

THE RHEO-OPTICAL FTIR STUDY OF POLYESTER-POLYETHER SEGMENTED COPOLYMER

WEN Zaiqing* (闻再庆), SHEN Deyan (沈德言) and ZHAO Hengqi (赵恒奇)

(Institute of chemistry, Academia Sinica, Beijing)

ABSTRACT

The polyester-polyether segmented copolymer has been investigated by rheo-optical FTIR during stretching for the information on strain induced crystallization of soft segment chains, hard and soft chain orientation.

At room temperature 15°C, the soft segment chains of polyester-polyether being to crystallize at 220% strain and the degree of crystallization increase with draw ratio, but there will not be any soft segment chains crystallization above 21°C even at higher strain. The average orientation of hard segment chains are higher than that of the soft chain at high strain level, both are positive oriented into the stretching direction at all over strain level. This indicates that the hard segment chains are dispersed into the elastomeric phase and without forming spherulite.

INTRODUCTION

To establish the relationship between the macroscopic properties of polymer and its microstructure is one of the basic goals in polymer society. A better comprehension of the molecular structural mechanism involved in many mechanical processes, such as stretching, extrusion, relaxation, required for new experimental techniques for the characterization of transient structural changes in real time. This requirement stimulated the development of rheo-optical spectroscopy and have been realized in many structural determination methods such as X-ray and light scattering.

The vibrational spectroscopy is a powerful technique to probe the microstructure of polymer chains. Information on localized level, such as functional group, conformation of segment, orientation of chain, and crystalline state can be obtained. With the advent of fast-scan FTIR, the rapid scanning capability offered the possibility to combine vibrational spectroscopy with mechanical measurement in analogy with other rheo-optical methods. The dynamical response of molecular chains to the mechanical deformation and relaxation can be reflected from the spectra simultaneously. In this case, spectroscopic properties changes, such as band frequency, intensity, dichroism can be directly related to the mechanical measurement parameters, stress, strain, draw ratio, draw rate and the macroscopic properties. Siesler is particularly active in the development of rheo-optical FTIR and many information on orientation of segment chain, crystal phase transformation and microphase separation have been obtained^[1].

This paper presents our studies on the polyester-polyether segmented copolymer by means of rheo-optical FTIR for probing the different dimensional structure changes under stretching deformation. This would be helpful to comprehend the unusual mechanical properties of the material at molecular level.

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* To whom correspondence should be addressed.

EXPERIMENTAL

The principle of rheo-optical FTIR has been well-demonstrated in the excellent review of Siesler^[2]. We have made a similar stretching device in our laboratory which can be fitted into the sample compartment of infrared spectrometer. The specimen to be tested is held between two clamps which are attached to force transducer and can be uniaxially drawn at variable elongation rates. The stress and strain can be simultaneously recorded.

The interferograms which are subsequently transformed to the corresponding spectra are recorded by a BRUKER IFS-113V FTIR spectrometer, which is a vacuum type with liquid nitrogen cooled MCT detector. Thus, interference of moisture and carbon dioxide are essentially eliminated. The scan velocity was set at 0.47cm/s. Spectrum resolution was 2cm⁻¹. Every spectrum were 8 scans averaged and taken in less than 5 seconds. This time interval is obviously the time resolution of the rheo-optical measurement which is related to the scan velocity and the signal to noise ratio of the interferometer. It can be changed with the decrease of signal to noise ratio. The limit of time resolution depends on the highest scan velocity. The data were collected by a ASPECT 3000

Table 1 The tentative vibrational assignment of main bands of polyester-polyether segmented copolymer.

Frequency cm ⁻¹	Intensity	Polariza- tion	Due to polyester segment chain ^[5]	Due to polyether segment chain ^[4]
2943	s	σ		ν_s CH ₂
2954	vs	σ		ν_s CH ₂
2797	m	σ		ν_s CH ₂
1722	vs	σ	ν_s C=O	
1578	w	π	ν_s C=C	
1504	m	π	19a	
1470	m	π	δ CH ₂	
1448	m	π	δ CH ₂	
1411	m	π	19b	
1371	m	π	r_w CH ₂	w CH ₂
1342	m	π	r_w CH ₂	
1272	vs	π	ν_s C—O	
1120	vvs	π	20a	ν_s COC
1020	m	π	18a	
995	m	σ		ν_s COC
973	m	π	ν_s C—O	
873	m	σ	17b	
730	s	σ	$\begin{array}{c} \text{C}=\text{O} \\ \diagdown \\ \text{O} \end{array}$ out of plane	

computer and stored on a hard disk and manipulated collectively after experiment.

