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Liquid Crystals

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Online publication date: 06 August 2010

To cite this Article Xu, Hui , Kang, Ning , Xie, Ping , Zhang, Rong-Ben and Xu, Duan-Fu(2000) 'Synthesis and characterization of a hydrogen-bonded nematic network based on 4-propoxybenzoic acid side groups grafted onto a polysiloxane', Liquid Crystals, 27: 2, 169 — 176

To link to this Article: DOI: 10.1080/026782900202930

URL: http://dx.doi.org/10.1080/026782900202930

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LIQUID CRYSTALS, 2000, VOL. 27, NO. 2, 169–176

Synthesis and characterization of a hydrogen-bonded nematic network based on 4-propoxybenzoic acid side groups grafted onto a polysiloxane

HUI XU, NING KANG, PING XIE, RONG-BEN ZHANG*
and DUAN-FU XU

Center for Molecular Science, Institute of Chemistry,
Chinese Academy of Sciences, Beijing 100080, PR China

(*Received 4 August 1999; accepted 19 August 1999*)

A polymethylsiloxane with 4-propoxybenzoic acid side groups was prepared by hydrosilylation of polymethylhydrosiloxane and methyl 4-allyloxybenzoate followed by hydrolysis. The existence of strong hydrogen bonding interactions in this polymer due to dimerization of the carboxylic acid groups was demonstrated by FTIR. The polymer exhibits a nematic mesophase at elevated temperatures due to the self-assembly of hydrogen-bonded mesogens (dimers). After cooling from its nematic melt, a stable hydrogen-bonded nematic network structure was formed, as demonstrated by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction. Temperature-variable FTIR analysis presents a convincing interpretation for the DSC thermogram of the polymer, and furthermore assists in understanding the process of formation of the nematic network and the reversibility of such hydrogen-bonded networks.

1. Introduction

Since Finkelmann *et al.* [1] first synthesized a side group type of liquid crystalline elastomer using a liquid crystalline polysiloxane, anisotropic polymeric networks have received a great deal of attention because of their potential applications in areas such as optical fibre coatings, chip encapsulation, non-linear optical (NLO) applications for frequency doubling, piezo- and pyroelectric sensors, the manufacture of new optical components, etc. [2–17]. In the past few years, we have also carried out much research on liquid crystalline networks based on side group and double side group polysiloxanes, as well as exploring their application for command and alignment layers for liquid crystal display (LCD) purposes [18–24]. Most of the polymeric networks were crosslinked through covalent bonds, which endow them with high mechanical and thermal stability. However, in recent years polymeric networks crosslinked by non-covalent bonds have attracted more interest thanks to their dynamic and reversible properties, that hold promise for their potential applications in the controlled release of medicines or catalysts, purification processes, and optoelectronic devices [25–30].

Hydrogen bonding, due to its stability, dynamics, and directionality, is one of the most important and widely used non-covalent interactions for the design and construction of supramolecular architectures [31]. Benzoic acid derivatives have long been known to exhibit liquid crystallinity as a result of dimer formation involving intermolecular hydrogen bonds [32–34]. By the introduction of benzoic acids into polymers, it is possible to obtain anisotropic polymeric networks by the self-assembly of hydrogen-bonded dimers. Blumstein *et al.* [35] prepared side group polymers containing benzoic acid moieties—poly[(*p*-acryloyloxy)benzoic acid] and poly[(*p*-methacryloyloxy)benzoic acid]—for the first time, but no anisotropic fluid mesomorphic state could be observed due to the lack of flexible spacers between the polymer backbone and the rigid aromatic mesogenic units, so restricting the arrangement of the hydrogen-bonded mesogenic units. Kato *et al.* [36] first reported smectic liquid crystalline polymer networks that show reversible smectic–isotropic phase transitions by introduction of long flexible spacers between the polymer main chain and the side group benzoic acid units. However, they concentrated their study on the liquid crystallinity of such polymers. The process of hydrogen-bonding self-assembly to form such anisotropic networks has not been analysed thoroughly, and this precludes us from further understanding the mechanism of formation and properties of such hydrogen-bonded networks.

In the present study, 4-propoxybenzoic acid, one of the benzoic acid derivatives that shows nematic liquid crystallinity, was grafted onto polymethylsiloxane.

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*Author for correspondence;
e-mail: zhangrb@infoc3.icas.ac.cn

Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2000 Taylor & Francis Ltd
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Through the self-assembly of hydrogen-bonded mesogens, an anisotropic polymeric network with a nematic state was formed and characterized by differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (XRD). In particular, the process of formation of the nematic network and the dynamic and reversible properties of the hydrogen-bonded network were systematically investigated by temperature-variable FTIR analysis.

