Polymer 42 (2001) 9045–9049

polymer

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Dynamic infrared spectroscopic studies on structure of segmented poly(urethaneurea)

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Received 9 March 2001; received in revised form 17 April 2001; accepted 17 April 2001

Abstract

We report the dynamic infrared spectroscopic studies on segmented poly(urethaneurea). In this study, we take into consideration not only the dynamic dichroic difference spectra but also the dynamic average absorption spectra, in order to detect dynamic change in concentration of hydrogen bondings. As a result, the similarity in shapes of spectra between the static and dynamic dichroic difference and the great difference of spectra between the static and dynamic average absorbances are obtained. It is concluded that stress along the urea carbonyl bonds, but not along the polymer chains, takes an important role on the negative orientation of the hard segment domains. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Dynamic infrared spectroscopy; Segmented poly(urethaneurea); Urea carbonyl group

1. Introduction

Rheo-optical techniques [1] have been developed so as to characterize the mechanical relaxation processes of the crystalline polymers and multi-phase polymer systems into more elemental molecular orientation and molecular motions. Namely, rheo-optics aims to explore the deformation mechanism of polymeric materials by measuring simultaneously the stress, strain and optical quantities (X-ray diffraction, birefringence, visible dichroism, etc.), which are directly related to orientation of the internal structure of the materials, as a function of time or frequency. Particularly, these techniques are suitable for investigation of semicrystalline polymers [2–4], which have the complex microscopic structures and rheological behaviors in contrast to amorphous polymers.

Dynamic X-ray diffraction [5,6] is the most powerful technique to reveal time-dependent deformation of crystalline phase and has been employed to characterize the relation between the mechanism of spherulite deformation [7,8] and the mechanical dispersion of semicrystalline polymers in detail. Also, rheo-optical investigation of amorphous phase [9] has been carried out by combining dynamic X-ray diffraction and birefringence [10,11], but those measurements have been done under the different mechanical conditions. On the other hand, dynamic infrared (IR) dichroism [12–14] is very useful to obtain information of the amorphous phase, therefore, IR dichroism can provide independently information on crystalline and amorphous phases of semicrystalline polymers. The dynamic IR dichroism can also be applied to multi-component polymer systems, such as polymer blends and block-copolymers. Noda et al. made extensive work on the dynamic IR dichroism by focusing on dynamic molecular orientation and extended this technique to two-dimensional IR correlation spectroscopy [15,16]. However, the dynamic IR dichroic measurements give not only the molecular orientation but also the wide variety of molecular information such as dynamic changes on concentration of functional group, dynamic internal stress onto chemical bond, and so on.

Here, we report on dynamic IR spectroscopic studies on a segmented poly(urethaneurea) (SPUU) consisting of soft and hard segments by taking all kinds of dynamic IR information into account. SPUU has been focused on as a medical and industrial material because of antithrombogenicity and high elasticity. Especially for use as a medical material, elucidation of fatigue mechanism under cyclic deformation also becomes important. Many workers have investigated the fatigue mechanism of SPUU [17–19].

2. Definition of rheo-optical functions

When a polymer film is subjected to the sinusoidal deformation, the resulting stress $\sigma(t)$ may vary sinusoidally

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PII: S0032-3861(01)00398-6

with the phase difference angle δ with respect to the dynamic bulk strain $\epsilon(t)$. These can be generally described as follows;

$$\epsilon(t) = \epsilon^0 + \Delta\epsilon \exp(i\omega t) \tag{1}$$

$$\sigma(t) = \sigma^0 + \Delta\sigma \exp[i(\omega t + \delta)] \tag{2}$$

where ϵ^0 and σ^0 are the static components, $\Delta\epsilon$ and $\Delta\sigma$ the dynamic components of the strain and stress, respectively, and ω the angular frequency of the strain in radians. The phase difference angle with positive sign means that the stress leads the prescribed strain; conversely, the negative sign represents a lag in phase.

