Siloxane-Containing Liquid-Crystalline Supramolecular Polymers: Preparation and Study of Thermotropic Behavior

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ABSTRACT: New hydrogen-bonding supramolecular polymers were obtained from 4,4′-bipyridine and different silicon-containing diacids. The formation and thermal stability of these complexes were verified with Fourier transform infrared spectroscopy following the specific absorption bands at 1950 and 2450 cm^{-1}. Their thermotropic behavior was investigated with polarizing optical microscopy and differential scanning calorimetry. All the obtained supramolecular compounds were liquid crystals within mesophase ranges that depended on the structure of the starting siloxane/silane diacid. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109:4000–4009, 2008

Key words: liquid-crystalline polymers (LCP); polysiloxanes; supramolecular structures

INTRODUCTION

The term *supramolecular chemistry* was introduced in 1978 by Jean-Marie Lehn[1] and was defined as “chemistry beyond the molecule.” It is based on the self- assembly of well-defined structures, following the models of natural molecular systems, and its ultimate aim is to create molecular devices.[1] Supramolecular polymers are macromolecules in which the monomer units are kept together by noncovalent interactions. In a broader sense, the term is also used for self-organized macromolecules of conventional polymers involving noncovalent interactions to determine their material properties.[2] Supramolecular polymers combine the features of supramolecular species with polymeric properties.

Several types of intermolecular interactions are effective in obtaining supramolecular structures: hydrogen bonding, arene–arene interactions, and metal coordination.[3] Although hydrogen bonds between neutral organic molecules are not very strong, they play a very important part in molecular recognition, self-assembly in biomacromolecules, increasing miscibility in polymers blends, organization in liquid crystals, and so forth. The directionality, fixed stoichiometry, and versatility of the hydrogen bonds are the major reasons for their importance in the design of supramolecular polymers.

It is well known that the physical properties of linear polymers and organic molecules are strongly modified when they contain associating end groups. Telechelic siloxanes bearing polar groups such as —OH or —COOH form supramolecular associations,[4,5] which may exhibit interesting mesomorphic and crystalline structures.[4] The ureidopyrimidone groups are known for their quadruple hydrogen bonding, which allows the preparation of very resistant supramolecular materials.[6] Polysiloxanes end-capped with such functional groups associate in a donor–donor–acceptor–acceptor array and behave like high-molecular-weight polymers.[7]

The self-assembly of carboxylic acids as proton donors with pyridyl fragments as proton acceptors is most frequently used in the formation of hydrogen-bonded structures.[8] Such supramolecular polymers have been obtained and investigated, especially for liquid-crystalline properties.[8–13] It has been observed that hydrogen bonding in supramolecular polymers is enhanced by liquid crystallinity and phase separation.[3] Siloxane-containing benzoic acids and bipyridine also form interesting supramolecular structures with cubic mesophases.[14] The formation of this rare type of liquid-crystalline phase has been explained by the chemical incompatibility between the polar aromatic part and the bulky, flexible, nonpolar siloxane moiety in the same mesogen, which are nanophase-separated.[15]

Here we report the preparation of a series of supramolecular polymers starting from 4,4′-bipyridine as an acceptor and different silicon-containing

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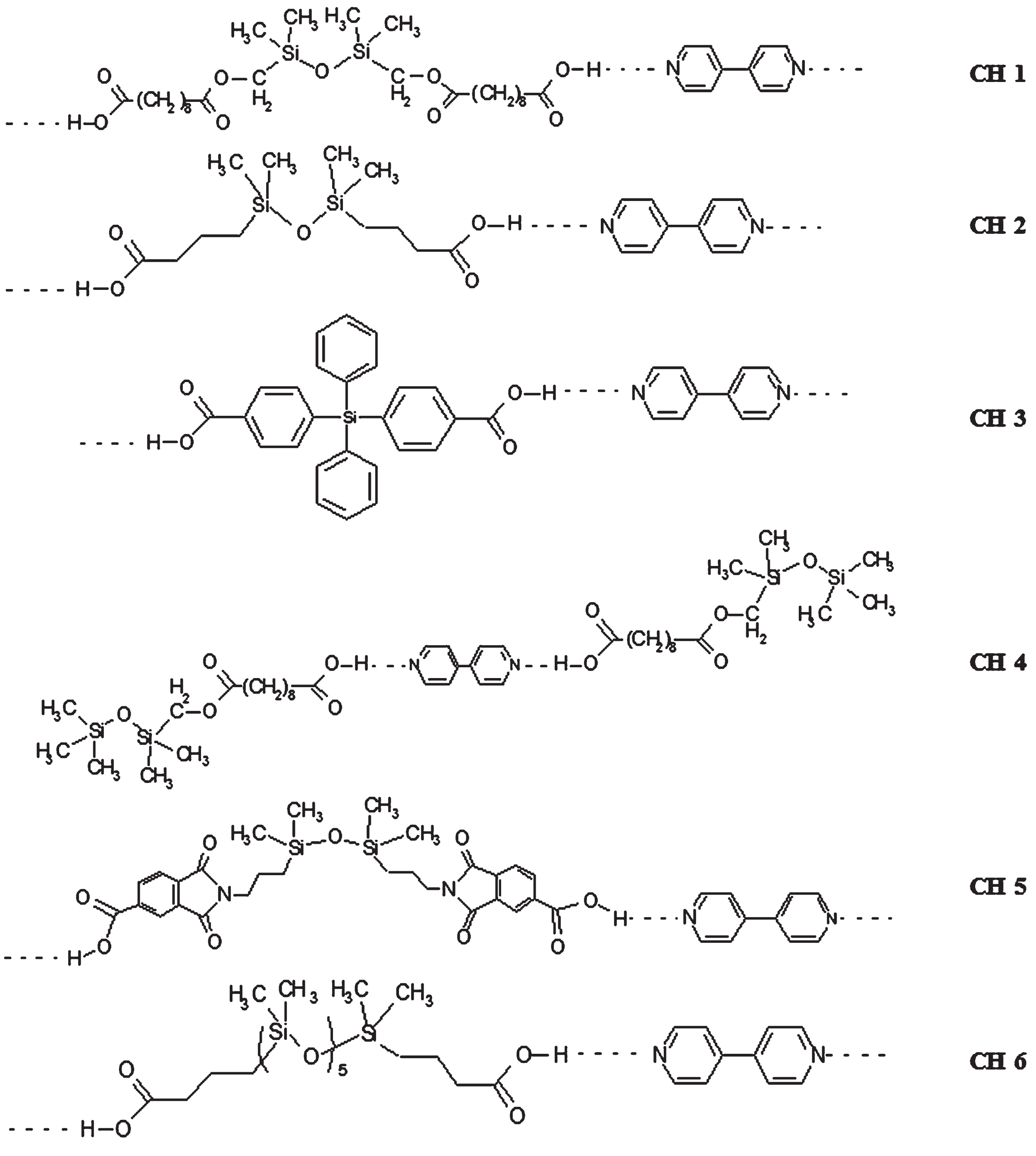