2. Experimental

2.1. *Materials*

Poly(methylhydrosiloxane) with the formula $(CH_3)_3SiO$-$[(CH_3)HSiO]_{\sim 35}Si(CH_3)_3$ was purchased from Fluka AG. The catalyst dicyclopentadienedichloroplatinum (Cp_2PtCl_2) was prepared by a literature method [37] and stored in a dry box. Allyl bromide, acetone, toluene, pyridine and tetrahydrofuran (THF) were obtained from the Beijing Chemical Co. and dried, followed by distillation, before use. Methyl 4-hydroxybenzoate, K_2CO_3, NaOH, hexane, dichloromethane, methanol, and hydrochloric acid (37%), all of analytical grade, were obtained from the Beijing Chemical Co. and used without further purification.

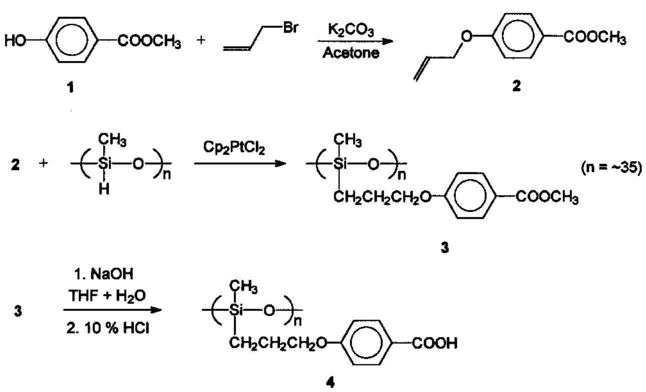
2.2. *Characterization*

^1H NMR spectroscopy was performed on a JNH-FX100 (JBOX) with DMSO-d_6 as solvent. FTIR spectra were recorded on a Perkin-Elmer 2000 FTIR spectrometer. Vapour phase osmometry (VPO) measurements were made on a KNAUER VP osmometer at 40°C with THF as solvent and poly(methylhydrosiloxane) as standard. DSC was carried out using a Perkin-Elmer DSC-7 differential scanning calorimeter at a heating rate of 10°C min^{-1}. POM was performed with a Xintian microscope model XP1A (China) equipped with a Mettler FP-82 hot stage and a RICOH F-2 camera. XRD was carried out using a Rigaku (Japan) D/max-2400 X-ray diffractometer (Cu K_α) and samples prepared as flat films on glass substrates. Temperature-variable FTIR spectra were recorded on a Nicolet 750 FTIR spectrometer equipped with a Mettler FP-84 hot stage at a heating rate of 10°C min^{-1}. The sample for measurement was prepared by casting a pyridine solution of a side group polysiloxane onto a KBr crystal to form a transparent film with thickness about 0.2 mm, which was dried *in vacuo* at 60°C for 20 h.

2.3. *Synthesis (see the scheme)*

2.3.1. *Synthesis of methyl 4-allyloxybenzoate 2*

To a 500 ml three-necked flask equipped with a reflux condenser and magnetic stirrer were added 61 g (0.41 mol) of methyl 4-hydroxybenzoate, 112 g (0.81 mol) of K_2CO_3, 200 ml of acetone, and 50 g (0.41 mol) of allyl bromide. The mixture was heated at reflux for 5 ~ 7 h, then cooled, filtered, and the filter pad was washed three times with ether. The filtrate and washings were collected and rotary evaporated to remove solvents and residual allyl bromide. The residual product was purified by flash silica gel column chromatography using dichloromethane/hexane (2:1) as eluent to give 70 g of a colourless oil, yield ~90%. ^1H NMR ($CDCl_3$, δ in ppm): 8.01 (aromatic, d, 2H), 6.92 (aromatic, d, 2H), 6.02 (=CH, m, 1H), 5.38 (CH_2=, m, 2H), 4.60 (OCH_2, d, 2H), 3.88 ($COOCH_3$, s, 3H). Elemental analysis: calc. for $C_{11}H_{12}O_3$, C 68.75, H 6.25; found, C 68.89, H 6.22%.



Scheme. The preparation of the side group polysiloxane with grafted 4-propoxybenzoic acids residues.