Polyester-polyether segmented copolymer was chosen as sample for it is an important thermoplastic polymer and has good mechanical properties and wide technical application. The multiple-segment character and rubber-like property is particularly suitable for rheo-optical testing. The synthesis of the copolymer and characteristic parameters is referred to [3]. The specimen chose for rheo-optical FTIR measurement contains hard segment polyester 20% in weight. The molecular structure of the segmented copolymer is shown as follows:

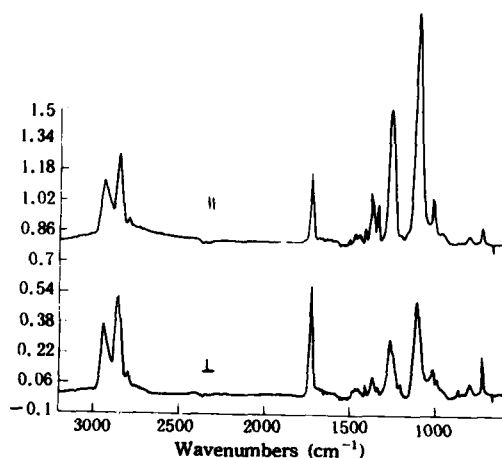
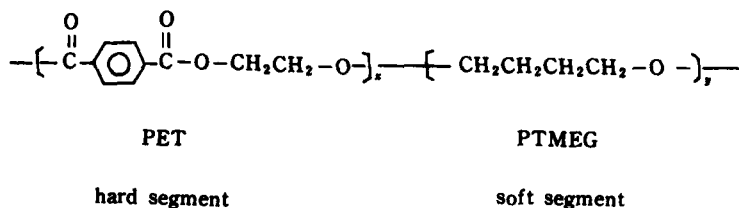


Fig 1 The polarized spectrum of polyester-polyether segmented copolymer
 || parallel to the stretching direction. ⊥ vertical to the stretching direction

The specimen film was solution-casted using chloroform as solvent. A homogeneous film was obtained after the solvent vapourized and the residue of solvent was removed by vacuum oven at room temperature for two days. The specimen was then cut into a gauge of 3cm × 1cm dummy bell shape for stretching testing.

RESULTS AND DISCUSSION

Fig 1 is the polarized spectra of high draw ratio film of polyester-polyether copolymer. The main vibrational bands of the copolymer are summarized in Table 1 for further discussion on the spectra changes during stretching. The spectrum can be considered as a combination of two components. One is the hard segment of polyethylene terephthalate, the other is the soft segment of polytetrahydrofuran. Some useful bands for characterizing the different dimensional structural changes are discussed.

Crystalline band: The 995cm^{-1} band is due to the symmetrical stretching vibration mode of C—O—C group in polyether chain. The band disappears when the segment chains are in the melted state and appears when crystallized^[4]. It is considered to be a crystalline band of polytetrahydrofuran chain and can be used as a characteristic band to monitor the crystallization of polyether segment chain in various thermal mechanical processes.

Segment orientation bands: As can be seen from Fig 1, some bands remain the character of components and are not overlapped with bands due to another component in the copolymer spectrum. The 1722cm^{-1} carbonyl stretching mode is relatively isolated and can be used to represent hard segment chain orientation^[5]. For the soft segment counterpart, there are not absolutely isolated band for the same purpose, however, at the methylene stretching mode regions the absorption bands due to polyester part are very weak and can be nearly neglected. The 2943cm^{-1} methylene stretching mode can thus be approximately chosen for characterizing the soft chain segment orientation.

For the detailed analysis of the series spectra taken during the rheo-optical experiment, some spectroscopic parameters should be evaluated based on the peak-maximum or integral intensity. The most important parameters involved in rheo-optical measurement are the structural absorbance which is defined as

$$A = (A_{//} + 2A_{\perp})/3 \quad (1)$$

the dichroic ratio R

$$R = A_{//} / A_{\perp} \quad (2)$$

and the orientation function

$$f = 2(R - 1)/(R + 2)(3\cos^2\theta - 1) \quad (3)$$

where $A_{//}$, $A_{\perp}$ are the absorbance of a band measured with incident light polarized parallel and vertical to stretching direction respectively. θ is the angle of a transition moment of a vibrational mode to the molecular chain axis. For a band having transition moment parallel or vertical to the chain axis, the equation (3) reduced to

$$f = (R - 1)/(R + 2) \quad (4a)$$

$$f = -2(R - 1)/(R + 2) \quad (4b)$$

The structural absorbance has been chosen as intensity parameter because it corrects the effect of stretching on the actual intensity of an absorption band. In general, the analysis band is compared with a proper internal reference band which is nearly insensitive to orientation. The relative ratio of two bands are calculated and related to the mechanical parameters or plotted as a function of time scale. The evaluation of spectra data are all followed in this way and can then be discussed on a normalized level.

