained at -50 °C. Narrow intense lines, dominating in these spectra, are typical for ordered crystalline polymers and evidently correspond to the modification having the most σ – σ conjugated all-*A* conformation of the Ge backbone [14]. On heating to T_c , the intensity of the strong lines, characteristic of the all-*A* modification, is gradually decreasing (Fig. 6b,c). At ca. 50 °C the Raman spectrum changes dramatically, confirming the PT at this point, and exhibits weak broad bands, typical for the modifications with a disordered polymer backbone (Fig. 6d–f).

The most modern highly sensitive Raman spectrometer T64000 used in our experiments permits registration of the Raman spectra of the same thin polymer films as were used for obtaining the UV spectra, thus allowing the strict comparison of the UV and Raman data. The identity of the room temperature Raman spectra of two films, one of the *hmw* polymer (exhibiting the UV band IV) and the second of the *lmw* polymer (with the band III predominant in the UV spectrum) is a strong evidence that the UV band III also corresponds to an ordered modification with an all-*A* conformation of the polymer main chain. Analogous phenomenon was observed for poly(di-*n*-hexylsilane), whose crystalline all-*A* modifications can exhibit in the UV spectra the narrow bands with λ_{max} either ca. 375 , or ca. 365 , or ca. 350 nm, or various superpositions of these bands

[24c,25]. The reason for their different λ_{max} values is not yet clear. We believe that this phenomenon for both polysilanes and polygermanes could be related to the polymer morphology, to peculiarities of the process of polymer crystallization, which depends on film preparation conditions. As a result, crystalline regions with different higher-order structure could be formed; the latter affects the length of effective *anti*-sequencies in the main chain, thus determining the degree of σ – σ conjugation and consequently the position of the UV band. The same point of view is reciprocated by Kyotani et al. [25]. Another possible explanation proposed by Michl and West is that only one modification of the polymer is truly all-*A*, the other forms have small irregular *transoid* deviations from it [11b].

Band assignment in the Raman spectrum of **1** can be made on the basis of the published data on vibrational spectra of organogermanium compounds [13b,26–30]. The position of the stretching vibrations of the Ge–C bonds (ν Ge–C) in the Raman spectra of alkylgermanes and the dependence of ν^s Ge–C on the nature of substituents were studied in [27,28]. Reliable information about the stretching vibration of the Ge–Ge bond (ν Ge–Ge) was presented by Fontal and Spiro [30] for $\text{Me}_3\text{Ge–GeMe}_3$. Its intense Raman line at 273 cm^{-1} was assigned to ν Ge–Ge on the basis of normal coordinate analysis, which showed, however, that this normal mode is not fully localized, the ν Ge–Ge coordinate being coupled with the δ CGeC deformation, but not with ν Ge–C. Using these data, the strong narrow lines in the region 200 – 300 cm^{-1} in the Raman spectrum of **1** can be assigned to ν Ge–Ge, whereas those in the region 580 – 650 cm^{-1} to ν Ge–C. Above 700 cm^{-1} , the lines corresponding to internal vibrations of "Hex groups are situated.

To elucidate the conformational state of the "Hex tails in **1**, it was useful to study the Raman spectrum of a model compound—a monomer "Hex₂GeBr₂ (analogous approach was applied by us to the polymer ["Hex₂Si]_n [24c,31]). The masses of Br and Ge atoms are of the same order of magnitude, so that the monomer is kinematically modelling to some extent the unit of the polymer **1**.



At room temperature, di(*n*-hexyl)dibromogermane is a liquid which should be an equilibrium mixture of various conformers due to hindered internal rotation about the Ge–C and C–C bonds. Thus, its spectrum in the region of internal vibrations of "Hex groups (800 – 1500 cm^{-1}) should be complicated. This is evident from Fig. 7a. A similar spectrum in this region is exhibited by all samples of **1** above T_c , pointing to a

disordered state of n Hex groups (Fig. 7b). Below T_c , the spectrum of **1** in this region becomes much simpler (Fig. 7c). It is especially notable that for the liquid n Hex₂GeBr₂ and for the polymer **1** above T_c two features in the region 1060–1080 cm⁻¹ are observed. The band at 1075 cm⁻¹ is usually associated with the *gauche* units in the aliphatic chain, while the neighbouring band at 1060 cm⁻¹ is characteristic of the *trans* units [13b,31]. Only the band at 1060 cm⁻¹ persists in the spectrum of **1** below T_c . These facts point to n Hex groups ordering during the phase transition.

2.3. Conclusions

The thermochromic phase transition of the *hmv* as well as *lmw* samples of the polymer [n Hex₂Ge]_n takes place on heating to ca. 50°C, at nearly the same temperature as for its Si and Sn congeners. This means that this phenomenon is governed not by the nature of polymetallane chain but by intermolecular interactions of the side *n*-hexyl groups.

