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Crystallization process of poly(ε-caprolactone)–poly(ethylene oxide)–poly(ε-caprolactone) investigated by infrared and two-dimensional infrared correlation spectroscopy

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Abstract

The crystallization of poly(ε-caprolactone)–poly(ethylene oxide)–poly(ε-caprolactone) (PCL–PEO–PCL) triblock copolymer was studied using FTIR and 2D FTIR spectroscopies. The weight ratio of PCL/PEO in the investigated sample was about 20:1. Although it is such a low amount of PEO that it cannot form any crystals, the PEO block undergoes some structural change in the cooling process. It was established that the PCL constituent crystallized quickly, and then forced the noncrystallizable PEO constituent to form a tighter structure (helical conformation) from the *trans* zigzag conformation. Besides, through the 2D IR analysis, more exact and detailed assignments of the overlapped CH_2 bands have been made – the 1193 cm^{-1} band is attributed to methylene next to the carbonyl group, whereas the 1162 cm^{-1} and 1295 cm^{-1} bands are assigned to other common methylenes.

Keywords: Crystallization; FTIR; Two dimensional correlation analysis

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1. Introduction

In recent years, a kind of amphiphilic triblock copolymer, poly(ε-caprolactone)–poly(ethylene oxide)–poly(ε-caprolactone) (PCL–PEO–PCL), has attracted much attention because of its environmental adaptability as well as potential capability as biomedical material. Both PCL and PEO constituents possess a number of outstanding physicochemical and biological properties which result in the fact that the copolymer mentioned above can be used as a drug delivery vehicle [1]. Furthermore, the hydrophilic PEO constituent is soluble in water while the hydrophobic PCL constituent can only dissolve in organic solvents. Thus, the copolymer PCL–PEO–PCL can form core–shell micelles through a self-assembly process in water.

A lot of research work has been made to investigate and promote the drug loading and delivery properties of the copolymer PCL–PEO–PCL. It was established that both biodegradability and drug permeability depend on the crystallinity [2]. However, there are only a few studies that have been published on the morphology and crystallization/melting properties of such block copolymer. Gan et al. [3] used WAXD, SAXS and DSC methods to investigate the isothermal crystallization and melting behavior of the PCL/PEO diblock copolymer. Besides the diblock copolymer, Bogdanov et al. [2] studied the isothermal crystallization behavior of three different types of PCL/PEG incompatible block copolymers including A–B, $(A)_2$–B, A–B–A types by DSC. Floudas et al. [4] synthesized and studied the structure and dynamics of structure formation of a model triarm star block copolymer composed of PEO, PCL and PS by several methods including X-ray scattering, optical microscopy, AFM, DSC and rheology.

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As mentioned above, a series of methods have been applied to study the crystallization behavior and properties of PCL/PEO block copolymers. But to the best of our knowledge, there are only few reports involving IR spectroscopy, a well-developed research method to investigate the conformation and local order of polymers. Since the real-time IR can give the information of structural evolution at the molecular level, the IR probe is widely used to reveal the structure and conformation changes during the crystallization and melting processes [5–8]. One of the reasons for the apparent lack of previous IR work may be due to the fact that the spectral region 1300–1000 cm^{-1}, mainly associated with ester groups, is highly overlapped, which makes the detailed analysis and assignment rather difficult. However, the generalized two-dimensional (2D) correlation spectroscopy developed by Noda [9,10] in 1993 in addition to conventional IR methods may be able to solve this problem. The theory and introduction to 2D IR can been found elsewhere [9–12]. 2D IR introduced the FTIR to a second dimension, provided additional useful information and thus enhanced spectral resolution and pertinent features of spectral changes [13].

PEO and PCL are both crystallizable polymers, however, when they are combined into one copolymer as two blocks, the crystallization behavior only depends on the block length ratio. When the blocks length ratio is 3 or higher, only the longer block will crystallize [4]. We have investigated a series of PCL–PEO–PCL copolymer samples with different PEO/PCL weight ratios. In this work, we studied the triblock copolymer PCL–PEO–PCL with a PEO/PCL ratio of 1:20 and try to elucidate how the shorter noncrystallizable PEO block affects the crystallizing process of the PCL blocks. Although the PEO blocks in this sample may not exhibit a crystalline phase, they may still form some ordered conformations on a molecular scale. The helical conformation composed of a 7/2 helix and the *trans* zigzag conformation composed of a 10/3 helix are two of the most common structures that exist in the PEO polymer [14]. 2D IR is used to reveal the correlation between different groups, especially in the region of 1300–1000 cm^{-1}. Samples with other ratios will be investigated in another paper, which is in preparation.

Quite different spectral patterns are found both in traditional IR and 2D IR analyses, which are believed to be produced by the dipole–dipole interaction between the C═O groups. Dipole–dipole interaction is a kind of inter- or intramolecular interaction between molecules or groups having a permanent electric dipole moment. The strength of the interaction depends on the strength and relative orientation of the dipoles, as well as on the distance between the centers and the orientation of the radius vector connecting the centers with respect to the dipole vectors [15]. Molecules will tend to align so that maximum attraction between dipoles is achieved. This occurs when the neighboring molecules have their dipoles anti-parallel, or the positive end of one dipole lies close to the negative end of another dipole.

