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Polymer 46 (2005) 11949–11957

polymer

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A novel aromatic polyimide with rigid biphenyl side-groups: Formation and evolution of structures in thermoreversible gel

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Received 9 July 2005; received in revised form 6 September 2005; accepted 6 October 2005
Available online 26 October 2005

Abstract

A new thermoreversible polyimide gel was prepared and characterized. This polyimide was synthesized from 4,4′-oxydiphthalicanhydride (ODPA) and 3,5-diamino-benzonic-4′-diphenyl ester (DABBE) via a one-step polymerization procedure in *m*-cresol. With lowering temperature, a gel from the polyimide (PI) solution was formed due to the solvation power decrease. On heating, a gel/sol transition could be observed by an endothermic peak of DSC curve, and the gel/sol transition enthalpy and temperature went up with the increase of the solution concentration. The original aggregation structure of the gel is amorphous. While the gel was kept at 15 °C, two kinds of order structure developed, which were determined by X-ray. One was layer structure which formed from aggregations of main chains with *d*-spacing of 15.7 Å ($2\theta = 5.64°$) or from side chains with *d*-spacing of 36.6 Å ($2\theta = 2.41°$); The other was crystallosolvate region formed within aggregation of main chains ($2\theta = 10–35°$), and the kinetics of isothermal crystallosolvate was analyzed by means of the Avirami equation. At the same time, a possible chain-packing model was suggested. Based on X-ray, DSC and FTIR experiments, the evolution of the ordered structure was also investigated in detail. The results imply that the hydrogen bonding interactions exist between solvent molecule and macromolecule, which is a possible mechanism of the formation of the above gels and order structures.

Keywords: Polyimide; Gel/sol transition; Layer structure

1. Introduction

Many years ago, Ferry defined gels as a substantially diluted system that exhibits no steady-state flow [1]. This phenomenological definition is independent of the gelation mechanism. Gels formation when the solvation power decreases drastically and a liquid–liquid phase separation may occur; usually through the solution temperature decreases. For example, flexible macromolecules systems such as poly(vinyl-chloride) [2,3], ultrahigh molecular weight polyethylene and various random copolymers form thermally reversible gels [4]. In addition, Yoshihito Osada et al. have been studied the hydrogel containing an *n*-alkyl acrylate and effects of carboxyls attached at alkyl side chain ends on the layer structure of hydrogels [5,6]. Polyimides with their cyclic and rigid molecular structures possess excellent heat resistance property and have shown wide applications [7–9]. Generally, polyimides are infusible materials, so the studies of polyimide structures are limited, specially, in the physical structure field. By the means of solution gelation, the studies on order structures of most infusible polyimide become possible. For example, polyimide/*m*-cresol solutions based on 2,2-trifluoromethyl-4,4′-diamino-biphenyl (PFMB) showed thermo-reversible gelation [10–13]. These articles focused on the establishment of the gel phase diagram, the influence of molecule weight on gel formation, investigation of the gel phase structure and morphology, changes of the gel/sol transition temperature.

Obviously, the researches on polyimide structures in gel are still not enough. The kinetics of crystallization from gel, the layer structure, which is formed through rigid mesogenic side chains and its structure evolution has not been found in our reviews. On the other hand, gelation can be used in spinning high performance fibers. As we known, it is the most successful application that the gel spinning process is used in ultrahigh molecular weight polyethylene, poly(vinyl-chloride), etc., [3, 4], which has greatly improved mechanical properties of the fibers. Recently, we have introduced this spinning process into the soluble polyimide that can form gels, and some interesting results have been obtained, which shows that gel-spinning

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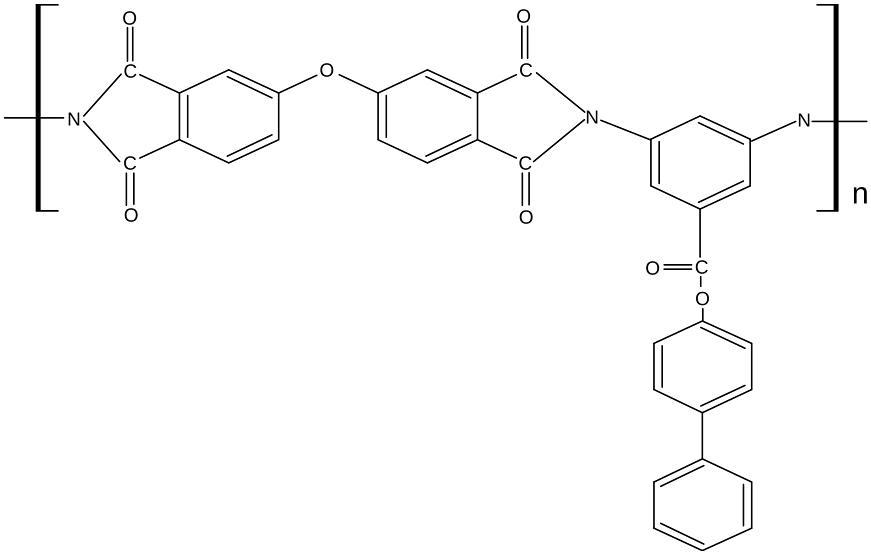
doi:10.1016/j.polymer.2005.10.031

process is very useful for the improvement of tensile strength and morphology of polyimide fibers. Thus, in order to understand more information of the gel spinning and control easily the gel spinning process, the formation and evolution of structure in the gel need to be studied in detail.