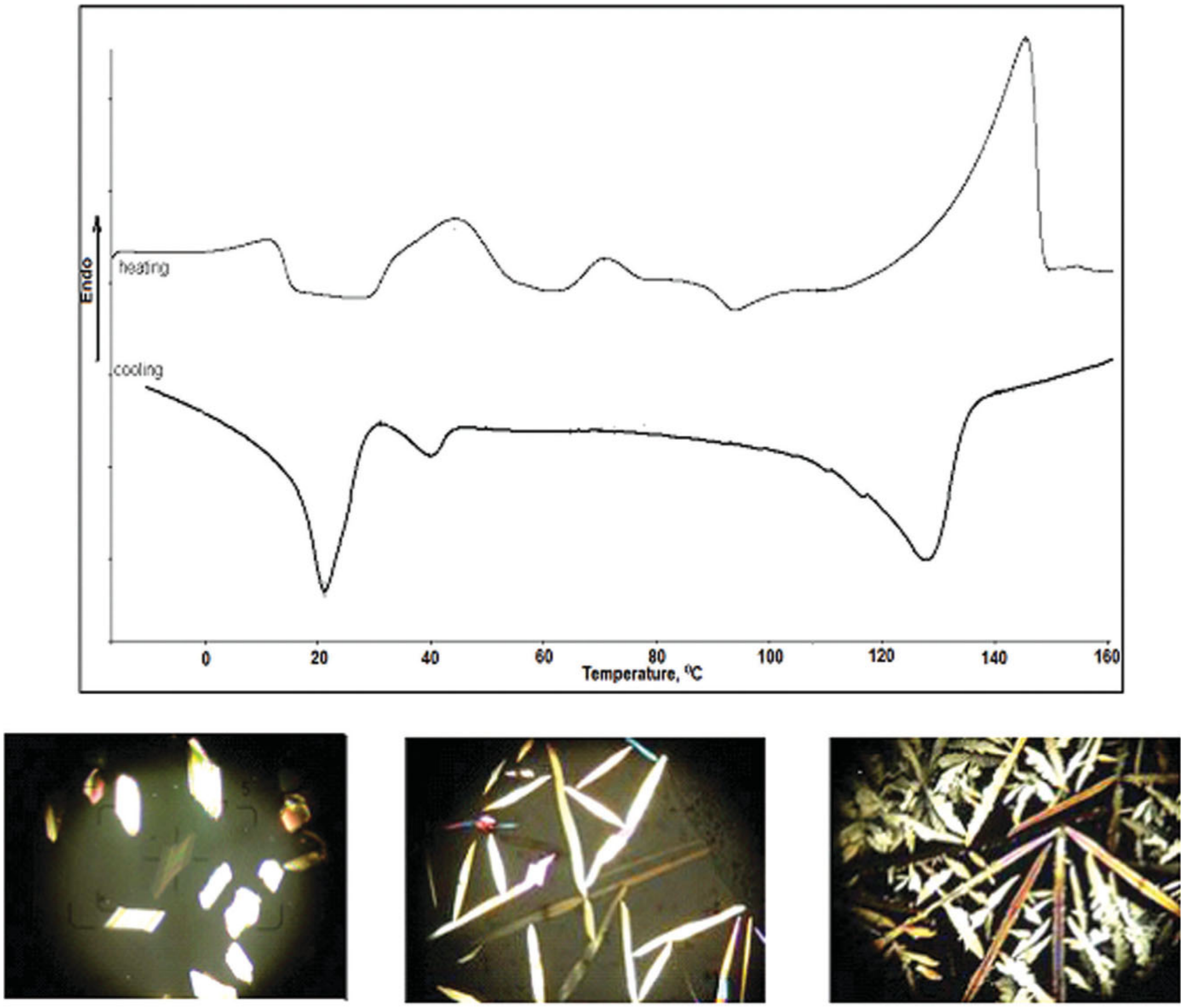
Scheme 1 Chemical structure of the supramolecular compounds.

carboxylic acids as hydrogen-donor molecules. Because neither of the starting compounds exhibit liquid crystallinity, it was interesting to observe the role of the hydrogen bonds in obtaining ordered mesophases. The structures of the siloxane diacids were chosen to ensure different levels of chain mobility, molecular polarizability, and free volume, which would impart different thermotropic behaviors, thus allowing the tailoring of the mesophase range. Another important perspective is that of possible phase separation in such siloxane organic structures, which would enforce the hydrogen bonding.[3]

TABLE I
Thermal Transitions of the Supramolecular Polymers (DSC Data on Heating)

Code	T_g (°C)	T_m (°C)	T_i (°C)
CH1	nd	20	146/170[a]
CH2	nd	68/62[a]	68[a]
CH3	167	210/200[a]	nd/270[a]
CH4	—	32	155
CH5	50	153/125[a]	165
CH6	8	48	69

nd = not determined.
[a] From POM observations.