2.3.2. *Synthesis of intermediate 3 by hydrosilylation*

A 50 ml Schlenk flask equipped with a reflux condenser and a magnetic stirrer was evacuated and charged three times with dry argon. Then to the flask were added by syringe 5 g (0.0266 mol) of methyl 4-allyloxybenzoate, 2 ml of a THF solution of Cp_2PtCl_2 (1 mg ml^{-1}) and 20 ml of dry toluene. The mixture was stirred at 50°C for 30 min before addition of 1.7 g (0.0255 mol of Si–H units) of poly(methylhydrosiloxane). The resulting mixture was stirred for 10 h at 80°C. The reaction was monitored by observing the disappearance of the SiH stretching band at 2160 cm^{-1} in the IR spectrum. After cooling, the reaction mixture was concentrated, and the excess of alkene **2** was separated from the polymer **3** by passing the reaction mixture through a flash silica gel column using dichloromethane/hexane (2:1) as eluent. The polysiloxane **3** was then eluted from the column using THF to afford a highly viscous oil after removal of THF. ^1H NMR ($CDCl_3$, δ in ppm): 7.85, 6.75 (aromatic), 3.82 (OCH_2), 3.78 ($COOCH_3$), 1.75 (CH_2), 0.60 ($SiCH_2$), 0.10 ($SiCH_3$). IR: 1710 cm^{-1} (C=O).

2.3.3. *Synthesis of side group polysiloxane 4 by hydrolysis*

3 g of polysiloxane **3** (11.58 mmol) was dissolved in 10 ml of THF, and then an aqueous NaOH solution

(10 ml) containing 0.47 g of NaOH (11.75 mmol) was added. The mixture segregated into two layers. The upper THF layer containing polymer **3** had a light yellow colour; the bottom aqueous layer was colourless. After heating gently under reflux at 65°C for 1 h, the colour in the upper layer moved to the bottom layer, indicating that the $COOCH_3$ groups had been converted into COONa groups giving a product which is soluble in water. After cooling, the upper THF layer was discarded and 10% aqueous HCl was added to the lower layer to acidify the COONa groups. Methanol was then added to the solution to precipitate polymer **4**. The resulting white solid was washed with water and subsequently with hexane and then dried under vacuum at 60°C for 20 h. ^1H NMR (DMSO-d_6, δ in ppm): 7.82, 6.85 (aromatic), 3.85 (OCH_2), 1.75 (CH_2), 0.60 ($SiCH_2$), 0.10 ($SiCH_3$). IR: 1680 cm^{-1} (C=O).

3. Results and discussion

3.1. *Preparation of 4-propoxybenzoic acid grafted polysiloxane*

Since the carboxylic acid group COOH is able to react with Si–H groups in the presence of Pt-catalyst to form COOSi≡ [38], the propoxybenzoic acid cannot be grafted to the polysiloxane by hydrosilylation of 4-allyloxybenzoic acid with polymethylhydrosiloxane directly. Therefore the alternative method shown in the scheme was adopted. This approach involves the hydrosilylation of methyl 4-allyloxybenzoate with polymethylhydrosiloxane followed by hydrolysis.

The hydrosilylation reaction catalysed by Cp_2PtCl_2 proceeds almost quantitively. The hydrolysis reaction also proceeds to completion, but it must be carefully performed in order to avoid or reduce side reactions such as the splitting of Si–O or Si–C bonds. The amount of alkali, the temperature, and the time of reaction play an important role in this regard. The final product is a white solid with a relatively high melting point due to the formation of dimeric structures between pendant side group benzoic acid moities through hydrogen-bonding [33]. The product is soluble in polar solvents such as THF, *N*,*N*-dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), but insoluble in non-polar solvents owing to the existence of carboxylic acid units.

The ^1H NMR spectrum of the final product confirms the structure of the side group polysiloxane (figure 1), but the signal for the carboxylic acid proton is difficult to detect owing to the influence of the solvent DMSO-d_6 with which the proton of the carboxylic acid could interact. The molecular mass of the polymer determined by vapour pressure osmometry (VPO) is about 7260 dalton, slightly lower than the theoretical value of 8500 dalton calculated on the assumption that all the Si–H sites have been grafted with 4-propoxybenzoic acid groups and that no side reaction occurs on hydrolysis. Based on the molecular mass result, it is considered that there are still side reactions occurring, but that their extent is not insignificant.

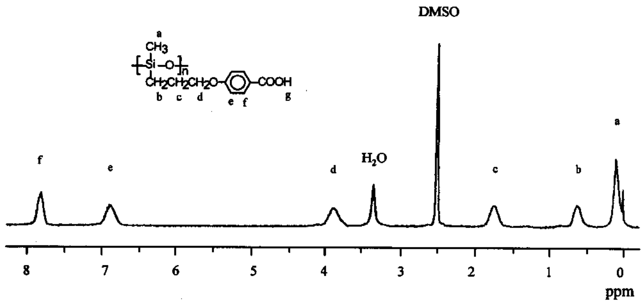


Figure 1. The ^1H NMR spectrum of 4-propoxybenzoic acid-grafted polysiloxane (in DMSO-d_6).