Similarly, the dynamic absorbance $A_k(t)$ can be defined as follows;

$$A_k(t) = A_k^0 + \Delta A_k \exp[i(\omega t + \alpha)] \tag{3}$$

where A_k^0 and ΔA_k are the static and dynamic components of the dynamic absorbance and α the phase difference angle with respect to the dynamic bulk strain ϵ. ΔA_k can be expressed by the in-phase and out-of-phase components, A'_k and A''_k, as follows:

$$A'_k = \Delta A_k \cos\alpha \quad \text{and} \quad A''_k = \Delta A_k \sin\alpha \tag{4}$$

Here $A_k(t)$ is applied to parallel and perpendicular absorbances, $A_\parallel(t)$ and $A_\perp(t)$, which are the absorbances under parallel and perpendicular polarization to the strain axis, respectively.

Under the static strain, $A_\parallel(t)$ and $A_\perp$, depend on the orientation of dipole moments of functional groups and are given by [20]

$$A_\parallel = kc\langle\cos^2\theta\rangle d \tag{5}$$

$$A_\perp = kc(1/2)\langle\sin^2\theta\rangle d \tag{6}$$

where k, c, and d are the molar absorption coefficient, molarity, and the optical path, respectively. $\langle\,\rangle$ means average over all orientations of the functional groups. θ is the angle between the dipole moment of the functional group and the polarization direction. By using the parallel and perpendicular absorbances, we can define the average absorbance A_{av} and the dichroic difference L as follows;

$$A_{av} = (A_\parallel + 2A_\perp)/3 = kcd \tag{7}$$

$$L = A_\parallel - A_\perp = kcd(3\langle\cos^2\theta\rangle - 1)/2 \tag{8}$$

Here, we can extend the averaged absorbance and the dichroic difference into the functions of time as follows:

$$A_{av}(t) = [A_\parallel(t) + 2A_\perp(t)]/3 = A_{av}^0 + \Delta A_{av} \exp[i(\omega t + \alpha)] \tag{9}$$

$$L(t) = A_\parallel(t) - A_\perp(t) = L^0 + \Delta L \exp[i\omega t + \alpha)] \tag{10}$$

$$L' = \Delta L \cos\alpha \quad \text{and} \quad L'' = \Delta L \sin\alpha \tag{11}$$

The dynamic average absorbance given by Eq. (9) has no contribution from dynamic orientation of functional groups, as derived from Eq. (7), so we can discuss the dynamic changes in concentrations of functional groups, such as the dynamic changes in bonding/breaking of hydrogen bonds and crystallization/decrystallization. The dynamic dichroic difference in Eq. (10) is given by the product of the dynamic changes of the concentration and orientation in a given functional group, as shown in Eq. (8).

By using Eq. (4), the in-phase and out-of-phase components of the dynamic parallel and perpendicular absorbances can be defined as follows:

$$A'_\parallel = \Delta A_\parallel \cos\alpha \quad \text{and} \quad A''_\parallel = \Delta A_\parallel \sin\alpha \tag{12}$$

$$A'_\perp = \Delta A_\perp \cos\alpha \quad \text{and} \quad A''_\perp = \Delta A_\perp \sin\alpha \tag{13}$$

3. Apparatus

The dynamic infrared spectroscopic system (DIR system) used in this study is composed of three parts, i.e. mechanical, optical and electrical systems, similar to the system used by Noda et al. [14]. All the systems are controlled by a personal computer. Fig. 1 shows a line drawing of the optics in our DIR system. The infrared radiation, which is generated from a silicon light source, passes through an optical chopper, a polarizer, a photoelastic modulator and specimen film deformed by sinusoidal strains within a temperature controlled chamber. The strain direction is inclined at 45° from the horizontal plane, in order to minimize machine polarization of a grating monochromator. The radiation from the specimen is dispersed by the grating monochromator (Japan Spectroscopic, Model CT-50), which is also controlled by a personal computer. Finally, the radiation from the monochromator is detected by a MCT infrared detector. Detailed data analysis was made using the same procedures as Noda et al. [21].