160°C first cooling 145°C second cooling 60°C third cooling

Figure 1 Thermotropic behavior of CH1: DSC scans and POM observations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

Besides the extreme facility of their preparation, these supramolecular polymers exhibit thermotropic liquid-crystalline behavior that could be tuned by the choice of the siloxane diacid. The hydrogen bonds are thermally stable within the mesophases. On the other hand, preliminary tests for using these compounds as sensing elements showed high sensitivity to gases such as NOx and CO_2, which would open another applicative perspective.

EXPERIMENTAL

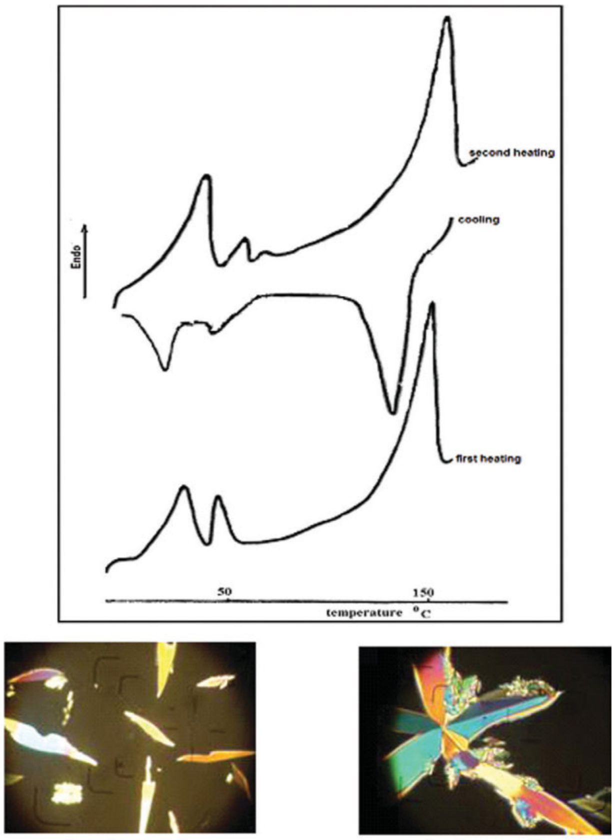
Materials

All reagents were high-purity compounds and were used as received.

The starting silicon-containing diacids were prepared by reported procedures as follows: 1,3-bis (sebacomethyl)tetramethyldisiloxane (mp = 125°C), sebacomethyl pentamethyldisiloxane (mp = 105°C),[16] 1,3-bis(carboxypropyl)tetramethyldisiloxane (mp = 50°C),[17] carboxypropyl-terminated siloxane oligomer,[18] dicarboxyphenyldiphenylsilane (mp = 265°C),[19] and 1,3-bis(carboxytrimellitylimido-*N*-propylene)tetramethyldisiloxane (mp = 200°C).[20]

Analyses

Fourier transform infrared (FTIR) spectra were registered on a Vertex 70 spectrophotometer (Bruker, Ettlingen, Germany). Polarizing optical microscopy (POM) observations were made with an Olympus (Tokyo, Japan) BH-2 microscope fitted with a THMS 600/HSF9I hot stage (Tadworth, Surrey, England). The differential scanning calorimetry (DSC) analyses were performed on a PerkinElmer differential



114°C, first cooling

88 °C first cooling

Figure 2 Thermotropic behavior of CH4: DSC scans and POM observations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

scanning calorimeter (Singapore) with heating and cooling rates of 10°C/min. ^{1}H-NMR spectra were registered on a JEOL C60-HL spectrometer (Tokyo, Japan) in $CDCl_3$. X-ray diffraction (XRD) patterns were obtained on a Philips PW 1830/PW 3710/PW 1050 powder diffractometer (Eindhoven, The Netherlands) with Cu Kα radiation.

The synthesis of the supramolecular polymers was performed through the mixing of stoichiometric amounts of 4,4′-bipyridine and siloxane or silane (di)acids in dry tetrahydrofuran (4–5 wt %) for 1 h at 50°C, followed by distillation of the solvent and vacuum drying.

As an alternative, the contact method was also applied: equimolecular amounts of 4,4′-bipyridine and 1,3-bis(carboxypropyl)tetramethyldisiloxane were finely ground together for a few minutes, and the resulted powder was analyzed.