In this paper, we report our recent results on a system consisting of a rigid-rod polyimide with biphenyl mesogenic side-groups and *m*-cresol as solvent. It possesses gel/sol thermally reversible transition and order structures depending on processing conditions. Its chemical structure is as following.



2. Experimental

2.1. Synthesis

The polymerization of DABBE and ODPA was carried out in refluxing *m*-cresol containing isoquinoline with a solid concentration of 15 wt%. Under these reaction conditions, the general intermediate poly(amic acids) cyclized spontaneously to the corresponding polyimides. The polyimide (PI) remained completely in solution when the polymerization was carried out. Until allowed to cool to below 20 °C, an opaque gel was gradually formed from the polyimide solution. The solutions with different PI contents were obtained by diluting or evaporating the solution as-polymerized to predetermined concentration.

2.2. Characterization

Differential scanning calorimetry (DSC) measurements were conducted on a Netzsch DSC 204. Samples exhibiting the gel state were tightly sealed in DSC pans, and scanned in a temperature range from −20–160 °C at a heating rate of 10 °C/min.

Polarized light microscopy (PLM) experiments were carried out with a XTP-7 (Jiangnan Photic Instrument Factory, China). The polyimide gel was placed between two glass slides. A hot stage was used with the PLM to observe the change of texture structure and gel/sol transition with rising temperature at 5 °C/min.

X-ray diffraction (XRD) experiments were conducted with a Philips X'Pert PRO MPD (Philips, The Netherlands). X-ray diffraction measurements were performed by reflection mode at room temperature using Ni-filtered Cu Kα radiation operated at 40 KV×40 mA. The chosen diffraction angle (2θ) ranged from 1.5–10° (SAXD) and 10–35° (WAXD), respectively. Layer-spacing was calculated by Bragg's equation. The crystallinity and background remove were proceeded by the Peakfit software (Sigma Company, USA).

FTIR studies were performed in KBr pellets using a Nicolet Magna 650 spectroscope at a resolution of 2 cm^{-1}. The scanned wavenumber range was 4000–400 cm^{-1}. The frequency scale was internally calibrated with a reference helium–neon laser to an accuracy of 0.2 cm^{-1}.

Scanning electron microscope (SEM) measurements were conducted with a LSM-5900LV (Japan) to determine morphologies of the gels. The SEM samples were prepared as following, the gel with 15 wt% solid content was dried in vacuum at room temperature for 72 h, and then at 80 °C lower than correspondent gel/sol transition temperature for 24 h up to constant weight to obtain powder samples.

3. Results and discussion

3.1. Formation of crystallosolvate structure

A thermoreversible gel from the polyimide (ODPA–DABBE) solution of *m*-cresol has been obtained while the temperature of the polyimide solution lowed down, due to the solvation power decreases drastically. The formation of gel is faster at higher concentration of polyimide solution, and the original aggregation structure of the gel is amorphous. It is

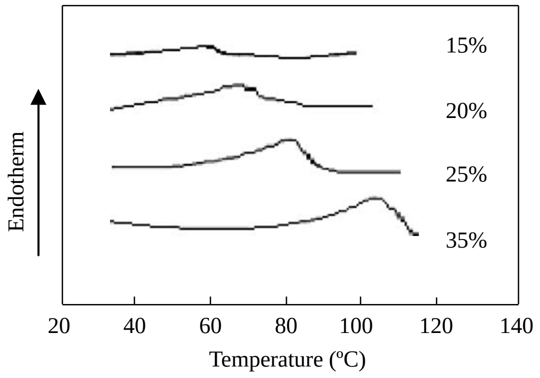


Fig. 1. DSC heating diagrams for the ODPA–DABBE PI/*m*-cresol system at different concentrations (heating rate, 10 °C/min, gel storing time is 7 days).

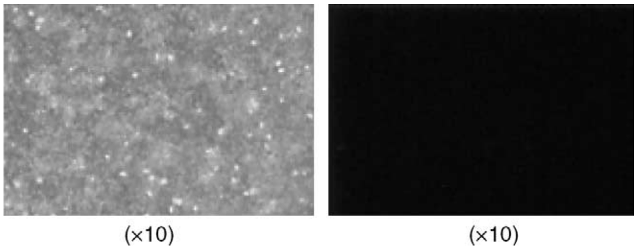


Fig. 2. PLM photograph of ODPA–DABBE/*m*-cresol system with 15% concentration at (left) 25 °C and (right) 90 °C.

clear that with increasing concentration, the gelation time decreases. But this decrease is not linear in the concentration region. It should be pointed out that during the sol/gel transition hysteresis found in this system. As all other polymer gels [5], the gel/sol transition temperature is higher than the sol/gel transition temperature.