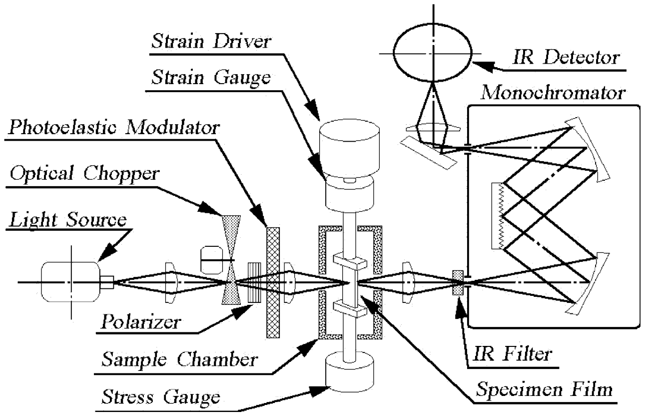

Fig. 1. A line drawing of optics of dynamic infrared spectroscopic system.

4. Experimental

The SPUU used in this study consists of poly(tetramethyleneglycol) (PTMG), 4,4′-diphenylmethane diisocyanate (MDI), and 1,2-propylene diamine (PDA). The number average molecular weight of PTMG in the soft segment is 856. The molar ratio of MDI, PTMG, PDA is 2:1:1 [17]. The average sequence numbers of the soft and hard segments were estimated as about 5 and 4.5, respectively.

10 μm of the thin films were prepared by casting a 4 wt% dimethyl formamide (DMF) solution onto a glass plate under the atmosphere of DMF vapor at 60°C. The films removed from the glass plate were dried in a vacuum oven at 60°C for a week so as to remove solvent and moisture. Sample size was 50 mm long and 20 mm wide. Gauge length was 30 mm.

Dynamic infrared measurements were carried out under the 10% static and 3.3% dynamic strains at −10 and 100°C and in the frequency of 32 Hz.

5. Results and discussion

Fig. 2 shows the static average absorption spectra over the wavenumber of 1550 and 1800 cm^{-1} at −10 and 100°C under the 10% static strain during the dynamic measurements. Here, we are focusing on three kinds of carbonyl (C=O) absorption bands at around 1640, 1710 and 1730 cm^{-1}, which are attributed to the hydrogen bonded urea (in the hard segments), the hydrogen bonded urethane (in the soft segments), and the free urethane C=O groups, respectively [22]. These bands shift to the higher wavenumbers with the higher temperature. Fig. 3 shows the static dichroic difference spectra obtained at the same time of Fig. 2. The dichroic differences give negative values at 1710 and 1730 cm^{-1} on the soft segments and positive values at 1640 cm^{-1} on the hard segments. The transition moments of the C=O groups for both the soft and hard segments are oriented along the perpendicular direction to the polymer chains or segments. This means that the soft segments are oriented to the strain direction, and contrary, the hard segments are directed perpendicular to the strain axis, due to the uniaxial deformation of the film. This kind of the orientation behavior has been reported in the segmented poly(urethaneurea)s and polyurethanes and explained by the disk-like model and/or the spherulite model [17–19,23,24].

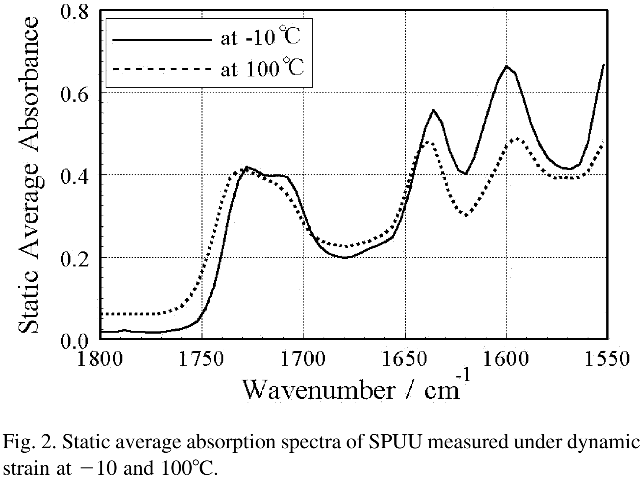

Fig. 2. Static average absorption spectra of SPUU measured under dynamic strain at −10 and 100°C.