[n Hex₂Ge]_n undergoes a complicated phase transition of order–disorder type with possible participation of

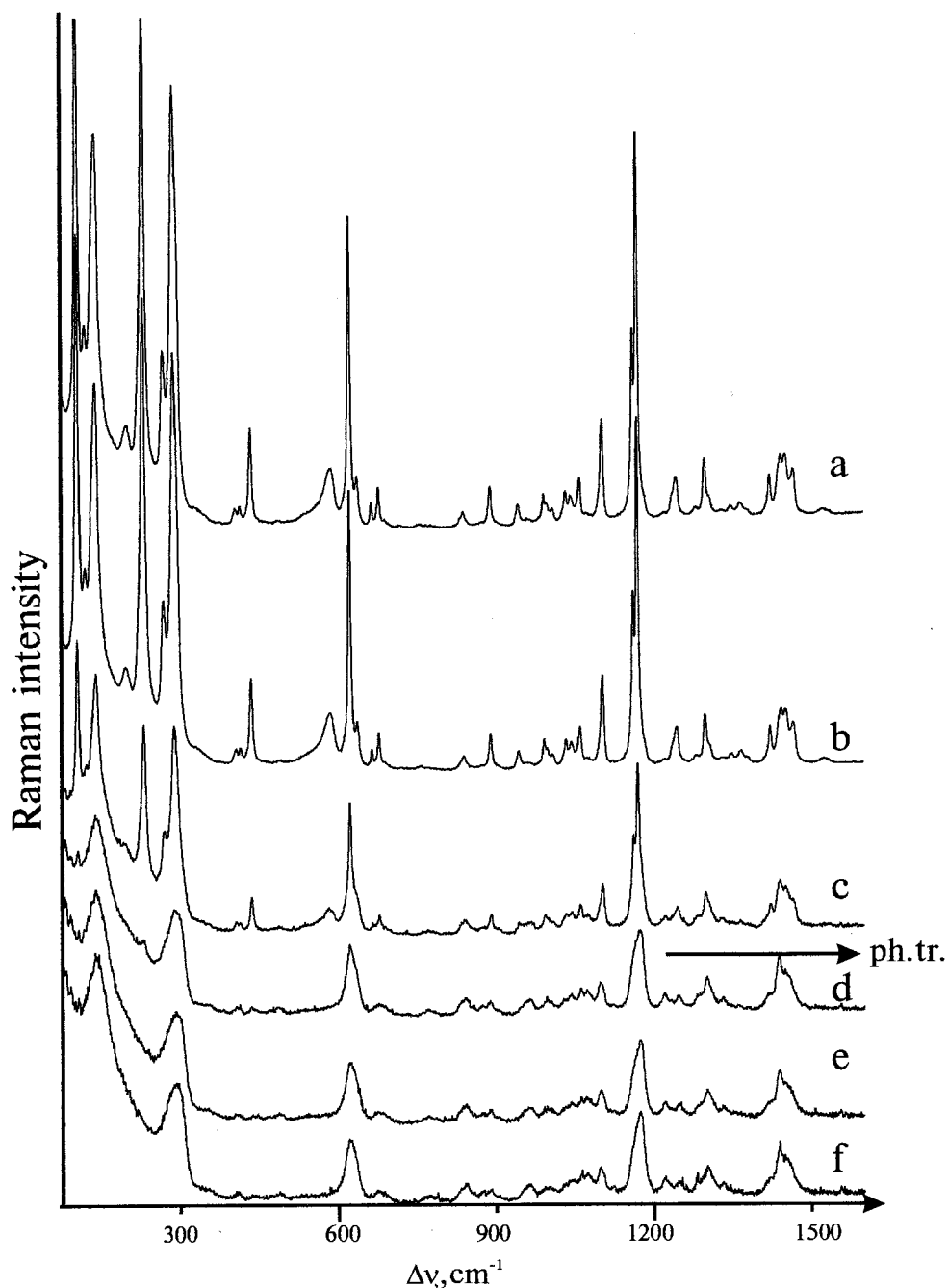


Fig. 6. Temperature evolution on heating of the Raman spectrum of [n Hex₂Ge]_n, common to all the samples studied. (a) 20 °C; (b) 35 °C; (c) 48 °C; (d) 50 °C; (e) 80 °C; (f) 100 °C.