Fig. 1 shows a set of DSC heating curves for the PI/*m*-cresol systems at different concentrations (15–35 wt%), and the samples have been stored for 7 days at about 15 °C. A single endothermic peak is observed in each trace, the gel/sol transition is also a typical transition of order/disorder. This phenomenon can be further proved by PLM observations. Below the gel/sol transition temperature, stronger birefringence occurs from these polyimide samples, but no obvious phase texture can be seen, as shown in Fig. 2. This birefringence disappears and the viewing area becomes dark when the temperature exceeds the transition temperature. In addition, in Fig. 1 it is also evident that, when the concentrations increase, both the gel/sol transition temperatures and the enthalpy of transition increase, suggesting a more order arrangement structure at higher concentrations in the region of 15–35 wt%.

For the detailed high birefringence and the order structure, WAXD experiments were carried out under the same conditions. As shown in Fig. 3, which is a gel containing 15 wt% polyimide, the WAXD patterns show a few diffraction; these results prove that some order structures exist. The effect of the storing time on the degree of order (X) is evaluated by Eq. (1) [14].

$$X = \frac{U_0}{I_0} \times \frac{I_X}{U_X} \times 100\ (\%) \tag{1}$$

U_0 and U_x denote the backgrounds of the reference sample and experimental sample while I_0 and I_x are integral intensities of diffraction lines of the reference sample and experimental sample, respectively.

As shown in Fig. 3, the intensity of diffraction peaks increases with increasing storing time at 15 °C, corresponding to $X = 2.3U_0/I_0$, $3.0U_0/I_0$, $4.2U_0/I_0$, respectively, which indicates that the degree of order structure in gel increases with the storing time increase. However, when the storing time exceeds 7 days, the degree of order structures reaches a plateau value. At the same time, the PLM experiments also suggest that the birefringence development of this system at 15 °C depends on the storing time of polyimide/*m*-cresol (15 wt%), which agrees with the WAXD results.

In addition, we find that the order structure is also affected by the solution concentration, as shown in Fig. 4. With concentration of the gel increasing from 10 to 35 wt%, the degree of order structure also increases; their crystallinities are 16, 25 and 34%, respectively. But when the concentration is higher to 50 wt%, the WAXD shows it is lower order structure and its crystallinity is down to 23%. The balance of macromolecular movability and interaction can explain these results. While the concentrations which are lower than 35 wt% increase, the distance and free volume between macromolecular chains decrease, which results in greater interaction between macromolecular chains and forces them to arrange more-extended chain conformation to advantageously develop higher order degree of aggregation structure.

In other words, the macromolecular interaction is a dominant factor in this region of concentrations (≤ 35 wt%). As we known, order structure development needs the macromolecules to have enough ability to move. When further raising concentration to 50 wt%, the macromolecular

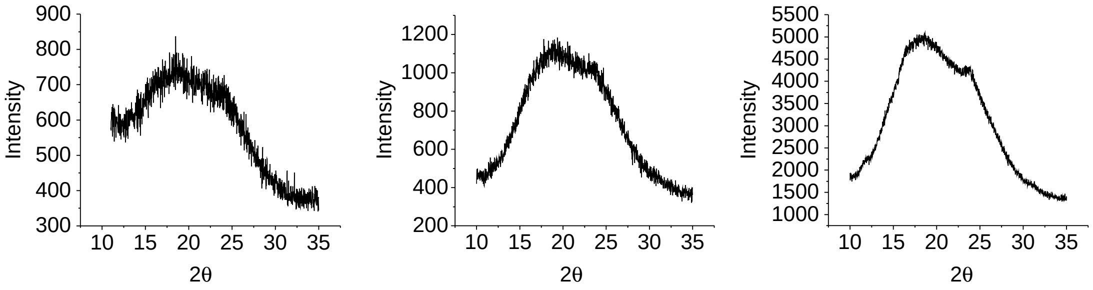


Fig. 3. WAXD patterns for ODPA–DABBE (15 wt%) at different storing time (after gelation) keeping at 15 °C (left: 6 h, middle: 30 h, right: 7 days).