2. Experimental details

2.1. Material and sample preparation procedures

The synthesis and purification of the triblock copolymer (PCL–PEO–PCL: $M_w \approx 40{,}000\ \text{g mol}^{-1}$, PCL/PEO = 20:1 in weight) were performed according to procedures reported in the literature [1]. The thin copolymer films were cast on KBr windows from a 1% (w/v) PCL–PEO–PCL chloroform solution. The KBr windows were placed under a culture dish outside the fume cupboard to ensure the evaporating rate was slow enough, so that we could produce perfect films. The majority of the solvent evaporated after 24 h, and then the films were placed under vacuum at room temperature for 48 h to completely remove the residual solvent.

2.2. FTIR spectroscopy

For studying the isothermal crystallization process of the triblock copolymer PCL–PEO–PCL, the sample was set in a temperature controlling cell, which was placed in the sample compartment of the FTIR Spectrometer Nexus 470. The sample was first kept at 80 °C ($T_m = 60$ °C) until it was completely molten, then the temperature decreased at a rate of 1.5 °C/min to 26 °C and was kept at 26 °C for about 120 min. The FTIR measurements were carried out at 26 °C, in 2 min intervals. The spectra were collected at a resolution of 4 cm^{-1} and 64 scans were accumulated. Before further analysis, all the spectra were baseline corrected.

2.3. Two-dimensional correlation analysis

The software for two dimensional correlation analysis in this present study is MATLAB7.0 (The Math Works Inc.). The correlation peaks are represented as pair (ν_1,ν_2) which refers, respectively, to the two independent wavenumbers involved. In all 2D correlation plots, the negative peaks are shaded while the remaining (unshaded) peaks are positive.

3. Results and discussion

3.1. Structure formation and bands assignment

The FTIR spectra of the investigated PCL–PEO–PCL sample at 26 °C (with comparatively high crystallinity) and at 80 °C (in the molten state) are shown in Fig. 1, reflecting large differences, especially in the region 1500–800 cm^{-1}. The assignments of several absorption bands are summarized in Table 1. It should be noted that there are some small differences in the peak positions between literatures and our results. For example, according to Zhu et al. [16], the assignment of the C═O stretching region is very simple and clear. Nevertheless, since hydrogen bonding is not the dominating factor in our system, the peaks located at 1724 cm^{-1} and 1735 cm^{-1} are assigned, respectively, to the crystalline state and the amorphous regions. Fig. 2, in which the transformation can be seen clearly in the spectra obtained during the cooling process in

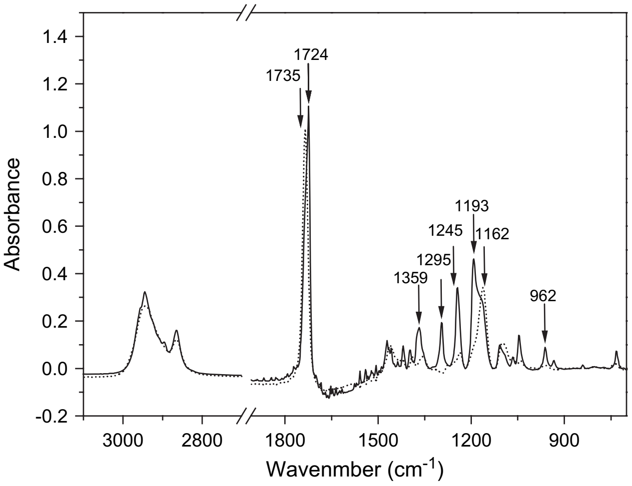


Fig. 1. FTIR spectra of the PCL–PEO–PCL sample in the molten (⋯) and crystalline states (—).

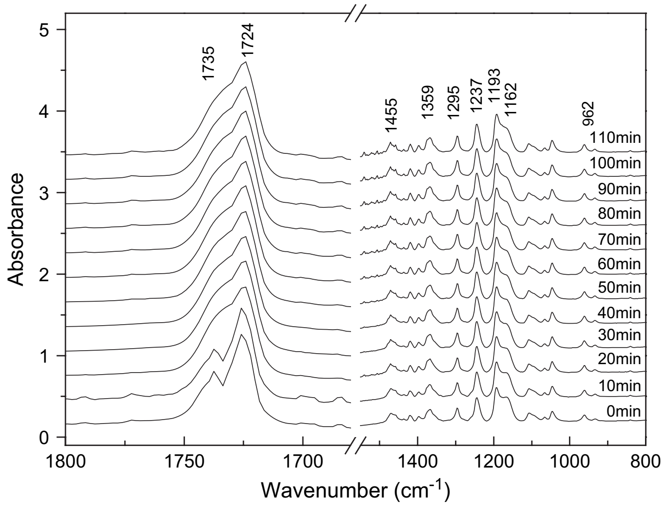


Fig. 2. Time-dependent FTIR spectra obtained at 26 °C of the investigated PCL–PEO–PCL sample in the region at around 1700 cm^{-1} and 1500–800 cm^{-1}.

10 min interval, shows the change of the IR spectra around the C=O stretching region as a function of the cooling process. It is very obvious that during the cooling process, the band at 1735 cm^{-1} decreases while the 1724 cm^{-1} peak increases at the same time. Since the change of the C=O band can represent the conformational transformation of PCL constituent (crystallizable block of the investigated copolymer) to a large extent, we will consider it as a reference in the further 2D IR analysis. Moreover, as labeled in Fig. 2, there are many significant absorption bands sensitive to the conformation of the copolymer in the wavenumber range of 1500–800 cm^{-1}. The peaks at 1455 cm^{-1}, 962 cm^{-1}, 1295 cm^{-1} and 1193 cm^{-1} which were attributed to CH_2 scissoring [17], CH_2 rocking [17], CH_2 rocking combined with C–O–C deformation [17] in PEO block and two significant absorptions of crystalline PCL block, respectively [18], increase gradually as the temperature decreases, whereas absorption bands of another group at 1359 cm^{-1} and 1235 cm^{-1} increase accompanied by a slight shift to a higher frequency. However, there is only one peak at 1162 cm^{-1} that shows significant attenuation during the cooling period, which is related to the amorphous phase in the PCL blocks according to literature [19].