The formation of dimeric hydrogen bonding in the side group polysiloxane is confirmed by FTIR spectroscopy (figure 2). It is noteworthy that there is a broad band of IR absorption in the range 2500–3400 cm^{-1}, which is attributed to the characteristic stretching vibration of associated O–H groups of COOH [39]. The stretching vibration of the carbonyl group (C=O) is located at 1680 cm^{-1} which means that the carbonyl group participates in the formation of hydrogen-bonding, further confirming the formation of hydrogen-bonded dimers in the polymer.

3.2. *Characterization of the nematic network*

The DSC curves for the side group polysiloxane are shown in figure 3. The data concerning the transition temperatures and the enthalpies for the transitions are collected in the table. It is found that in the first heating run there is a glass transition at 63°C and an endothermic peak at about 174°C; in both the cooling and second

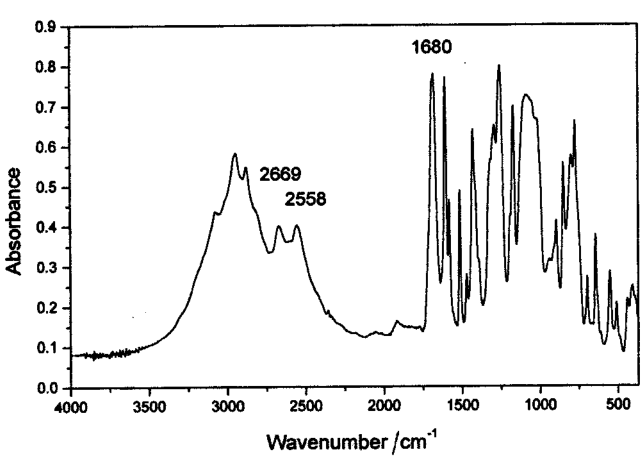


Figure 2. The FTIR spectrum of 4-propoxybenzoic acid-grafted polysiloxane.

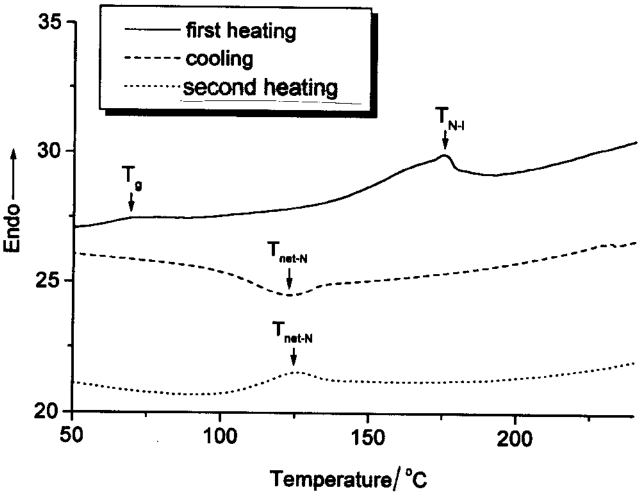


Figure 3. The DSC thermogram of the side group polysiloxane.

Table. Thermal properties of the 4-propoxybenzoic acid-grafted polysiloxane.

Scanning run	T_g^{a}/ °C	$T_{net\text{-}N}^{b}$/ °C	$T_{N\text{-}I}^{c}$/ °C	ΔH/ J g^{-1}
First heating	63	undetectable	174	15.7
Cooling		122	undetectable	− 19.3
Second heating		124	undetectable	6.9

[a] T_g, glass transition temperature, detectable only during the first run.

[b] $T_{net\text{-}N}$, nematic network–nematic liquid crystalline phase transition temperature.