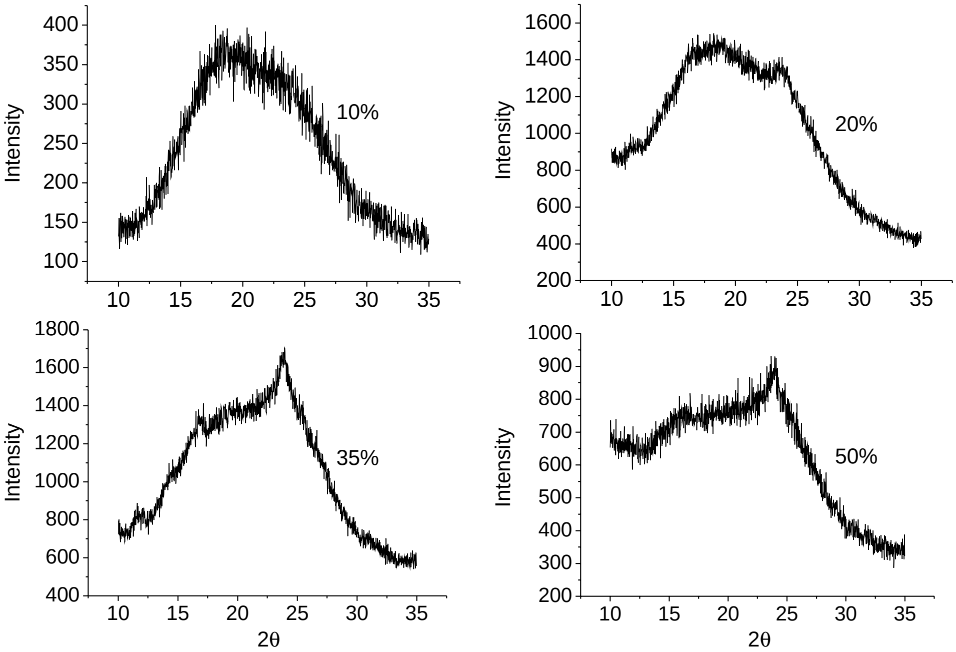


Fig. 4. WAXD patterns for ODPA–DABBE/*m*-cresol at different concentrations (7 days keeping at 15 °C).

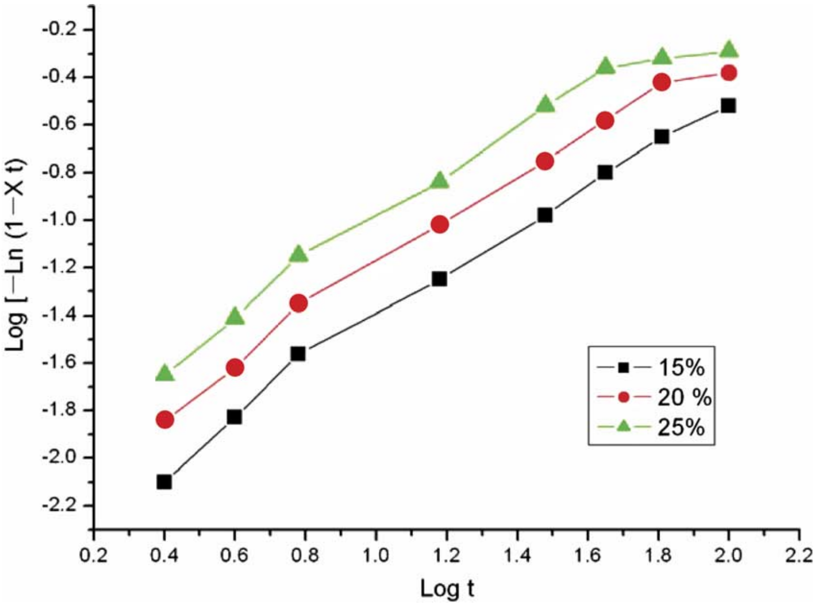


Fig. 5. Plots of Eq. (3) for the determination of Avrami parameters of crystallization for samples storing isothermally (keeping at 15 °C).

movement decreases greatly at 15 °C, which results in difficulty for the order arrangement of macromolecules. Thus in this region of concentrations, movability of macromolecules is dominant factor. It is the reason why the gel structure at 50 wt% concentration is a lower order structure compared to 10–35 wt% concentrations during the same storing time.

Combination of these results of PLM, WAXD, and gelation time, we can conclude that the decrease of solvation power firstly leads to the formation of gel when the temperature of solution lowers down, and then the order structures which depend on the storing time and concentration develop.

3.2. Kinetics of isothermal crystallosolvate of the gel

Reviewing previous literatures, studies of crystallization kinetics always were carried out in melted polymers. As for

Table 1
Isothermal crystallization parameters for the gels

Concentrations (%)	n^{a}	$Z\times 10^{3}$ (h)$^{1/na}$
15	1.09	2.5
20	0.99	6.3
25	1.03	11.3

[a] The range linearity of storing time is between 2.5 and 50 h ($0.4<\log t<1.7$).

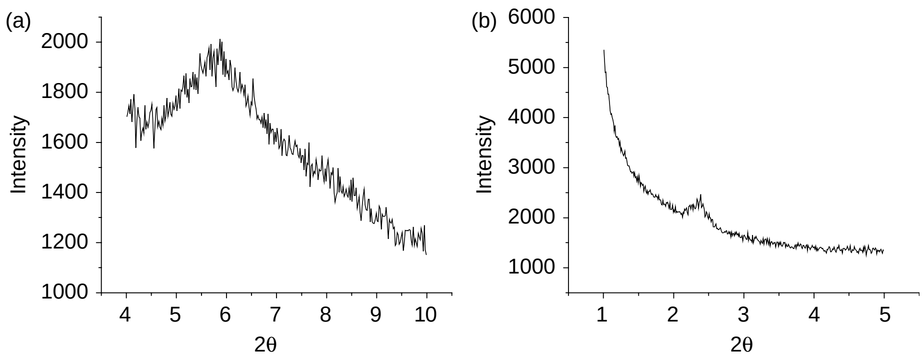


Fig. 6. SAXD diagrams of the PI gel (ODPA–DABBE).

polyimides, only a few kinds of polyimides have melting temperature, such as NEW-TPI, LARC-TPI, etc., [15,16]. By the means of gelation, the studies of crystallization kinetics of most infusible polyimide become possible.