The second-derivative IR spectra are also calculated for the amorphous state and the highly crystalline state. Several overlapped bands at around 1245 cm^{-1}, 1455 cm^{-1}, 1067 cm^{-1} and 1045 cm^{-1} can be found in both phases with a shift to a higher frequency in the crystalline state compared to the amorphous one.

To investigate the detailed mechanism of segmental motion taking place during the crystallization process, normalized peak heights of several characteristic peaks of different blocks are plotted as a function of cooling time, which is shown in Fig. 3. The 1295 cm^{-1} and 1193 cm^{-1} are both characteristic peaks of the PCL crystalline phase [18], the 1367 cm^{-1} and 1045 cm^{-1} absorptions are both considered as characteristic of a 7/2 helical conformation in the PEO blocks, while 962 cm^{-1} and 1245 cm^{-1} represent a 10/3 helical conformation [17]. It could be clearly seen in this picture that the crystallization process mainly took place within the period of 10 min after being cooled for an hour. Nevertheless, although the six bands

Table 1
Band assignments of amorphous and crystalline PCL and PEO blocks [16–19]

Band	Wavenumber (cm^{-1})		Assignment	
	PCL	PEO		
C=O	1736 [16]		C=O stretching (amorphous phase)	
	1724 [16]		C=O stretching (crystalline phase)	
C–H		1468 [17]	CH_2 scissoring	–
		1359 [17]	CH_2 wagging	Helical conformation (7/2 helix)
		1242 [17]	CH_2 twisting and C–O–C stretching	*trans* Zigzag (10/3 helix)
		1060 [17]	CH_2 rocking and C–O–C stretching	Helical conformation (7/2 helix)
		964 [17]	CH_2 rocking	*trans* Zigzag (10/3 helix)
	1162 [19]		C–O–C stretching of PCL amorphous phase	
C–O–C		1242 [17]	CH_2 twisting and C–O–C stretching	
		1060 [17]	CH_2 rocking and C–O–C stretching	
	1295 [18]		Significant absorption of PCL crystalline phase	
	1192 [18]		Significant absorption of PCL crystalline phase	

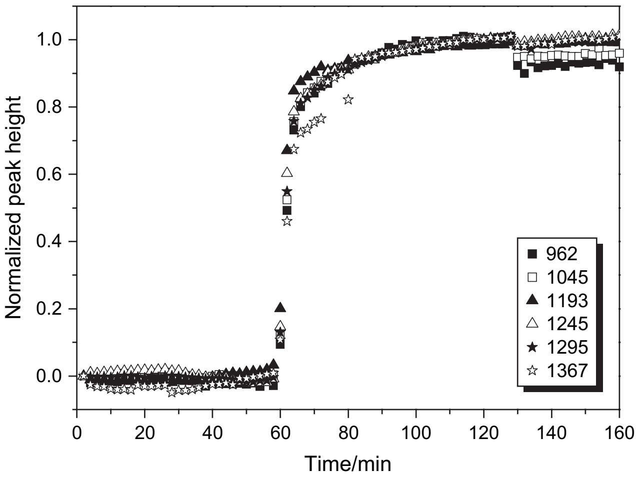


Fig. 3. Normalized peak heights of the characteristic peaks of the PCL crystalline phase at 1295 cm^{-1} and 1193 cm^{-1} and of different PEO conformation at 1367 cm^{-1}, 1245 cm^{-1}, 1045 cm^{-1} and 962 cm^{-1} as a function of time of the isothermal crystallization process calculated from the spectra shown in Fig. 2.

are attributed, respectively to different conformations of the PCL or PEO blocks, there are hardly any differences between the lines in Fig. 3. Obviously, the one-dimensional analysis is not able to provide sufficient evidence. We use in this study 2D IR correlation spectroscopy to elucidate the detailed crystallization mechanism of the block copolymer.

3.2. Two-dimensional FTIR analysis

The synchronous and asynchronous correlation spectra of PCL–PEO–PCL of the C═O stretching region are shown in Fig. 4. The two autopeaks shown in the synchronous spectra locate at (1736 cm^{-1},1736 cm^{-1}) and (1724 cm^{-1},1724 cm^{-1}), respectively. Since the 2D calculations always obtain average results, the center of the cross peak may slightly shift from the peak in 1D reference spectra. The negative area in Fig. 4A centers at (1740 cm^{-1},1724 cm^{-1}). Thus, there are obviously two kinds of C═O bands existing in the IR spectrum, one of which can be found in the region of a higher wavenumber at around 1740 cm^{-1} while the other at a lower wavenumber at around 1724 cm^{-1}. Furthermore, the 2D analysis also indicates that the peak appearing at higher wavenumber alters in the opposite direction to the peak at lower one, similar to the observation in the 1D IR analysis.