RESULTS AND DISCUSSION

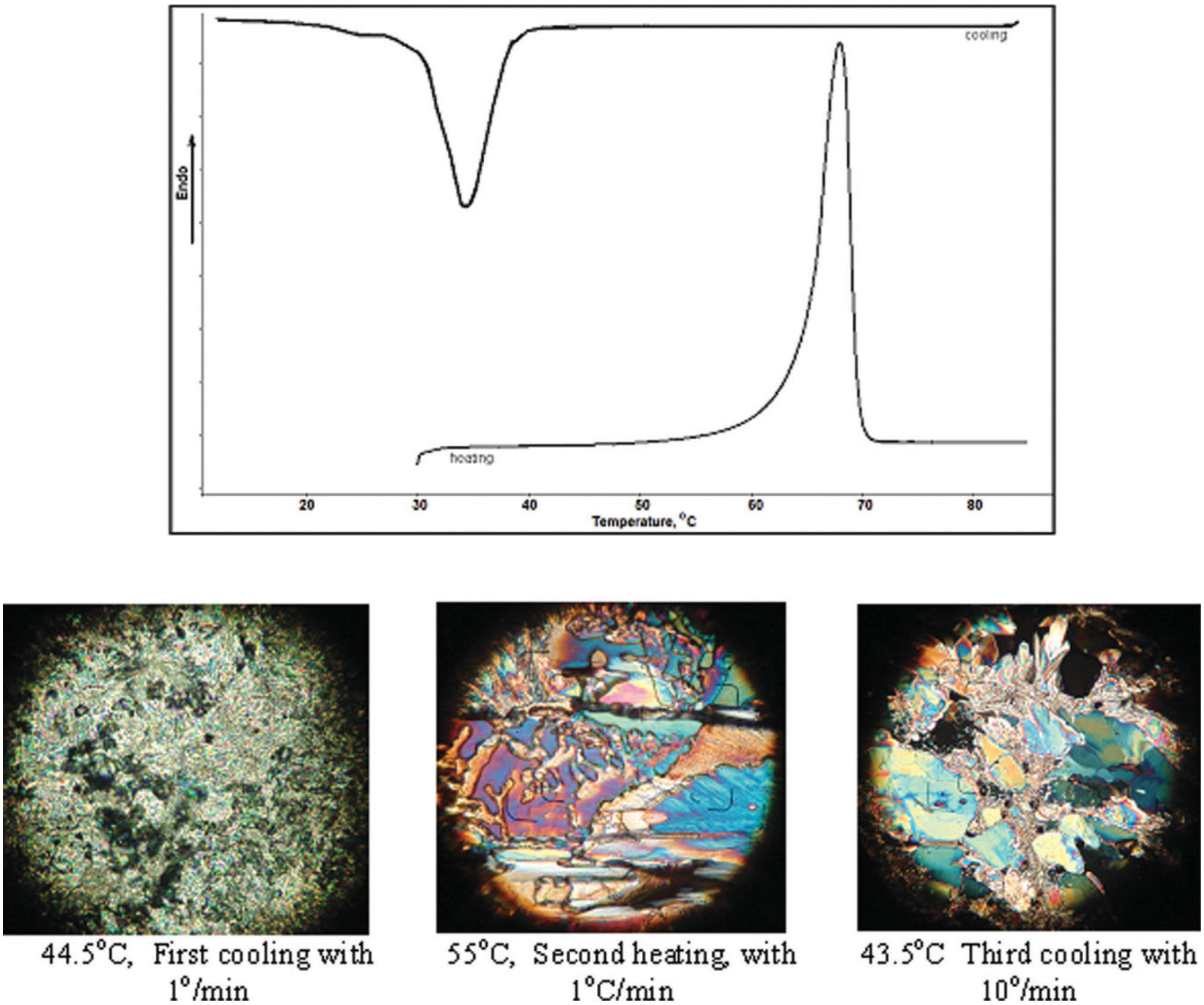
Starting from 4,4′-bipyridine and silicon-containing carboxylic acids dissolved in a common nonpolar solvent, five supramolecular polymers and one model dimer were obtained with the structures depicted in Scheme 1. The preparation method followed a reported procedure based on a slow-evaporation technique.[10] Because the association of a carboxylic acid and a pyridine derivative through hydrogen bonding is stronger than that of carboxylic acid dimerization,[21] the preparation of supramolecular polymers in nonpolar solvents is extremely easy.

The formation of the hydrogen bonds was primarily verified by FTIR spectroscopy, which showed two specific absorption bands[10] around 1950 and 2450 cm^{-1} that were concomitant with the disappearance of the broad OH absorption between 3000 and 3500 cm^{-1}. All the other bands corresponding to the proposed structures were present: asymmetric siloxane Si—O—Si at 1030 cm^{-1}, CH_3 deformation at 1250 cm^{-1}, CH_3 rocking at 812 cm^{-1}, and —C=C— stretching vibration in aromatics at 1600 cm^{-1}. The carboxyl band was shifted toward lower wave numbers in the supramolecular complexes in comparison with the starting diacids, except for the polymer CH3, which showed the reverse tendency.

We also tested the feasibility of the contact method: through the simple mixing of a siloxane dicarboxylic acid and bipyridine in stoichiometric quantities in a grinding mortar, without the addition of any solvent, hydrogen bonding occurred within a few minutes. The FTIR spectrum, registered after 30 min, was identical to that of the same compound (CH2) obtained by evaporation from tetrahydrofuran.

^{1}H-NMR spectra showed one set of signals, indicating that the polymers were stable in chloroform, at least on the analysis timescale. The signal of the carboxylic proton was visibly shifted in the supramolecular polymer in comparison with the starting compounds (all spectra were obtained in $CDCl_3$), thus indicating the change of the neighborhood polarity (from 10 to 8.6 ppm in the case of CH1, from 8.9 to 10.3 ppm in the case of CH2, and from 10.2 to 8.3 ppm in the case of CH3).