Crystallization kinetics is commonly analyzed by means of the Avirami equation [17,18].

$$X_t = 1 - \exp(-Zt^n) \tag{2}$$

Where X_t is the relative volume fraction of crystallized material at time t, Z a rate constant, and n the Avrami exponent.

There is considerable doubt as to the validity of a simple Avrami equation alone describing the total crystallization behavior of bulk polymers. Despite this, however, analyses based upon Eq. (2) are justified, as a means of comparison. Eq. (2) can be rearranged as:

$$\mathrm{Log}[-\mathrm{Ln}(1 - X_t)] = \mathrm{Log}\,Z + n\,\mathrm{Log}\,t \tag{3}$$

The Avrami parameters can then be conveniently extracted from the slope and intercept of the straight line in a plot of $\mathrm{Log}[-\mathrm{Ln}(1-X_t)]$ vs. $\mathrm{Log}\,t$.

Measurements of crystallization exotherms are restricted by sensitivity of the calorimeter and the limitation of sample size. It is possible, however, to study the kinetics of crystallization by measuring the crystallinity developed in various time, base on the results of WAXD.

Plots of Eq. (3) for the gels treated isothermally at three different concentrations are shown in Fig. 5. A straight line can be satisfactorily determined by the least-squares fit for each set of data. The Avrami parameters extracted from the fits are tabulated in Table 1. It is noted that the values of n are in the vicinity of 1.0 but independent of concentrations. This apparently indicates that the dimensionality of the crystal grown at different concentrations is essentially unchanged. The crystallization rate constant, Z, becomes smaller at lower concentration, which agrees with the WAXD results. Moreover, the increase of the crystallinities at primary stage is faster but levels off at 7 days later (as shown Fig. 5), this kinetics shows a typical nucleation-controlled process.

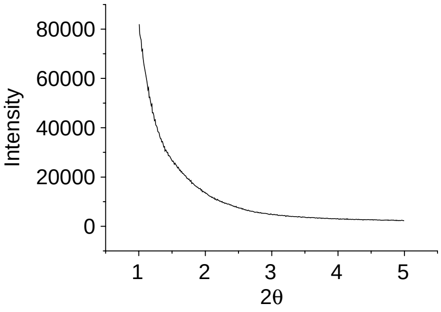


Fig. 7. SAXD diagram for the PI film (ODPA-mPDA).

3.3. Layer structure in gel

In this section, the polyimide gel sample investigated has gel concentration of 15 wt%, and the storing time is 2 weeks at 15 °C.

As shown in Fig. 6(a), the SAXD of the ODPA–DABBE/*m*-cresol shows a diffraction peak at $2\theta = 5.64°$, which corresponds to a d-spacing (d_1) of 15.7 Å [19]. Generally speaking, the small angle diffraction can be indexed as the diffraction of the layer structure [5,18,19]. On the basis of computer modeling, the biphenyl side-groups are almost perpendicular to that of the main chain. The calculated length of the biphenyl side-group is 10.2 Å (n_2), and the thickness of main chains is 5.0 Å (n_1). One should notice here that the d-spacing ($d_1 = 15.7$ Å) in the gels is nearly 0.5 Å (n_3) larger than 15.2 Å ($n_1 + n_2$). This indicates that the solvent molecules in the polyimide gel are preferentially absorbed between two aggregations of the main chains. It means that the support of the biphenyl side-groups results in formation of the layer structure ($2\theta = 5.64°$) between the aggregations of main chains.

At the same time, the SAXD patterns also show another diffraction peak at $2\theta = 2.41°$ (Fig. 6(b)), corresponding to d-spacing (d_2) of 36.6 Å. What causes the diffraction? The PI film of ODPA-*m*PDA (*m*-phenylenediamine) whose backbones

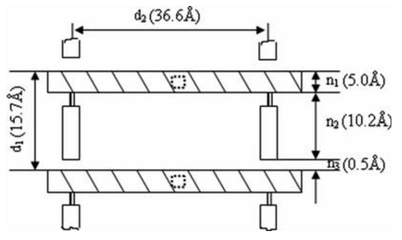


Fig. 8. Schematic representation of the layer structures region with cross hatching = aggregation of main chains; rod with curved ends = biphenyl side-chain of in-plane; ⬚ = biphenyl side-chains of out-of-plane.