The negative asynchronous cross peak Ψ(1735 cm^{-1}, 1724 cm^{-1}) developed in Fig. 4B indicates that the intensities of two dynamic bands at 1735 cm^{-1} and 1724 cm^{-1} vary out of phase, and provides the information on the sequential order of intensity changes between these two peaks. According to the publications of Noda [9], if the product of the intensity of a synchronous peak and its corresponding asynchronous peak is positive (a concise expression of this sentence is: $\Phi(\nu_1,\nu_2)\cdot\Psi(\nu_1,\nu_2) > 0$), band ν_1 varies prior to band ν_2. Contrarily, if $\Phi(\nu_1,\nu_2)\cdot\Psi(\nu_1,\nu_2) < 0$, band ν_2 varies prior to the band ν_1. It should be mentioned that all peaks in this paper are the peaks appearing in the top-left region of the maps, except for those maps without a top-right to left-bottom symmetry axis. The cross peaks Φ(1735 cm^{-1},1724 cm^{-1}) and Ψ(1735 cm^{-1}, 1724 cm^{-1}) are both negative, that is, the product of these two peaks are positive (Φ(1735 cm^{-1},1724 cm^{-1})$\cdot\Psi$(1735 cm^{-1}, 1724 cm^{-1}) > 0), therefore the band at 1735 cm^{-1} varies prior to the band at 1724 cm^{-1}. Moreover, similar to Zhang et al.'s study [5], there is a so-called "butterfly pattern" in the C═O stretching region in the asynchronous correlation spectra. Usually, the appearance of this pattern is attributed to a peak shift combined with the intensity changes or band splitting [20,21].

Fig. 5 shows the 2D correlation spectra of the highly overlapped 1380–900 cm^{-1} region. In principle, we should be able to extract useful information about the crystallizing process of the copolymer system from these data. Among many cross peaks shown in Fig. 5A (synchronous spectrum), only the

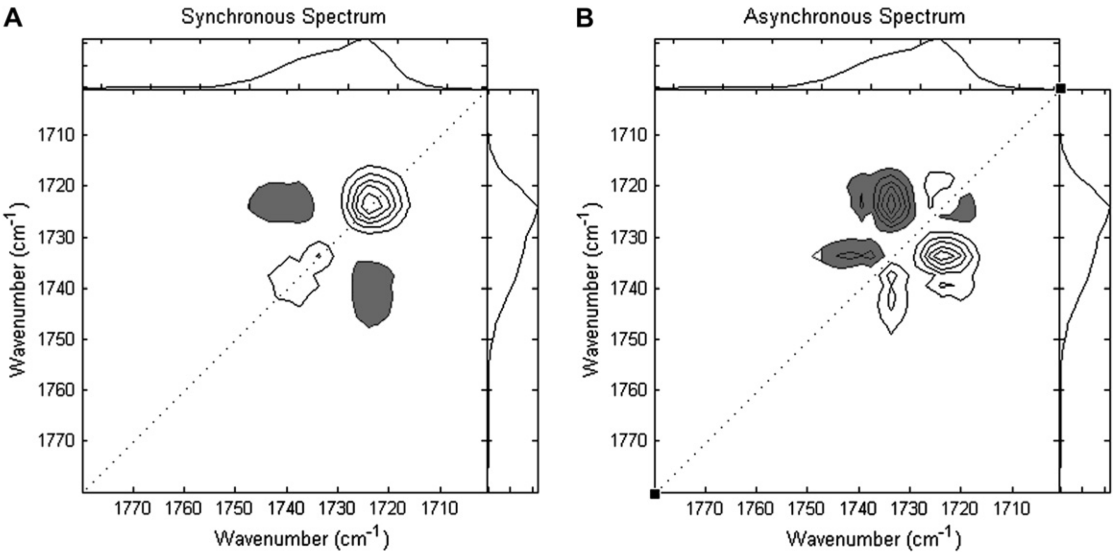


Fig. 4. Synchronous and asynchronous 2D correlation spectra of PCL–PEO–PCL copolymer at 1780–1700 cm^{-1}.