[c] $T_{N\text{-}I}$, nematic–isotropic transition temperature for the first heating run, contributed to mainly by a quasi-crystalline–isotropic transition.

heating runs there appears only one peak at about 122°C and 124°C, respectively. From POM observations, this can be seen as a softening point at about 120°C. Above the softening point, the sample shows poor fluidity and birefringence, the latter becoming brighter after annealing for a period of time. When the temperature is elevated to above 175°C, the birefringence disappears gradually. As the temperature returns to below 175°C, the birefringence reappears. Apparently, the temperature of 175°C, which corresponds to the endothermic peak in the first DSC run, is the liquid crystalline–isotropic transition temperature. In the temperature range 120–175°C therefore, the sample is in a liquid crystalline state. The XRD pattern of the sample at 140°C, figure 5 (*a*), shows only two diffuse peaks at $2\theta = 10°$ and 20°; no peak exists at small angles, indicating that the liquid crystalline state of the sample should be assigned as nematic. On dropping the temperature to below the softening point, the fluidity of the sample is frozen out and a stable hydrogen-bonded network structure is formed; the birefringence of the sample remains throughout (figure 4). The XRD pattern of the sample at room temperature after cooling, figure 5 (*b*), is similar to that of the nematic melt (no crystalline diffraction peaks appear), indicating that the network preserves the nematic state of its precursor melt. The peaks in the cooling and second heating DSC runs, occurring at temperatures

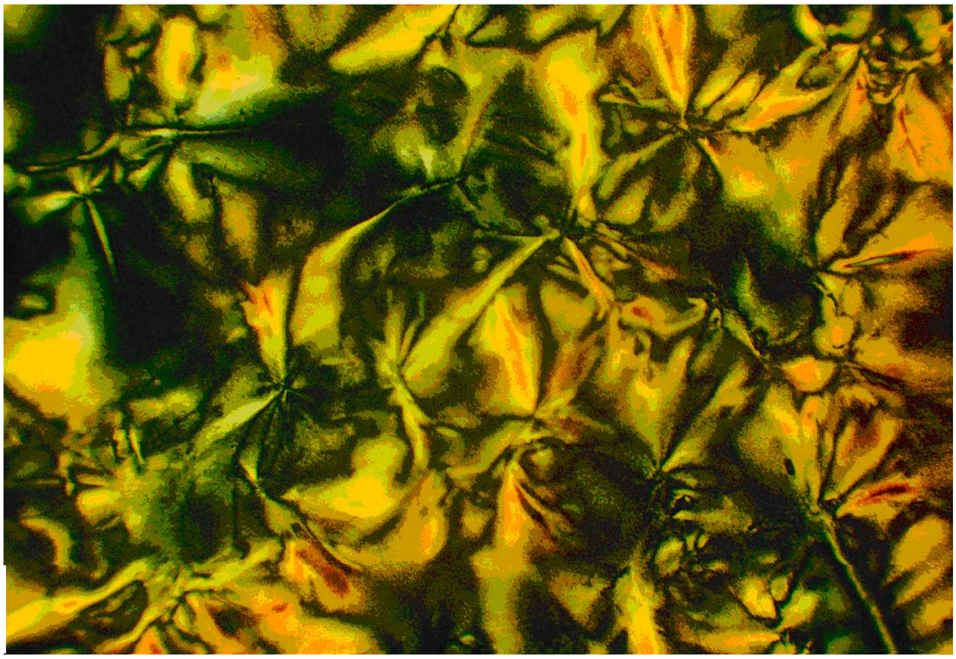


Figure 4. Polarized optical micrograph of the side group polysiloxane at room temperature after heat treatment, 100 ×.

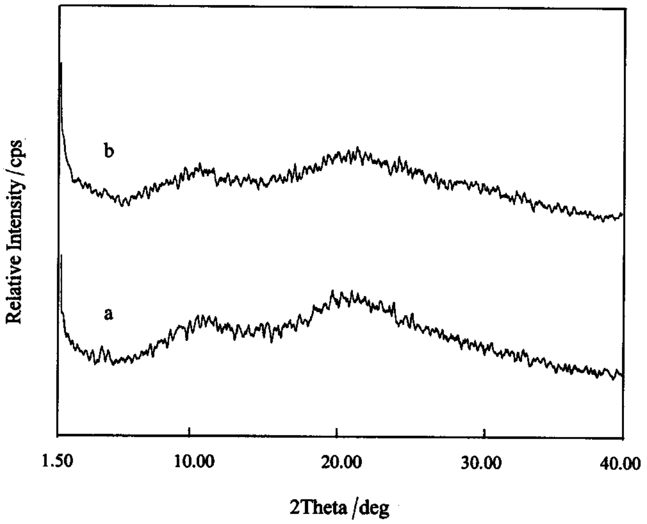


Figure 5. The XRD pattern of the side group polysiloxane at (*a*) 140°C, and (*b*) room temperature after cooling from 140°C.

near to the POM softening point, should therefore correspond to the nematic network–nematic liquid crystalline transition ($T_{\text{net-N}}$) as discussed later.