The thermal behavior of the obtained hydrogen-bond complexes was completely different from that of the starting compounds. For some of them, glass transitions were detected by DSC above room temperature. The melting temperatures (T_m's) of the supramolecular polymers (Table I) were between those of 4,4′-bipyridine (112°C) and the corresponding diacids, with the exception of CH1 and CH4, which had T_m values lower than those of the starting acids. As observed by POM and DSC measurements, all the obtained supramolecular polymers exhibited thermotropic behavior, although the separate components did not. Because of the characteristics of the hydrogen bonds, the liquid-crystalline phase in the supramolecular polymers is stabilized by the increased aspect ratio of aggregates in



44.5°C, First cooling with 1°/min

55°C, Second heating, with 1°C/min

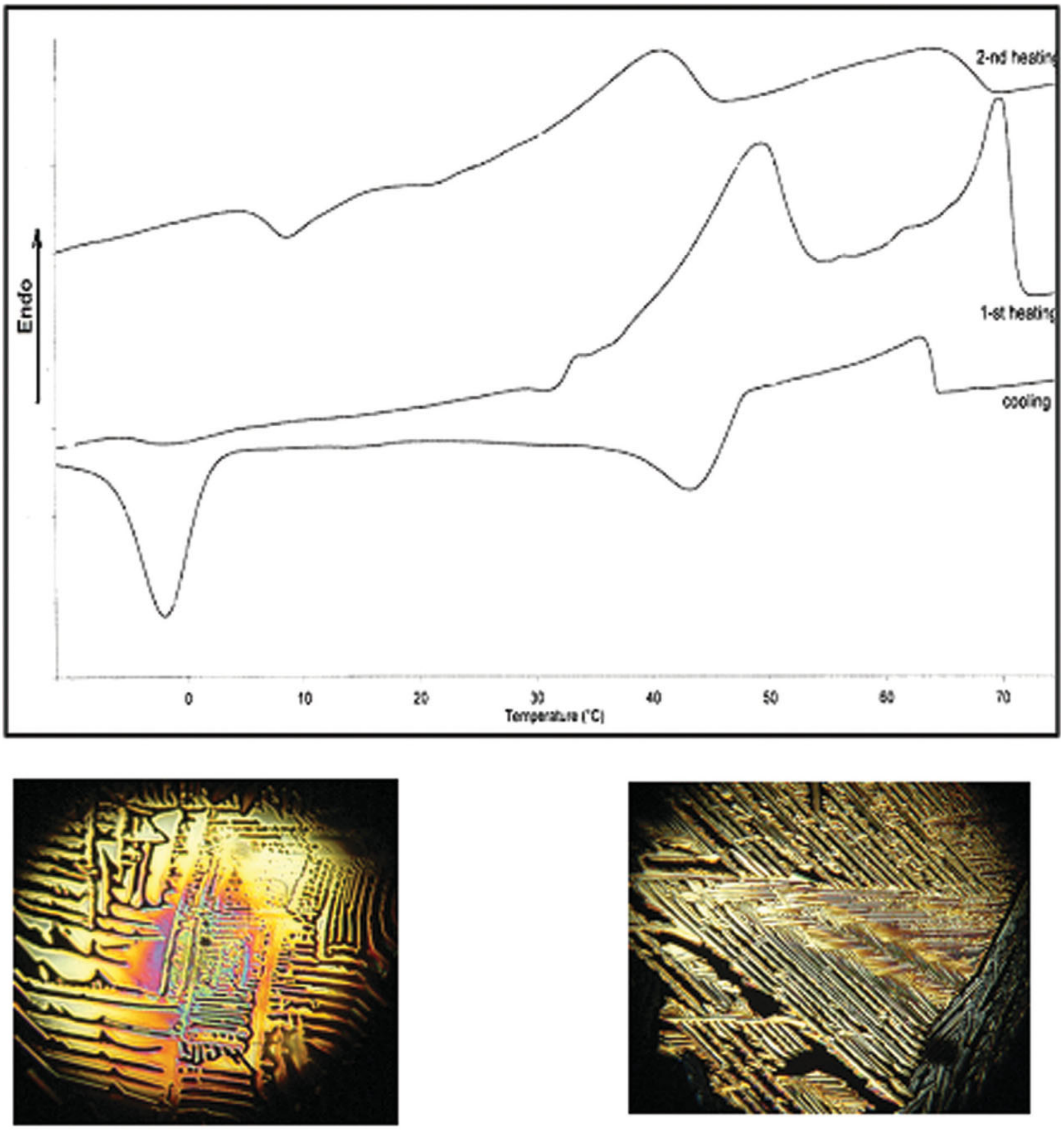
43.5°C Third cooling with 10°/min

Figure 3 Thermotropic behavior of CH2: DSC scans and POM observations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

comparison with the constituent molecules.[3] On the other hand, it is known that the anisotropy in liquid crystals enhances the degree of polymerization in hydrogen-bonded molecules, so a strong cooperative relationship exists between association and mesomorphism.

In Table I, the thermal transitions (from DSC) of the obtained supramolecular compounds are collected: T_m and the isotropization (clearing) temperature (T_i) from the first heating scan and the glass-transition temperature (T_g) from the second heating scan. The thermotropic transitions from DSC were generally confirmed by the POM observations. The differences between the two methods are partly due to the differences in the measurement principles and partly due to the specific behavior of the samples having large transitions. With DSC, T_m and T_i were taken at the peak maxima, whereas from POM observations, we considered the onset of melting and the end of the isotropization process. Nevertheless, the two methods gave complementary results, which are summarized as follows. In Figures 1–6, we have collected the DSC scans and POM observations (200× magnification) for each supramolecular polymer, and we discuss the mesophase features.