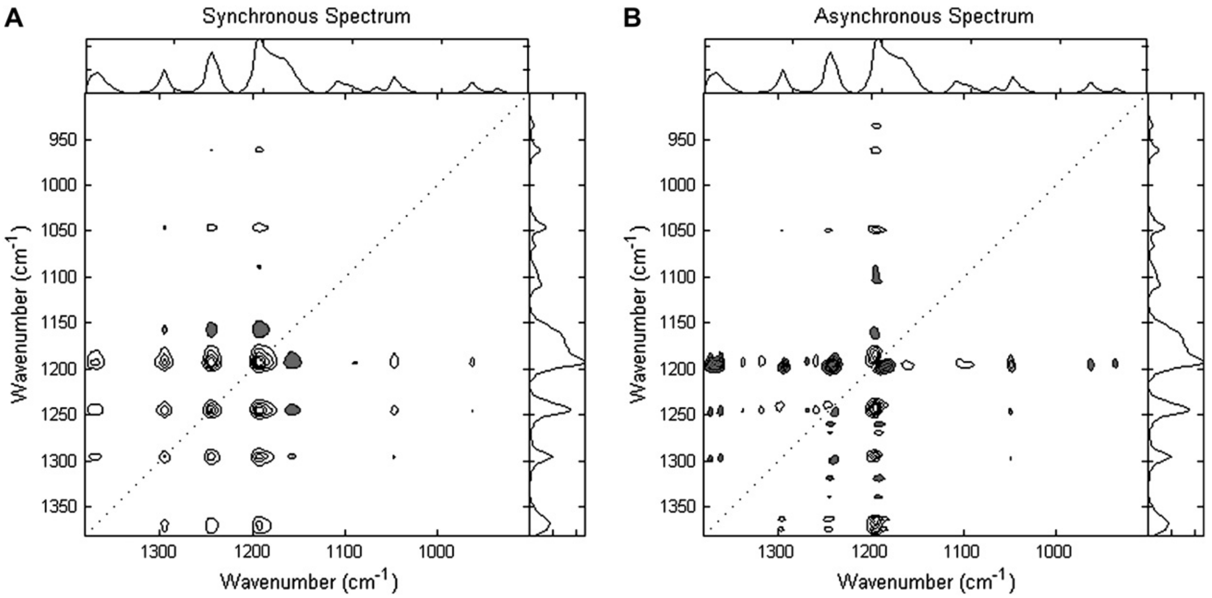


Fig. 5. Synchronous and asynchronous 2D correlation spectra of PCL–PEO–PCL copolymer at 1380–900 cm^{-1}.

cross peaks at 1162 cm^{-1} are negative, which suggests that the majority of peaks in the range of 1380–900 cm^{-1} alter in the same direction, whereas the peak at 1162 cm^{-1} changes oppositely. As outlined before, the 1162 cm^{-1} band is assigned to the amorphous PCL phase [19]. Based on the above analysis, it is easy to understand that the peaks altering in the opposite direction to the band at 1162 cm^{-1} should be attributed to the formation of a more regular conformation. However, the PEO block cannot take the conformation of the crystalline phase because the block length ratio of PCL/PEO is much higher than 3 [4].

It is, however, somewhat difficult to pick out the fine structure of the spectrum in Fig. 5, when such a broad spectral region is displayed. The full advantage of the contour map representation of 2D correlation spectra will not be realized until the technique is performed on a limited portion of the spectral map. Parts A and B of Fig. 6 are the close-up view of the contour maps shown in Fig. 5 in the spectral region between 1380 cm^{-1} and 1230 cm^{-1} in one dimension and between 1280 cm^{-1} and 1170 cm^{-1} in another dimension. Thus, more detailed features become apparent.

After the analysis of the asynchronous correlation spectrum in Fig. 6B, several cross peaks (denoted as a, b and c) are found to contain interesting information. The positions of these three peaks are as follows: a (1367 cm^{-1},1245 cm^{-1}), b (1295 cm^{-1},1193 cm^{-1}) and c (1295 cm^{-1},1245 cm^{-1}). Peaks (a) and (b) are negative, whereas (c) is positive. The corresponding synchronous cross peaks are all positive. Following

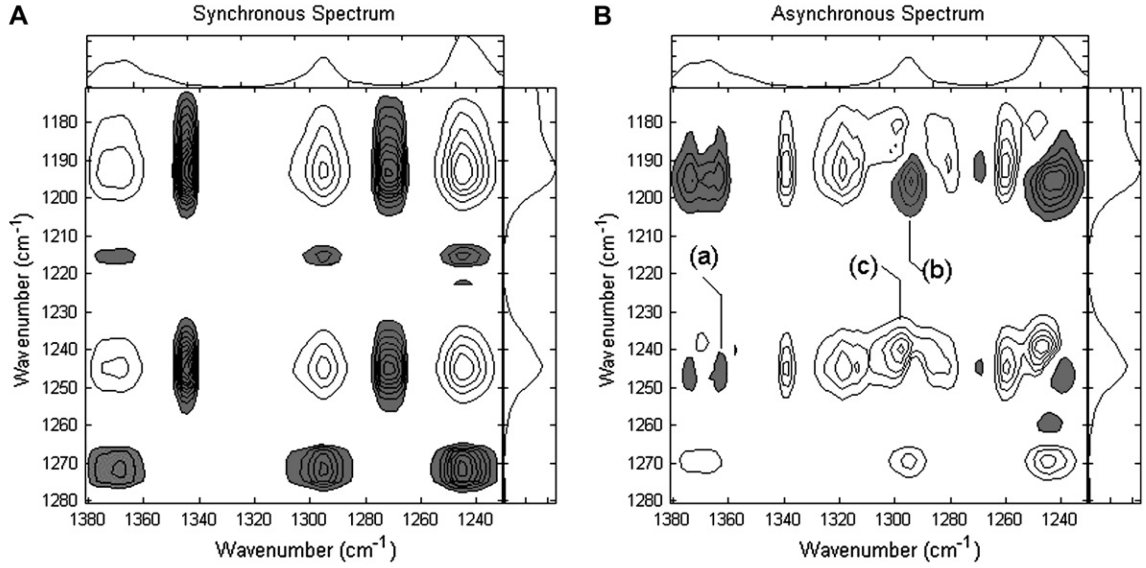


Fig. 6. The signs of cross peaks appearing in the expanded view of the contour maps shown in Fig. 5.