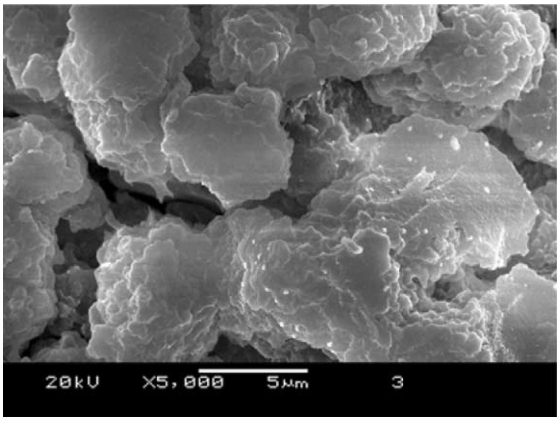


Fig. 9. SEM picture of the dried gel.

are the same with that of the PI (ODPA–DABBE), but only not with side-groups, was scanned, its SAXD figure as illustration in Fig. 7. Comparing Fig. 6(b) with Fig. 7, the SAXD diffraction at $2\theta = 2.41°$ in Fig. 6(b) may results from the biphenyl side-groups themselves. On the basis of the computer modeling, the length of two main-chain repeating units is 36.6 Å and equal to the *d*-spacing (d_2), which also suggests that the side-chains form layer structure by themselves with a thickness of 36.6 Å, and the side-chains take alternation alignment (in-plane or out-of-plane) to agree with the results of SAXD. This is quite reasonable, since adjacent biphenyl side-chains in the backbone are not able to take the *meso* configuration (or isotactic diad) in the flat plane but take racemic (or syndiotactic diad) and non-coplanar configuration. In addition, the biphenyl groups have a natural tendency to form order structure through microphase separation, special in solution. The schematic representation of two kinds of layer structures ($2\theta = 2.41$, $5.64°$) is as shown in Fig. 8.

In addition, SEM experiments of the gel have been carried out, as shown in Fig. 9. The result can further prove the existence of the layer structures in gel from macroscopical view.

3.4. Structure evolution

When the gel (15 wt%) was dried in vacuum at room temperature, which is lower than correspondent gel/sol transition temperature for 72 h, and then at 80 °C for 24 h up to constant weight (dried-gel), some fine powders were obtained. XRD shows

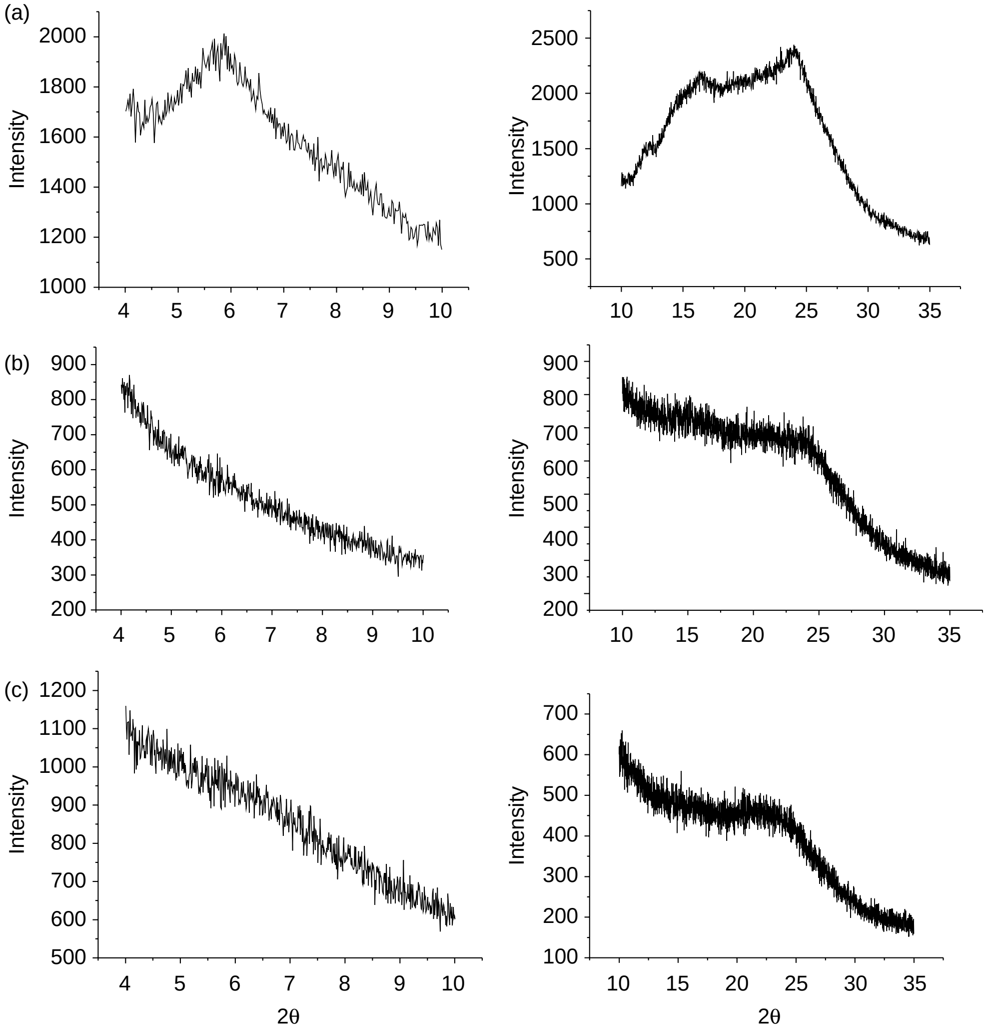


Fig. 10. XRD diagrams for the PI (ODPA–DABBE)/*m*-cresol system at different conditions (a): dried gel; (b): annealed gel; (c): extracted gel.