As have discussed above, from detail analysis of whole spectrum of the copolymer, one would expect that microstructural responses to external force at different dimensional level can be well characterized.

1. Soft segment chain crystallization induced by strain and temperature

The mechanical properties of polyester-polyether segmented copolymer are strongly influenced by thermal-mechanical history. The elastic recovery of the polyester-polyether elastic fibres are dramatically reduced in winter and the reason has been ascribed to the low temperature crystallization. The polyester-polyether thermo-plastics having 20% in weight of hard segment crystallized at about -5°C . With this understanding, our attention is focused on the crystallization band region in the rheo-optical experiment. The 995cm^{-1} band are expected to appear when the

specimen undergoes stretching. This is approved by the results shown in Fig 2. The appearance of 995cm^{-1} band is an indicator of soft chain segment crystallization induced by strain. The data clearly demonstrate the nature of strain induced crystallization and allow to assign a strain value of about 220% to the onset of crystallization. The degree of crystallization increases with increase of strain. The stretching has evidently elevated the crystallization temperature about 20°C . This result is similar to the case of sulfur-crosslinked natural rubber^[6]. Fig 3 shows the relative ratio of structural absorbances of the 995cm^{-1} and 1020cm^{-1} bands plotted as a function of strain. The adjacent band 1020cm^{-1} is taken as a thickness reference band. The whole process of strain induced crystallization of soft segment chain can be well-illustrated.

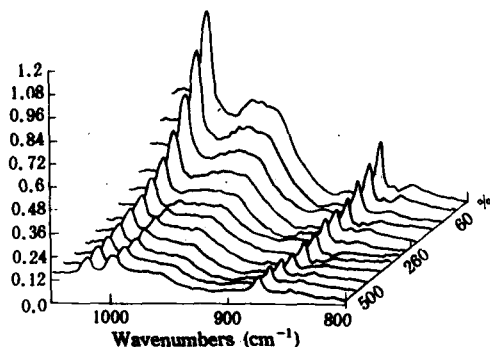


Fig 2 The series spectra of polyester-polyether segmented copolymer at the region between 1050cm^{-1} to 800cm^{-1} . The 995cm^{-1} band appears at the strain 220%. The draw rate is 1.3cm/min , draw temperature 15°C

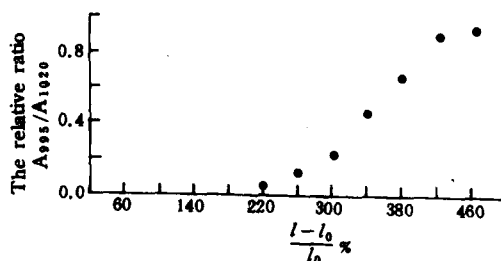


Fig 3 The relative absorbance ratio of $995\text{cm}^{-1}/1020\text{cm}^{-1}$ plotted as a function of strain

As concerned with temperature dependence of the soft chain segment crystallization, we carried out another set of experiments at elevated temperature but at the same draw rate and draw ratio. The spectra data are shown in Fig 4. This time the 995cm^{-1} band did not appear even at higher strain. It can be understood that the soft chain segments are in the melted state at the experimental temperature. The melting point of pure polytetrahydrofuran is about 30°C . With this in mind, the experimental phenomena can be born-out and understood.

There is another important factor which is the influence of the relative content of hard segment on soft chain crystallization. Cooper et al^[7] have made extensive studies on polyester-polyether and polyurethane based thermoplastics. They did not mention the soft segment crystallization. This might be the fact that their attention are mainly focused on the crystallization of hard segment and its effect on the macroscopic properties. The samples they studied contain relatively higher content of hard segment. This would greatly reduce the critical point of the crystallization of soft chain segments. Hence, at the ambient experiment condition, the soft chain segments crystallization:

would not take place. It can be predicted that it would take place at lower temperature and higher strain. This is indeed proved by the experiment on the polyester-polyether segmented copolymer having content of hard segment 30% in weight at temperature of -30°C . Thus, the picture on crystallization of soft chain segment and its effect on mechanical properties is intuitive. The critical point of crystallization depends on multiple factors which are the temperature, the strain and the relative content of hard segment and its chemical structure in the copolymer. The loss of elastic recovery in winter is attributed to the soft chain segment crystallization induced by the combination factors of temperature and strain. This result is practically useful for the manufacture and technical application.