All these results prove the formation of a nematic network in the side group polysiloxane below $T_{\text{net-N}}$. The nematic network could be represented as shown in figure 6. The formation of a nematic but not a smectic network could be ascribed to the short flexible spacer which may result in weak decoupling between the polymer main chain and the mesogenic units, so making the free arrangement of the mesogenic moieties into a more highly ordered mesophase difficult.

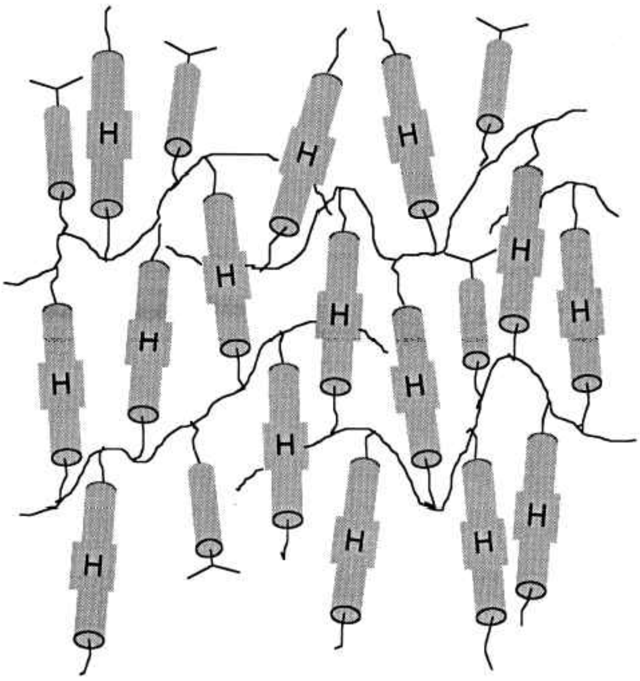


Figure 6. Schematic representation of the nematic network of the side group polysiloxane.

3.3. *Temperature-variable FTIR analysis of the nematic network*

Although the formation of a nematic network in the side group polysiloxane has been demonstrated by a set of characterization techniques, there are still quite a few questions that needed to be clarified, such as why the glass transition appears only in the first heating DSC run, why there appears only $T_{\text{N-I}}$ but no $T_{\text{net-N}}$ transition in the first heating run, while in the cooling run and the second heating run there appears only $T_{\text{net-N}}$ but no $T_{\text{N-I}}$ transition, and how the nematic network is formed. Answers to these questions would be helpful to our understanding of the process of formation of the nematic network and the reversible and dynamic properties of the hydrogen bonding self-assembly.

The nematic network is formed by crosslinking through hydrogen-bonding, and therefore by monitoring the variation of hydrogen bonding, it is possible to gain an insight into the nematic network. The hydrogen-bonding, specifically the dimeric hydrogen-bonding of carboxylic acids, can be analysed through the stretching vibration of the carbonyl group (C=O) in FTIR spectra. The peak for the carbonyl group of the dimer is located at around 1680 cm^{-1}, while if the dimer dissociates to monomer, there should appear a new peak at around 1730 cm^{-1}. The stronger the peak at 1730 cm^{-1}, the greater is the extent of dissociation of the dimer. Temperature-variable FTIR studies can reflect all these changes with change of temperature and provide an effective method for this investigation.

The temperature-variable FTIR spectra of the side group polysiloxane obtained in the range about 1650–1850 cm^{-1}, in which the carbonyl stretching falls, during first and second heating runs, are shown in figures 7 (*a*) and 7 (*b*), respectively. It is noted that there is no peak for monomer acid (1730 cm^{-1}) below 100°C, but at 130°C an obvious peak appears at 1730 cm^{-1} and strengthens with rise in temperature, which means that the hydrogen-bonding starts to dissociate at around 130°C following which the sample enters into the liquid crystalline state. Actually, the starting temperature for the hydrogen-bonding dissociation should correspond to the $T_{\text{net-N}}$ transition in the DSC thermogram.