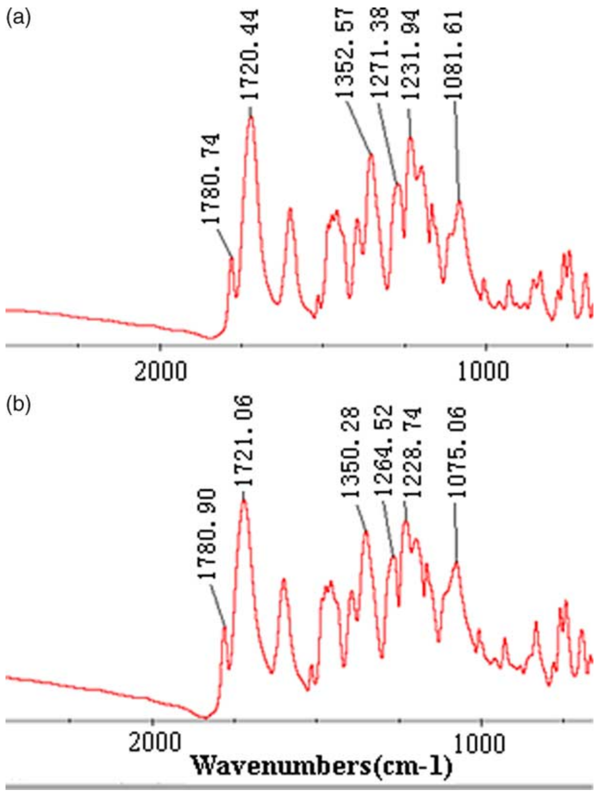


Fig. 11. The 2500–600 cm^{-1} region of the gel FTIR spectrum: (a) extracted-gel; (b) dried-gel.

that the original order structures in powders are retained (Fig. 10(a)). After the powders are further annealed at above 300 °C (annealed-gel), the order structures disappear almost (Fig. 10(b)) though the powders do not have any melting transition throughout the entire stage of annealing. Moreover, the solvent in gel was completely extracted by ethanol or methanol (extracted-gel), and then the extracted-gel was dried further at 80 °C in vacuum for 24 h. The XRD of the extracted gel shows that no order structures exist almost (Fig. 10(c)). These results imply that some solvent molecules participate in the formation of order structures in gel and the interactions exist between solvent molecule and macromolecule.

In order to detail the interactions, FTIR experiments were carried out, as shown in Fig. 11. In the 1800–1700 cm^{-1} region, the characteristic doublet due to the symmetric and asymmetric stretching of the imide carbonyls (1780 and 1720 cm^{-1}, respectively) was observed. Broader, conformationally sensitive bands appear at 1380–1100 cm^{-1} [20].

A very small effect was detected in the carbonyl region, which is reasonable because of small amount of residual solvents [20], but some obvious shifts of the dried-gel samples towards lower wavenumbers, comparison to the extracted-gel samples, were observed at the 1380–1100 cm^{-1} region on which we focused in the analysis, as shown in Table 2. These peak shifts towards lower wavenumbers found in the dried gel strongly suggest the formation of hydrogen bonding interaction between the solvent molecule and macromolecule.

In order to understand clearly the relationship of the order structures and solvent molecules in gel, DSC experiments of the dried gel were carried out under a heating rate of 10 °C/min, as shown in Fig. 12(a). Three endothermal peaks were observed, denoted 1, 2 and 3, correspondent temperatures are 95, 148 and 178 °C, respectively.

Table 2
The peak shifts observed in FTIR spectra of extracted-gel and dry-gel

Extracted-gel (cm^{-1})	Dried-gel (cm^{-1})	Shifts (cm^{-1})
1352	1350	2
1271	1264	7
1231	1228	3
1081	1075	6

Obviously, peak 3 is the endothermic evaporation of solvent. A sudden jump of the endothermic transition temperature at 148 °C (peak 2), as well as the enthalpy of transition, may be an indication of the change of the crystalline structures (i.e. crystallosolvate). Peak 1 is located at lower temperature, as well as the largely lower enthalpy of transition, may be contribute to a breaking of the weaker hydrogen bonding interaction. To prove our opinion, the samples of dried-gel were annealed at 100 °C which is between the temperatures of peak 1 and peak 2 for 3 h. Then the annealed samples were characterized by XRD, as shown in Fig. 13. Compared with Fig. 10(a), the intensity of diffraction peak at $2\theta = 5.64°$ which is considered as layer structure largely decreases, but that at $2\theta = 10–35°$ which is considered as the crystalline structure is almost constant. Then further raising the annealing temperature higher than 160 °C, the diffraction peak at $2\theta = 10–35°$ also disappears almost, which is the same as the results shown in Fig. 10(b). Thus the breaking procedure of interaction includes two stages, the first is the destroying of layer structure (long-range order), which needs lower energy and temperature; the second is the destroying of the short-range order, which needs more energy and higher temperature. These results maybe indicate that two different strength of hydrogen bonding interactions occur, which arises from the difference in electron affinity existing between solvent molecule and macromolecule; because the longer hydrogen-bonding distance is, the weaker hydrogen-bonding interaction and energy will be.