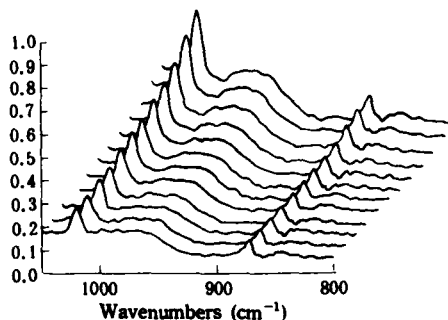


Fig 4 The series spectra of polyester-polyether segmented copolymer at draw rate 1.3cm/min, but draw temperature 21°C .

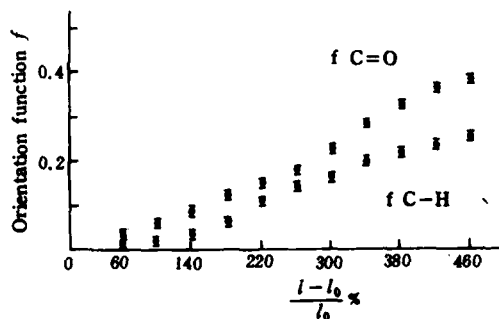


Fig 5 The orientation function of hard and soft segment chains as a function of strain.

2. The orientation of the hard and soft segment chain

From the polarized spectrum of high draw ratio of the copolymer, there is a difference of dichroism values between soft segment and hard one. It is possible to evaluate the orientation function of each component from the dichroism and the whole orientation process of the segmented copolymer can be followed in time scale. The calculation of normalized orientation function was completed by taking the dichroic values of 1722cm^{-1} band of polyester which represents the orientation of hard segment and 2943cm^{-1} one of methylene stretching mode of polyether which indicates the soft counterpart. The angle between the transition moment of carbonyl group and polyester chain axial is taken as 79° and the methylene one is vertical to its chain direction.

For minimizing the possible error caused by different thickness of specimens in experiments, the two specimens for vertical and parallel measurements were cut from the same casting film. The initial band intensity of two specimens before stretching were recorded and the relative intensity ratio of these two spectra was taken as a scale factor for normalization. The normalized orientation function of C=O carbonyl group and CH_2 methylene bands have been plotted in dependence of

strain in Fig 5. It is apparent that at the ambient temperature up to the maximum stretching ratio the hard segment demonstrated a higher average chain alignment in the direction of stretching than the soft one. Both hard and soft segments oriented positively into the stretching direction at all strain level. This is different from the case of polyurethane based thermoplastics and also the polyester-polyether segmented copolymer having higher content of hard segment and the case when film were prepared by casting from 1,1,2-trichloroethane solution where the hard segment chains are initially negatively oriented and then changed to the orientation to the stretching direction positively. It is believed that the orientation of hard segments is closely related to the crystalline morphology. It might be suggested that the positive orientation of hard segments at all over strain level are mainly due to the relative lower content in the copolymer and the film casting method. The sample have been estimated to have an average hard segment length of four monomer units by NMR and they might be isolated by the rich soft segment chains and could not form into a hard segments crystalline domain in the chloroform casting preparation. The morphology of chloroform casting film is nonspherulitic as characterized by microscopy. That the hard segments shown a positive orientation in the whole process means its morphology is different from the model proposed based on polyurethane thermoplastics where the strong interchain interaction through hydrogen bonding play an important role to associate with each other for hard segment chains^[8]. It might be more closed to the micelles picture where the hard segments are likely dispersed into the soft chain segment elastomeric matrix.

In conclusion, rheo-optical FTIR study on polyester-polyether segmented copolymer provide a more detailed insight into strain induced crystallization and segmental orientation. It also contributes a better comprehension of the unusual mechanical properties of thermoplastics and an optimization of their chemical structure and technical application. It can probe the microstructural changes at different dimensional levels under external force action and correlate macroscopic properties to microscopic nature at time scale which is significant in engineering.

Keywords:

Rheo-optical FTIR; Segmented copolymer; Polyester-Polyether.

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