Polymer CH1 and model CH4 with a similar structure had broad mesophases starting around room temperature and extending over 120°C. The textures observed by POM were also similar: bâtonnets specific to the smectic mesophase were observed both on heating and on cooling, and the textures and temperatures were quite reproducible within three heating–cooling treatments in the microscope. No nematic features were observed, but only lances and bâtonnets, which could be deformed on pressure, were found; this confirmed the molten



56 °C on heating

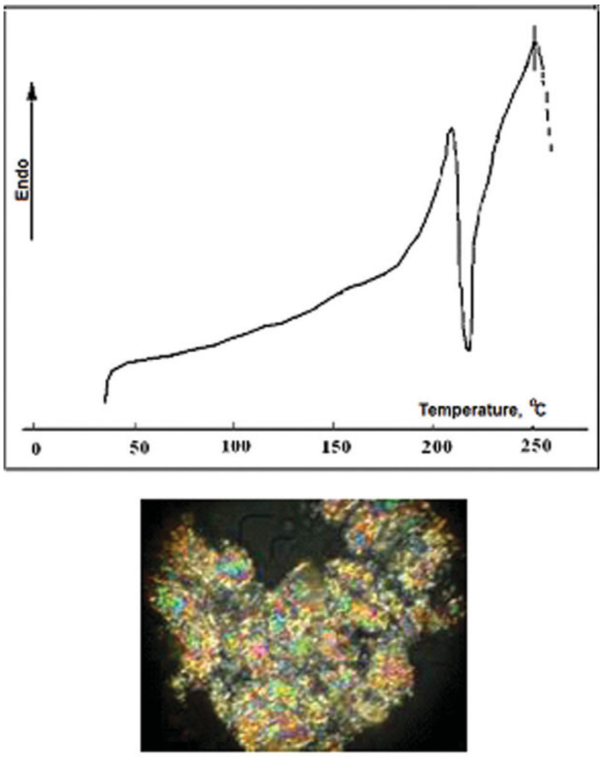
65 °C first cooling, 40x

Figure 4 Thermotropic behavior of CH6: DSC scans and POM observations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

state of the material. The DSC analyses showed more than two endothermal peaks for these compounds, which denoted polymorphic transitions that could not be assigned by POM observations.

The mesomorphic behavior of these compounds is intriguing if one considers the short hard segment. We believe that the liquid-crystalline order could be enhanced by the phase separation within the soft segment and also by the involvement of the ester groups in intermolecular interactions.

Polymers CH2 and CH6 contain carboxypropyl siloxanes with siloxane segments of different lengths. Low transition temperatures but narrow mesophases were obtained for these supramolecular polymers. In the case of CH2, we observed a liquid-crystalline phase within 6°C by POM. By



214 °C, first heating

Figure 5 Thermotropic behavior of CH3 on heating. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

DSC, a single, asymmetric, very intense peak was registered both on heating (at 68°C) and on cooling (at 34°C). Nevertheless, the heating/cooling rate is very important in this case; a thermal treatment with a rate of 1°C/min during microscopy observations revealed the textures shown in Figure 3 (left and middle microphotographs), which are indicative of a mesophase, whereas at 10°C/min, a paramorphotic phase (liquid-crystalline and crystalline) can be seen (Fig. 3, right photograph). Because all the pictures were taken at temperatures above the crystallization peak and below the melting peak in DSC, the most plausible explanation is that the liquid-crystalline phase transition was probably too weak to be detected by DSC at 10°C/min.

The XRD analysis at room temperature confirmed the smectic nature of the mesophase observed in this case only by optical microscopy. The presence of diffraction peaks in the low-angle region without a previous thermal treatment is indicative of a remanent smectic mesophase. It is known that in certain cases such peaks can be observed at room temperature because of the thermal history of the sample.[21–25] As can be seen in Figure 7, besides the crystalline nature of the sample CH2, a peak corresponding to a *d*-spacing of about 19 Å was registered in the low-angle region, suggesting a layered ordering of a smectic mesophase.

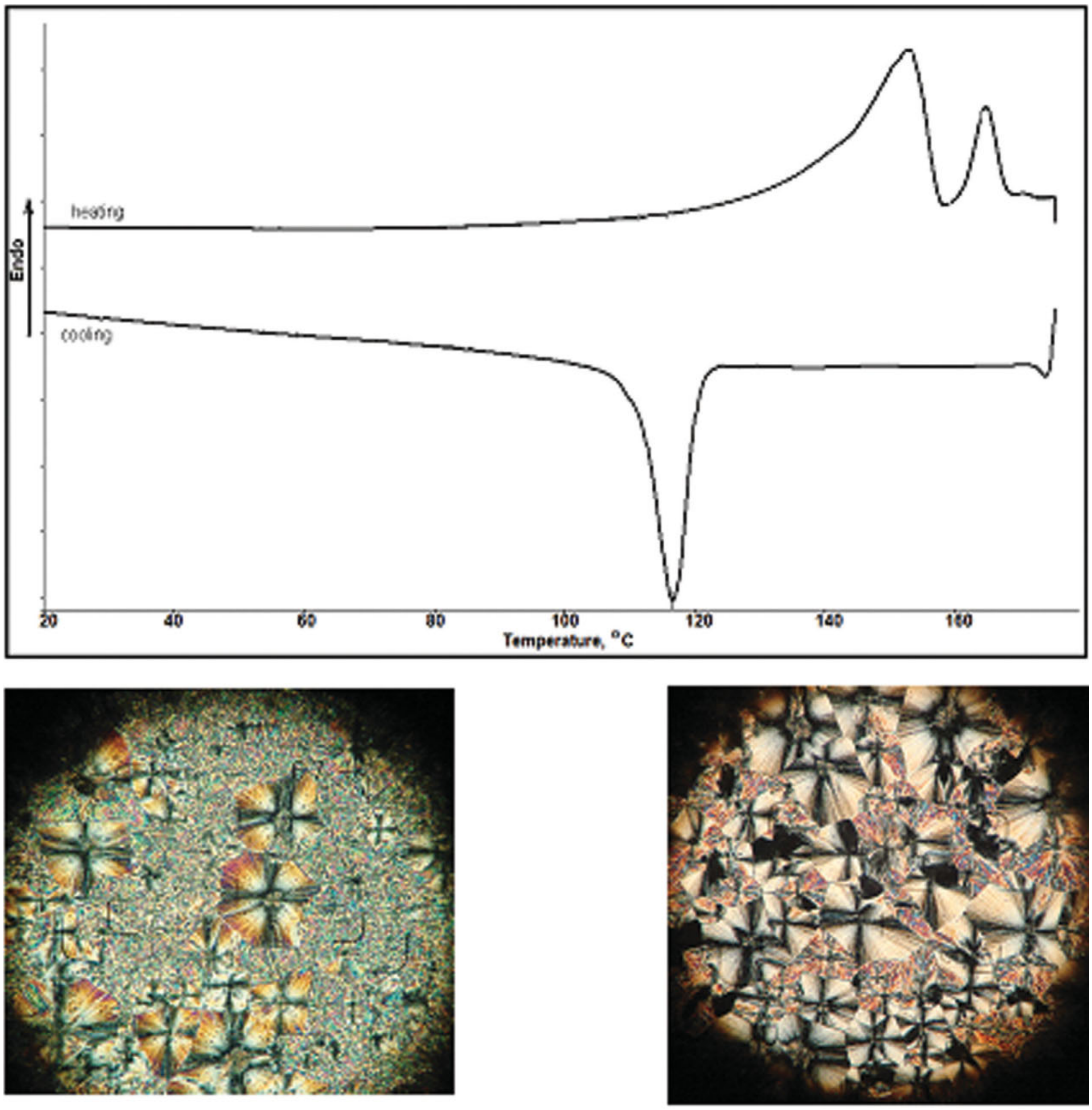
For CH6, the XRD analysis showed a *d*-spacing of 20.7 Å and a lower crystallinity (the amorphous halo was more pronounced). This was an expected result because CH6 contains a longer siloxane segment as a spacer between the hydrogen-bonded mesogenic units. In this case, lowering of T_m was also observed, which is a general trait in liquid crystals with polysiloxane spacers. The thermotropic behavior of sample CH6 is presented in Figure 4. The mesophase was detected in this case by DSC, although the soft segment is much longer than that in CH2. Once again, the tendency of microphase separation probably influenced this behavior.