Moreover, there is only one T_g transition at 260 °C on the DSC curve (Fig. 12(b)) of the powder PI whose solvent was completely extracted by ethanol or methanol, which further proves that the order structure will disappear without existence of solvent molecules.

Based on the foregoing results, the possible mechanism of the formation of gels can be put forward. It is imaginable that macromolecules and the solvent molecules pack in a network of hydrogen bonding which forms between the electron-donor (OH) and electron-acceptor groups (C=O, –O–, –N–). This hypothesis is reasonable, because the biphenyl side chains are pendant on the backbone chains through ester group bonds, and should have two aspects of function. One is the formation of hydrogen bonding between ester groups of the side chains and solvent molecules, the other is the increase of free volume to favor more solvent molecules insert inter-chains and form hydrogen bonding between main chains and solvent molecules.

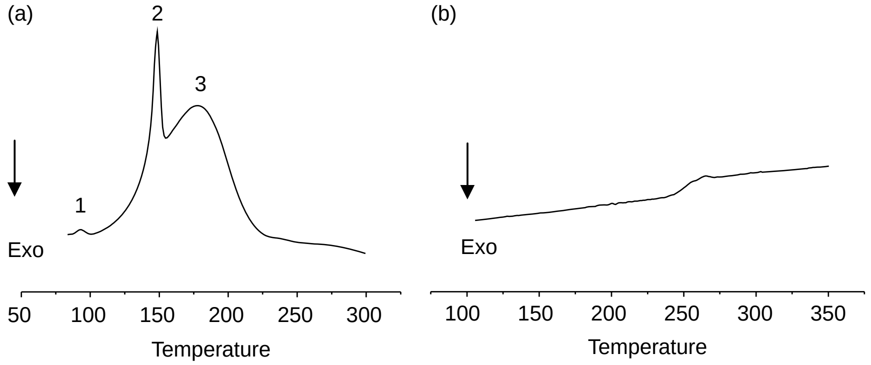


Fig. 12. DSC curves of dry-gel and extracted gel (a) gel dried in vacuum (b) gel extracted by methanol.

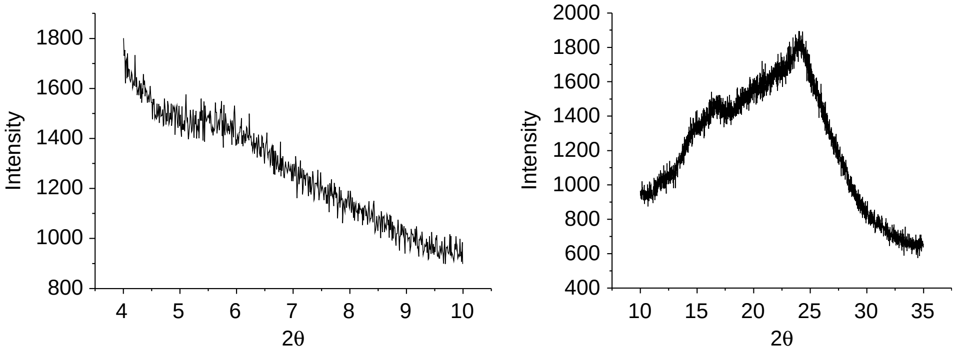


Fig. 13. XRD of annealed samples at 100 °C for 3 h.

Additionally, it is obvious that the directions of hydrogen bonds are impossibly co-planar, because of steric hinder effects.

It is also interesting that the other kind of layer structure at $2\theta = 2.41°$ is independent of the annealing conditions, which indicates that solvent molecules should not participate in the formation of this kind of layer structure. It is possible that the mesogenic biphenyl side chain groups have a natural characteristic that they can arrange order structure by them without assistance of solvent. But the detailed reasons need to be further explored.

4. Conclusion

ODPA–DABBE/*m*-cresol PI solution shows a thermoreversible gelation, and the gel/sol transition depends on solution concentration and storing time. With decreasing temperature, the solvation power decreases drastically resulting in the formation of gel by a network of hydrogen bonding. With the storing time increasing after gelation, the two kinds of order structure develop from the gel state and depend on the gel solution concentration. One is layer structure which is formed from the aggregation of main chains ($2\theta = 5.64°$) or from side chains ($2\theta = 2.41°$); the other is crystallosolvate region which is formed within aggregation of main chains ($2\theta = 10–35°$), the kinetics of isothermal crystallosolvate is analyzed by means of the Avirami equation, which indicates the dimensionality of the crystal grown at different concentrations is essentially unchanged and the crystallization rate constant, *Z*, becomes smaller at lower concentration. Based on WAXD, DSC and FTIR experiments, the results imply that the solvent molecules participate in the formation of order structures and the hydrogen bonding interactions exist between solvent molecule and macromolecule. At the same time, the breaking procedure of interaction includes two aspects, the first is the destroying of layer structure at $2\theta = 5.64°$ (long-range order), which need lower energy and temperature; the second is the destroying of the short-range order, which need more energy and higher temperature.

Acknowledgements

This work was supported by the National Science Foundation of China (Grant No.20274026 and 50433010).

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