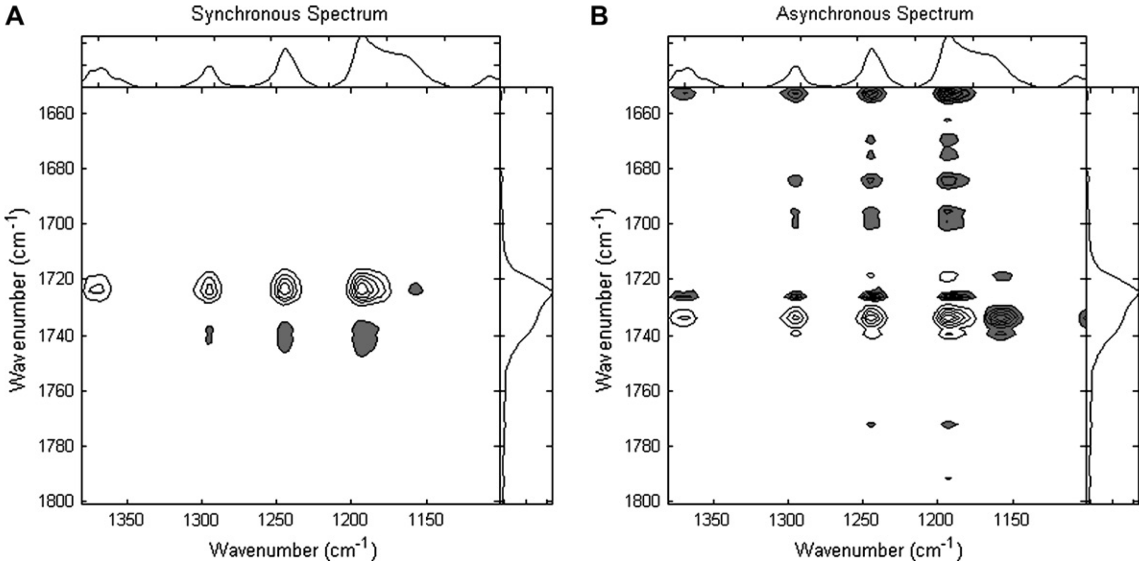


Fig. 7. Synchronous and asynchronous 2D FTIR correlation spectra of PCL–PEO–PCL copolymer obtained during the isothermal crystallization process between 1380–1100 cm^{-1} and 1800–1650 cm^{-1}.

the rule mentioned above, a conformational transformation sequence among the bands involved is obtained: 1193 cm^{-1} > 1295 cm^{-1} > 1245 cm^{-1} > 1367 cm^{-1}. The significance of this sequence notation will be discussed later.

Additionally, 2D correlation spectra between different ranges are acquired to achieve information about the relationship between different groups in the copolymer. The 2D spectra between the C═O stretching region and the highly overlapped region mainly associated with ester groups are shown in Fig. 7. In the synchronous spectra (Fig. 7A), all peaks involving the 1724 cm^{-1} band are positive and those involving the 1735 cm^{-1} band are negative, except for the 1162 cm^{-1} band. From the asynchronous spectrum, we inferred that a band split occurs in the C═O stretching mode, which always represent a dipole–dipole coupling when the molecules form an ordered structure [5]. This result goes consistent with what we get from the self-correlation analysis of the C═O stretching region. Also, the changing sequence can be obtained easily so that the bands at 1735 cm^{-1} and 1724 cm^{-1} vary prior to all the peaks in the range of 1380–1100 cm^{-1}.

To investigate the role of different C–H groups in the crystallization process, 2D analysis between regions containing information of C–H and C–O–C bands is performed. Fig. 8

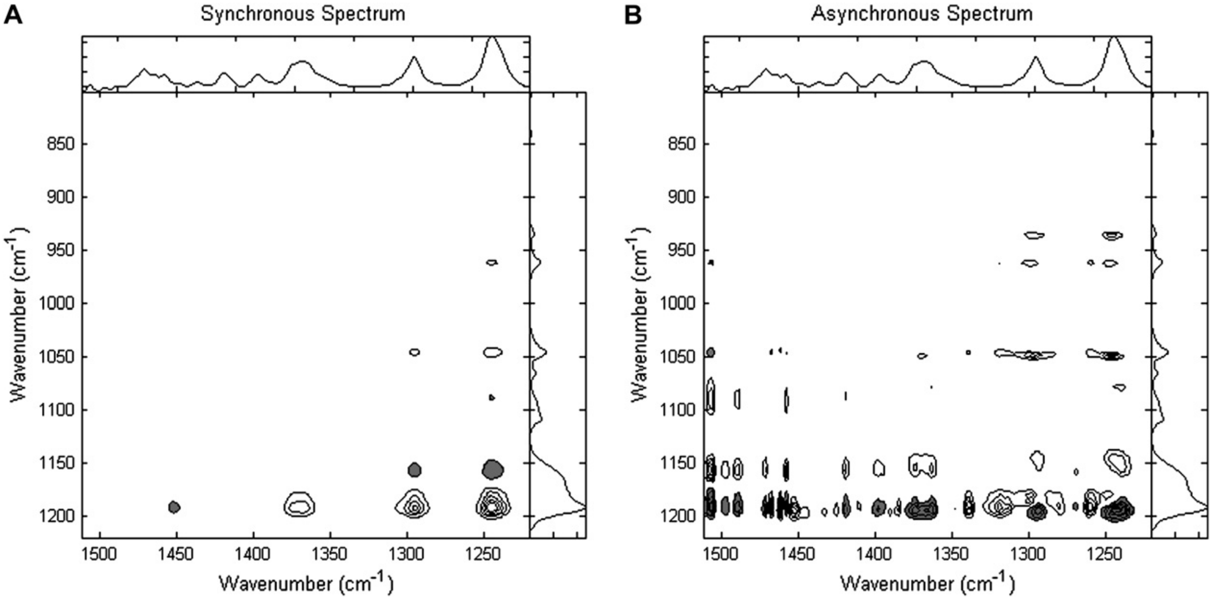


Fig. 8. Synchronous and asynchronous 2D FTIR correlation spectra of the investigated PCL–PEO–PCL copolymer obtained during the isothermal crystallization process between 1210–800 cm^{-1} and 1510–1220 cm^{-1}.