Supramolecular polymers CH3 and CH5 exhibited higher transition temperatures, and this is in agreement with the reduced flexibility in comparison with the other compounds. The more rigid structure is the explanation for the T_g values observed above room temperature, whereas for the other supramolecular polymers, they were most likely below room temperature (not determined). In the case of CH3 (Fig. 5), T_i was overlapped by the decomposition, as observed by POM. For this reason, the DSC heating scan was stopped before the completion of the isotropization process.

In the case of sample CH5, the DSC scan with 10°C/min (Fig. 6) on heating showed two endotherms (153 and 165°C), whereas on cooling only one peak at 116.5°C was present, with a shoulder at 110°C. However, this exothermal peak was very little influenced by the cooling rate (main peak at 108°C with cooling at 40°C/min). It is known that modification of the cooling rate may induce great variations of the crystallization temperature but very small differences in mesophase transitions. Additional information was obtained by POM. A grainy mesophase was observed on heating, whereas on cooling from the isotropic state, a focal conic texture of a smectic mesophase formed, starting at 125°C, which was similar to that reported for other hydrogen-bonding polymers.[14] This texture froze on further cooling, whereas a crystallization process was overlapped at some point, although the exact temperature of this transition could not be observed.

To verify the thermal stability of the supramolecular hydrogen-bonding complexes in the mesophase, variable-temperature infrared studies were carried out for all polymers (except for CH3 because of its very high T_m value).

The results were similar for all the samples and showed that the hydrogen bonding was stable over the entire mesophase range. This finding is in agreement with other reported data referring to



123° C, first cooling

110° C/min, third cooling

Figure 6 Thermotropic behavior of CH5: DSC scans and POM observations. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

complexes formed with bipyridine derivatives and benzoic acids.[26] Nevertheless, some changes did occur in the infrared spectra above T_m: in all cases, a band at about 2150 cm^{-1} appeared just after the melting; it was present over the entire mesophase and disappeared on cooling. In Figure 8, the FTIR spectra of CH2 are presented (the region of interest); they were registered at room temperature, at T_m, just above isotropization, and after cooling at room temperature. A broadening of the 3000–3500-cm^{-1} region began at 60°C and was more obvious at 70°C after the isotropization; it was accompanied by a diminution of the hydrogen-bonding bands and a shift of the carboxylic band toward a higher wavelength. A similar result was reported by St. Pourçain[26] and explained by the presence of acid dimers as a result of increased mobility in the isotropic liquid state. This explanation seems to be reasonable because the observed modifications were reversible on cooling.