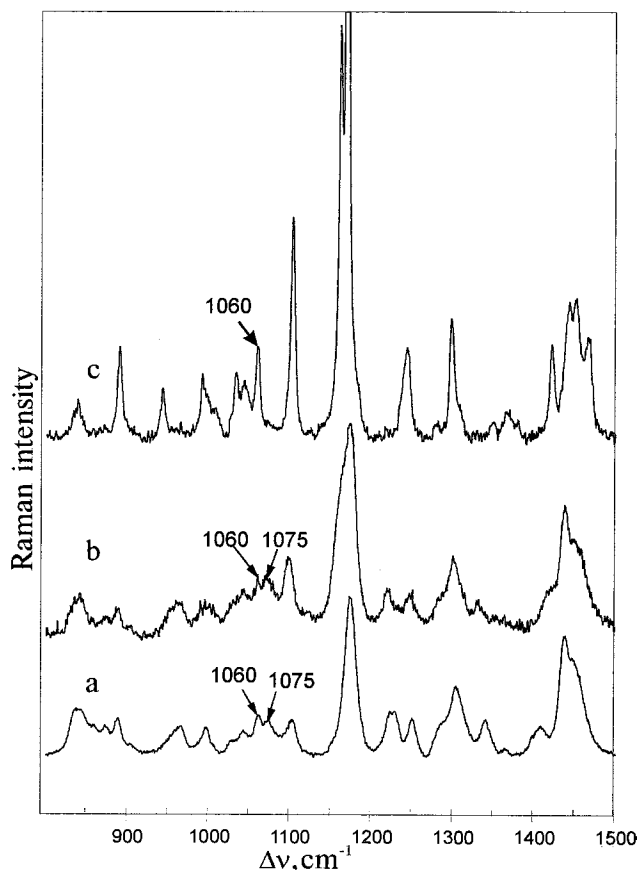


Fig. 7. Comparison of the Raman spectra in the region of internal vibrations of *n*-hexyl groups. (a) Liquid $^{70}\text{Hex}_2\text{GeBr}_2$; (b) $^{70}\text{Hex}_2\text{Ge}$, above T_c (at 80 °C); (c) $^{70}\text{Hex}_2\text{Ge}$, below T_c (at 20 °C).

several polymer modifications, which differ in intermolecular ordering and in main chain and side chain conformations. Particular characteristics of a given phase transition depend on the molecular weight of the sample, its prehistory, and the rate of heating or cooling.

3. Experimental

GPC was performed on a Bruker LC 21 chromatograph, using toluene as an eluent at the rate 1 ml/min. Molecular weights are presented relative to polystyrene standards.

^1H - and ^{13}C -NMR spectra were recorded on a Bruker AC-200 instrument in CDCl_3 .

The UV–vis studies were carried out using a computerized M-40 Carl Zeiss spectrophotometer. The samples were thin polymer films cast from solutions in hexane. The details of the procedure of sample preparation (temperature, concentration, the rate of solvent evaporation) were found to strongly influence the initial UV pattern observed.

The Raman spectra were registered using laser Raman spectrometers Jobin-Yvon U-1000 and T64000 with excitation by 514.5 nm line of an Ar^+ laser Spectra Physics 2020. A prism monochromator and interference filters were applied for filtering laser lines. Both photomultiplier and CCD detectors were used for spectra registration. The samples for Raman investigations were either small polymer chunks sealed in glass capillaries in vacuo, or just the same polymer films as used for the UV measurements. To avoid sample destruction in the laser beam, the latter was defocused and minimum light density was applied (exciting laser power less than 10 mW).

The films of **1**, which were studied by the UV and Raman methods, were free of oxidative destruction products because their IR spectra contained no broad IR band in the region 800 cm^{-1} , corresponding to $\nu^{\text{as}}\text{GeOGe}$ (to identify the latter mode, the IR spectrum of the cyclic $^{70}\text{Hex}_2\text{GeO}_3$ was obtained).

The IR spectra of the polymer **1** films and of $^{70}\text{Hex}_2\text{GeO}_3$ were registered, using a computerized M-82 Carl Zeiss spectrophotometer.

For variable-temperature measurements, various cryostats and heated cells were used. Temperatures were generally maintained to within ± 1 °C.

All reactions were carried out under dry Ar atmosphere. Solvents (toluene, hexane, *i*-PrOH) were dried and distilled before use by standard methods.

$^{70}\text{Hex}_2\text{GeBr}_2$, poly(di-*n*-hexylgermane) (**1**) and $^{70}\text{Hex}_2\text{GeO}_3$ were obtained as described in Ref. [13a]. The polymers with *lmw* and *hmw* were isolated from different reactions. In the reaction, leading to *lmw* sample, a simple propel stirrer, while in the reaction leading to *hmw* polymer a wire stirrer were used.

GPC data for *lmw* polymer: M_w 73940, M_n 24180, polydispersity 3.05; for *hmw* polymer: M_w 259660, M_n 211190, polydispersity 1.22.

^1H -NMR (δ , ppm): 0.85 (t), 1.25 (m); ^{13}C -NMR (δ , ppm): 14.24 (CH_3), 17.61, 23.03, 28.76, 31.95, 34.39. ^1H and ^{13}C -NMR spectra were identical for *lmw* and *hmw* polymers. Anal. Calc. for $\text{C}_{12}\text{H}_{26}\text{Ge}$: C 59.12, H 10.79, Ge 29.88; Found (for *lmw*): C 59.50, H 10.85, Ge 29.67.

Acknowledgements

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