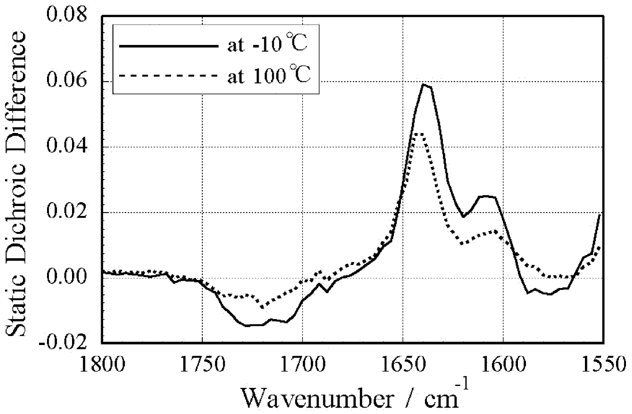

Fig. 3. Static dichroic difference spectra of SPUU measured under dynamic strain at −10 and 100°C.

Fig. 4 shows the dynamic dichroic difference spectra. The general features of the in-phase curves at both temperature of −10 and 100°C are similar to the static spectra in Fig. 3 except for the magnitude of the curves. This means that both the hard and soft segments are oriented by the dynamic strain in the same manner as under the static strain. The out-of-phase curve at 100°C (almost rubbery state) is almost zero in this wavenumber range, however, one at −10°C (near glassy state) gives positive and negative peaks crossing zero within the urea C=O band. This type of change comes from the dynamic peak shift [6].

Figs. 5 and 6 show the dynamic parallel and perpendicular absorption spectra. The spectra of in-phase components give the positive orientation of hard segments and the negative orientation of the soft segments as shown in the dynamic dichroic difference. The out-of-phase components

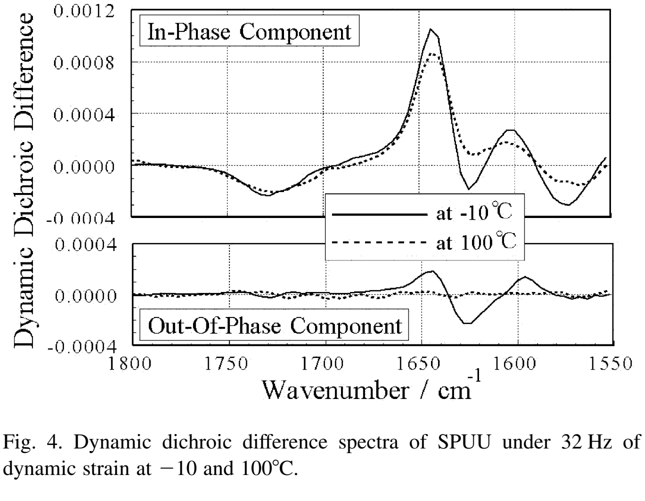

Fig. 4. Dynamic dichroic difference spectra of SPUU under 32 Hz of dynamic strain at −10 and 100°C.

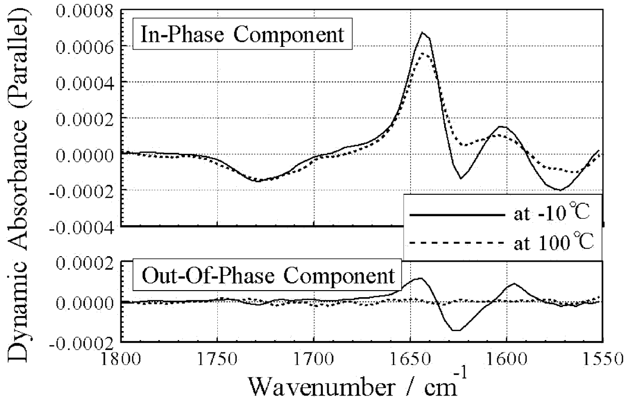

Fig. 5. Dynamic absorption spectra of SPUU (parallel direction to strain axis) under 32 Hz of dynamic strain at −10 and 100°C.