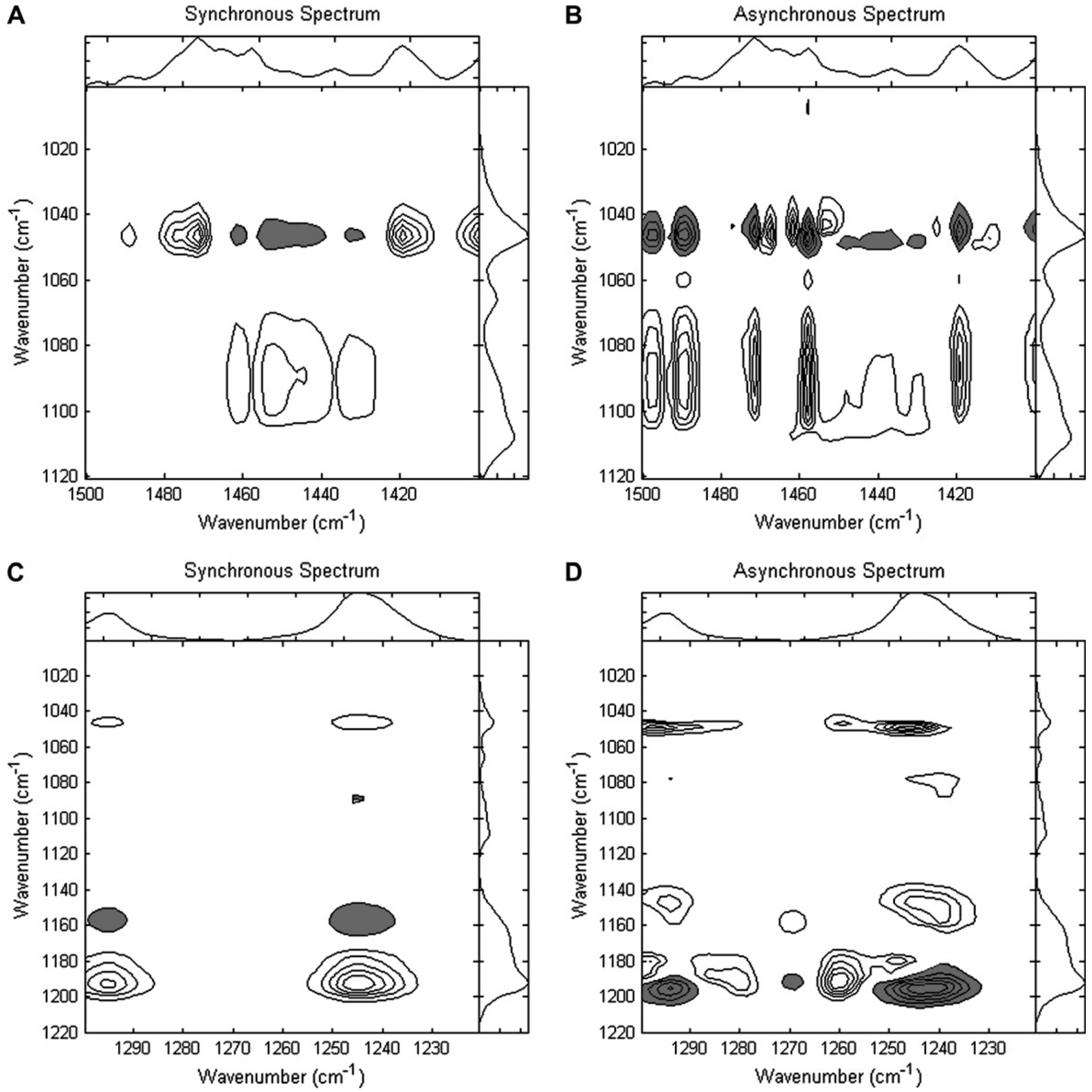
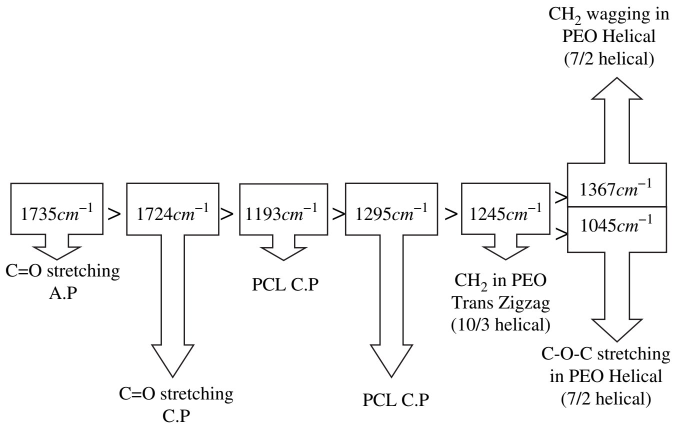


Fig. 9. The signs of cross peaks appearing in the expanded view of the contour maps shown in Fig. 8.