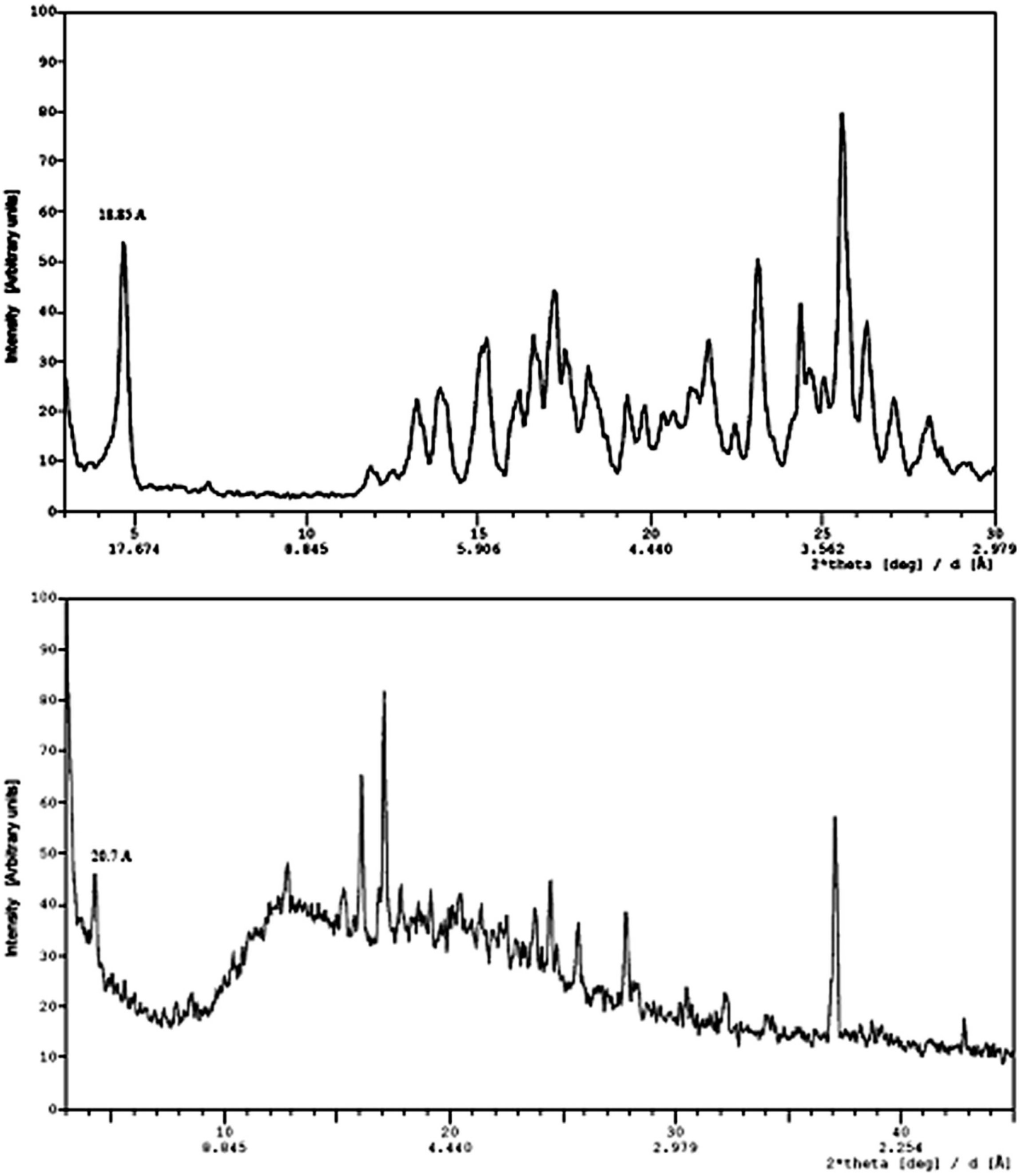


Figure 7 XRD spectra of polymers (top) CH2 and (bottom) CH6.

The supramolecular polymers were used as sensing elements in a device sensor made with thick-film technology. The preliminary tests proved a high sensitivity to NO_x and CO_2, the sensor developing high voltage values in the first minutes upon exposure to gas (hundreds of millivolts). These results will be reported in another article.

CONCLUSIONS

Hydrogen-bonding supramolecular polymers were easily obtained from 4,4′-bipyridine and different silicon-containing diacids and were investigated for thermotropic behavior. All the obtained complexes were liquid crystals within different mesophase ranges depending on the structures of the diacids. Smectic mesophases were observed by optical microscopy and confirmed by XRD.

The hydrogen bonds were stable within the mesophase ranges, and this proved that the observed thermotropic behavior belonged to the new compounds, the supramolecular polymers, and not to inert mixtures of the starting compounds.

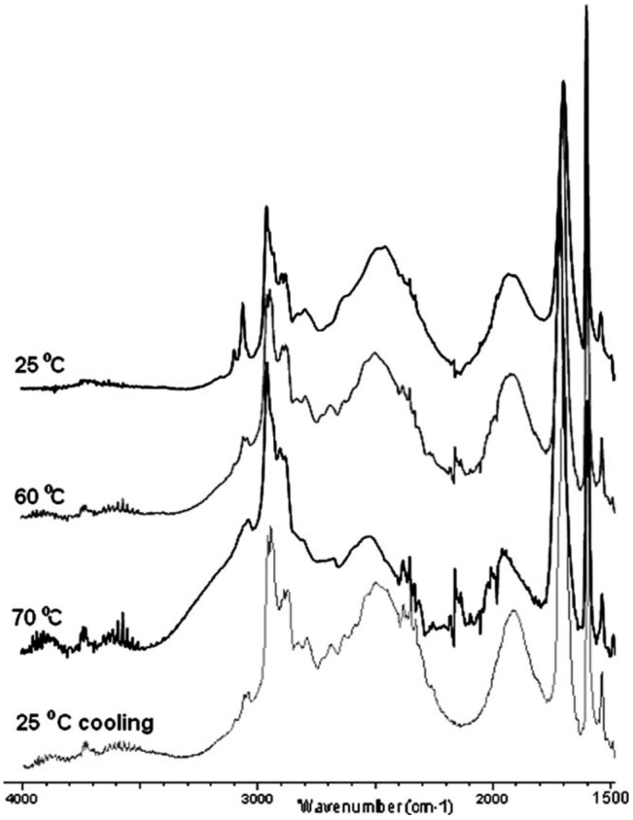


Figure 8 FTIR spectra of polymer CH2 at different temperatures.

Preliminary testing of the supramolecular polymers as gas sensors gave promising results.

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