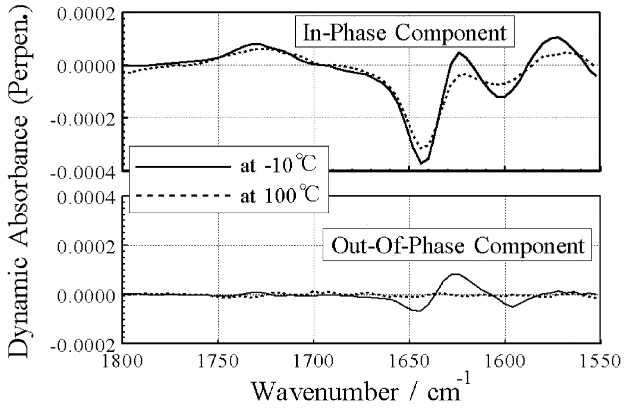

Fig. 6. Dynamic absorption spectra of SPUU (perpendicular direction to strain axis) under 32 Hz of dynamic strain at −10 and 100°C.

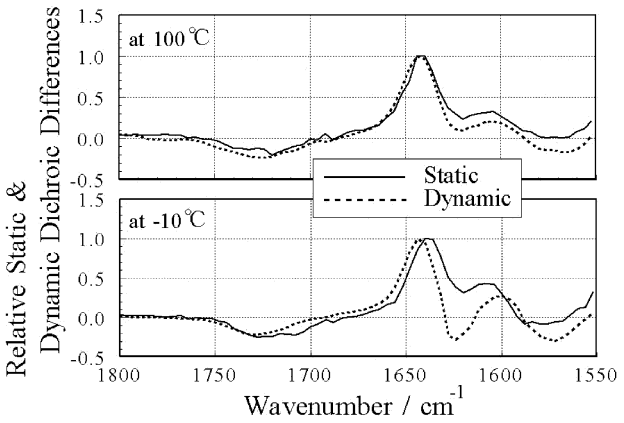

Fig. 7. Relative static and dynamic dichroic difference spectra normalized at the peak height around 1640 cm^{-1}.

of the urea C=O groups at −10°C give the dynamic peak shift of the opposite directions for the parallel and perpendicular polarizations along the strain axis.

Fig. 7 shows the relative static and dynamic dichroic difference spectra normalized by the peak height of the urea band. Here the dynamic components are converted by Eq. (14) so as to take into account the out-of-phase components before the normalization

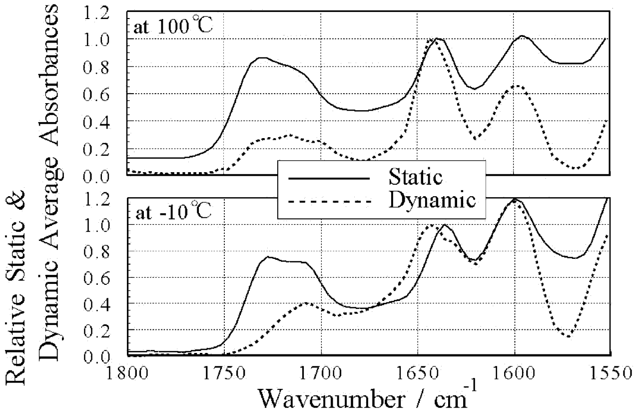

Fig. 8. Relative static and dynamic average absorption spectra normalized at the peak height around 1640 cm^{-1}.

$$L_{\mathrm{d}} = (L'/|L'|)(L'^2 + L''^2)^{-1/2} \tag{14}$$

The static and dynamic spectra are in good agreement except at a lower wavenumber than that at the urea band. On the other hand, the same normalized spectra for the average absorbances shown in Fig. 8 give a clear difference between the soft and hard segments. Here the dynamic average absorbance spectra are shown as the absolute values and the in-phase components are generally negative values. It is derived from this difference that the hydrogen bonds of the urea C=O are broken by the dynamic strain along the bonding.

6. Conclusions

From above discussion on the similarity between the static and dynamic dichroic difference spectra and the difference between the static and dynamic average absorption spectra, it is concluded that stress along the urea C=O bonds, but not along the polymer chains, takes an important role on the orientation of the hard segment domains. That is, the soft segments as a matrix component orient toward the strain direction, however, the hard segments make perpendicular orientation to the strain axis due to the stress along the urea C=O bond, which is perpendicular to the hard segment chain.

Acknowledgements

We acknowledge partial financial support of the Japanese Ministry of Education, Culture, Sports, Science, and Technology (Grant No. 11450370 to Shunji Nomura).

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