shows the 2D correlation spectra between 1210–800 cm^{-1} and 1510–1220 cm^{-1}. Since the whole region is too large for the 2D calculation to get a satisfactory result, several localized views are made in addition as shown in Fig. 9. The parts A and B in Fig. 9 are synchronous and asynchronous 2D IR spectra between 1120–1000 cm^{-1} and 1500–1400 cm^{-1}, while the parts C and D represent the regions between 1220–1020 cm^{-1} and 1300–1220 cm^{-1}. Three meaningful cross peaks can be found in the two asynchronous spectra (Fig. 9B and D) at the position of (1452 cm^{-1},1045 cm^{-1}), (1295 cm^{-1},1045 cm^{-1}) and (1245 cm^{-1},1045 cm^{-1}). The first one is negative while the other two are positive. And the corresponding synchronous cross peaks are negative, positive and positive, respectively. Thus, another band variation sequence can be achieved: 1045 cm^{-1} varies after the other three bands at 1295 cm^{-1}, 1452 cm^{-1} and 1245 cm^{-1}.

Summing up the conformational transformation sequences obtained during the 2D correlation analysis, a final result is attained which can be described by the following scheme:



Here, A.P means *amorphous phase* whereas C.P means *crystalline phase*.

In this sequence, 1735 cm^{-1} and 1724 cm^{-1} are attributed to the C=O stretching band in the amorphous and crystalline phases, respectively [16]. The bands at 1193 cm^{-1} and 1295 cm^{-1} are related to absorptions of the PCL crystalline phase [18]. The 2D results revealed the information that we cannot get from the 1D analysis shown in Fig. 3. The band at 1245 cm^{-1} is assigned to a CH$_2$ twisting vibration of PEO in the *trans* zigzag conformation [17]. The band at 1367 cm^{-1} is attributed to a CH$_2$ wagging motion in the PEO helical conformation [17]. The band at 1060 cm^{-1}, which appears at 1045 cm^{-1} in our polymer system, is also attributed to the helical conformation but mainly relates to the C–O–C stretching vibration [17].

According to the above data, we can derive on a molecular level that, in the cooling process, the structural adjustment of the PCL blocks occurs faster than that of the PEO blocks, which means that the PCL blocks are able to form a crystalline phase more easily. The detailed mechanism in each one of these two kinds of blocks are: in PCL blocks, the carbonyl groups alter faster than the CH$_2$ groups, and there are also some differences between different CH$_2$ groups in the PCL blocks; in the PEO blocks, the CH$_2$ groups vary prior to the C–O–C groups, and what is more important, a conformational transformation is uncovered which indicates that the PEO segments change from an incompact conformation into a tighter one.

We consider that it is the dipole–dipole interaction between the carbonyl groups that cause the C=O groups change prior to others. To prove this interaction actually exists in our system and is strong enough to affect the crystallization process of the block copolymer, we have two evidences. Firstly, as has been mentioned in several literatures references [6,22], the dipole–dipole interactions always result in a band splitting for polymer systems when the molecules form an ordered structure. Furthermore, the high-frequency shift of the C=O stretching band is usually due to the dipole coupling of the C=O bonds in the crystalline state. From both the traditional spectra (Fig. 2) and the 2D correlation analysis of C=O stretching region, we can derive that in our system, there is obviously a band splitting taking place together with a high-frequency shift of the C=O stretching band. Secondly, the carbonyl group has the largest dipole moment of almost all chemical bonds. The value of the dipole moment of the carbonyl group is 2.3–2.7, whereas the one of the O–H bond in water is 1.85, which determines that the dipole–dipole interaction between carbonyl groups is stronger than the hydrogen-bonding effect. These two evidences substantiate the existence and the possible effect of dipole–dipole interaction in our system, which is very helpful to explain the mechanism brought forward through our analysis. The carbonyl groups with strong polarity have a comparatively strong trend to congregate first and produce the driving force for the neighboring molecular chain to form an ordered state. It is obvious that, in this process, the CH$_2$ groups located near the carbonyl groups will be affected more easily compared to those which are located further away from the carbonyl groups. With reference to the transformational sequence we obtained from the two-dimensional analysis of both the bands at 1193 cm^{-1} and 1295 cm^{-1}, which were both attributed to absorptions of the crystalline PCL phase, we suppose that the 1193 cm^{-1} band can be attributed to the methylene group next to the carbonyl group, whereas the 1295 cm^{-1} band should be assigned to other common methylene groups.

As we have mentioned in the analysis of Fig. 3, the crystallization process occurs very quickly, which indicates that the crystallizable segments of the PCL block form regular structure in a very short period of time. In this process, the noncrystallizable segments of the PEO block are separated between the ordered PCL segments, and will be certainly influenced by the PCL crystallization process. It is probably this effect that influences the conformational transition of the PEO blocks.

4. Conclusion

FTIR and 2D FTIR spectroscopies have been applied to study the crystallization behavior of a PCL-rich PCL–PEO–PCL copolymer. The PEO blocks are in such a low amount that they cannot perform crystallization. However, we investigated the role of the PEO blocks in the copolymer and put forward hypothesis of the crystallization process. The carbonyl groups of the PCL blocks first congregate and force the neighboring chains to form an ordered state. The squeezing effect produced during the crystallization process of the PCL blocks forces the PEO blocks to form a tighter and more ordered state, which appears as the transformation from the *trans* zigzag (10/3 helical) to the helical conformation (7/2 helical). Besides, some more exact and detailed assignments have been made. The 1193 cm^{-1} band is attributed to methylene next to the carbonyl group, whereas 1295 cm^{-1} bands are assigned to other common methylenes.

Acknowledgements

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