The intensities of the carbonyl stretching for the monomer at 1730 cm^{-1} plotted as a function of temperature, during the first and second heating runs, are shown in figures 8 (*a*) and 8 (*b*), respectively. For the first heating run, the sudden change in the curve occurs at about 170°C, which is consistent with $T_{\text{N-I}}$. For the

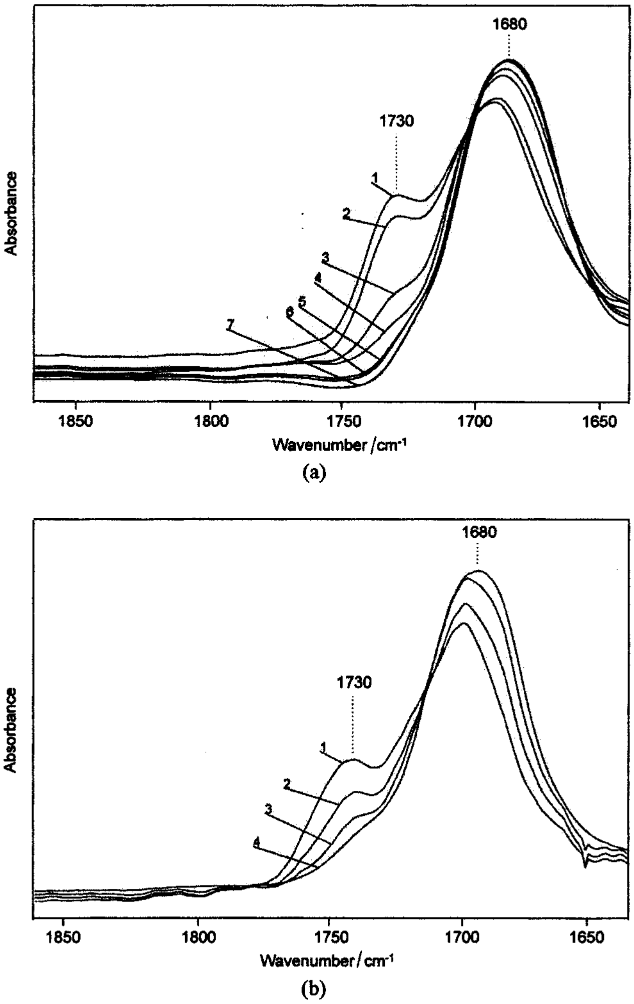


Figure 7. The temperature-variable FTIR spectra of the side group polysiloxane in the range about 1650–1850 cm^{-1}. (*a*) First heating, 1: 190°C, 2: 175°C, 3: 150°C, 4: 130°C, 5: 100°C, 6: 70°C, 7: room temperature; (*b*) second heating, 1: 175°C, 2: 150°C, 3: 130°C, 4: 100°C. (Some curves are omitted for clarity.)

second heating run, the sudden change in the curve occurs at about 120°C which is consistent with $T_{\text{net-N}}$. Also, the extent of the sudden change for the first heating run is larger than that for the second heating run, consistent with the fact that the enthalpy of the first heating run is higher than that of the second heating run. All the FTIR results conform well with the DSC thermograms, indicating that all the transitions result from the fluctuations of hydrogen-bonding.

The difference between the first heating and the second heating DSC runs can now be interpreted as below. When the sample film is prepared from a solution, many quasi-crystalline regions may form via aggregation involving intramolecular hydrogen-bonding, whereas the intermolecular hydrogen-bonding which should lead to network structure is relatively minor. The existence of quasi-crystalline regions is supported by the XRD pattern of the cast film (figure 9), in which there appear several small peaks. Since no large dimensional network structure is formed in the film cast from solution, movement of chain segments of the polymer is possible and

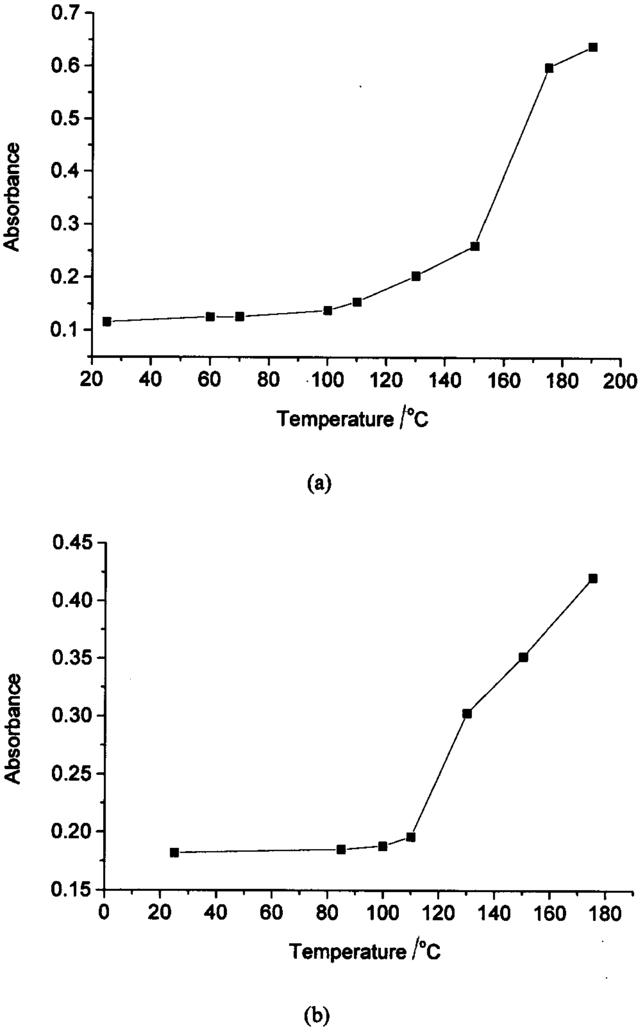


Figure 8. The intensity of the carbonyl stretching of monomeric carboxylic acid groups at 1730 cm^{-1} as a function of temperature. (*a*) First heating; (*b*) second heating.

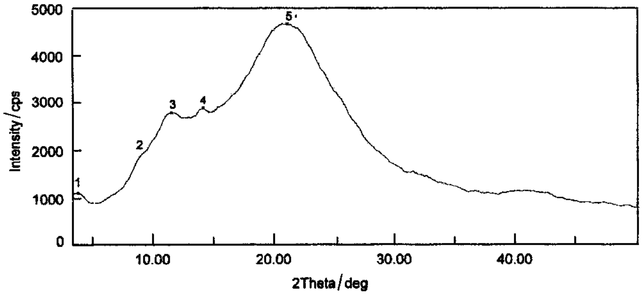


Figure 9. The XRD pattern of a film of the side group polysiloxane cast directly from pyridine solution.

hence the glass transition appears in the first heating process. The formation of quasi-crystalline regions in the polymer would strengthen those hydrogen-bonds, that dissociate at relatively high temperatures—up to about 170°C as shown in figure 8 (*a*)—and the sample enters the isotropic state directly after melting. The temperature happens to tally with the $T_{\mathrm{N\text{-}I}}$ value, but as a matter of fact, the large endothermic peak is at 174°C during the first heating run and could result mainly from the quasi-crystalline–isotropic and not the nematic–isotropic transition. There are probably small parts of network structure in the film due to a little intermolecular hydrogen bonding; however the amount is small so that $T_{\mathrm{net\text{-}N}}$ cannot be observed by DSC during the first heating run, but is detected by the temperature-variable FTIR.

In the second heating run, a large amount of nematic network has been formed through extensive intermolecular hydrogen bonding. This restricts the movement of chain segments of the polymer, and consequently the glass transition of the polymer disappears. In addition, the formation of large domains of nematic network make the $T_{\mathrm{net\text{-}N}}$ detectable in the DSC thermogram. Nevertheless, the $T_{\mathrm{N\text{-}I}}$ peak is difficult to detect in the second heating since the enthalpy for the hydrogen-bonding-based nematic–isotropic transition is basically low.

From the temperature-variable FTIR analysis, we get a general conception of the process of formation of the nematic network. With the temperature dropping to below $T_{\mathrm{N\text{-}I}}$, the nematic mesophase is gradually formed through the self-assembly of the hydrogen-bonded mesogenic units, a process that proceeds through the repeated dissociation and re-association of the dynamic hydrogen bonds. When the temperature is below $T_{\mathrm{net\text{-}N}}$, the dissociation of hydrogen-bonding ceases, resulting in the stable network structure and freezing of the nematic mesophase in this network. The formation of the network structure prevents the mesogenic side groups from further arrangement, so preventing crystallization.

4. Conclusions

A side group polysiloxane containing 4-propoxybenzoic acid residues as pendant groups gives the self-assembly of hydrogen-bonded dimers of the carboxylic acid groups and forms a nematic liquid crystalline mesophase at elevated temperature. With decreasing temperature below $T_{\mathrm{net\text{-}N}}$, a stable hydrogen-bonded nematic network structure was obtained, which was characterized by DSC, POM, and XRD. The formation of the nematic network restricts the movement of the chain segments and side group mesogenic units of the polymer, and therefore the glass transition of the polymer disappears and crystallization of the polymer at low temperatures is also prevented. The phase transitions of the polymer are ascribed to the dissociation and association of dimeric hydrogen-bonding which was analysed by temperature-variable FTIR. This kind of polymer with a nematic network structure, has potential applications as an oriented host in NLO materials, the controlled release of catalysts, the alignment layer in a liquid crystal display and other areas.

This project is financially supported by NSFC (No. 29874034). We also appreciate Dr Li Cui's assistance with the POM measurements and helpful discussions on hydrogen-bonding self-assembly.

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