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Poly(carbonate-g-styrene) 공중합체의 유리전이 영역에서의 동적 점탄성과 광학 특성

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Dynamic Viscoelasticity and Optical Properties of Poly(carbonate-g-styrene) Copolymers in the Glass Transition Zone

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요 약

Polystyrene/polycarbonate 조성이 약 50/50인 3종류의 Poly(carbonate-g-styrene) 공중합체의 동적 탄성율, E*(ω)와 동적 스트레인-광학계수, O*(ω)을 유리전이 영역 부근의 여러 온도에서 동시에 측정하여 연구하였다. 두개의 공중합체는 각각의 스티렌 그라프트 쇄에 5, 10 wt%의 MAH를 함유하고 있다. 이들 공중합체의 E*(ω)와 O*(ω) 완화거동과 그라프트 공중합체의 상용성과 연관하여 비교 고찰하였다. 공중합체들의 E*(ω)는 전형적인 무정형 고분자의 유리전이 완화거동을 보였으며 정성적인 차이를 발견할 수 없었다. 그러나 고강도의 단일 tanδ 분산의 저주파수 영역에 미세 분산을 나타내, 공중합체는 2상으로 분리되어 있음이 추정되었다. 폴리스티렌 그라프트체에 무수 말레인산 함유량이 증가함에 따라, 저주파수 영역의 미세피크가 α-주분산에 병합되어 성분 고분자 간의 상호 협동성이 증가함을 알 수 있었다. 3 공중합체의 유사한 기계적 특성과는 달리, 광학적 완화 스펙트럼 O*(ω)는 정성적으로 명확한 차이를 보여, 공중합체들의 광학 완화 거동이 명확히 다름을 나타냈다. 기계적 특성보다는 광학적 특성이 공중합체 내의 성분 고분자의 미세한 완화 거동에 훨씬 민감한 응답을 나타냈다. 이러한 특성적인 공중합체의 O*(ω) 차이를 공중합체의 조성 단일 고분자 PS, PC의 O*(ω)의 가성성을 가정하여 모사하였다. 모사에서 구한 광학적 부분 기여 파라메터를 사용하여 공중합체의 상용성을 고찰하였다.

Abstract— In the glass-to-rubber transition zone over a wide temperature range, we simultaneously measured the complex Youngs modulus, E*(ω), and the complex strain-optical coefficient, O*(ω), of three poly(carbonate-g-styrene) copolymers. Two of them include 5 and 10 wt% of maleic anhydride (MAH) in their grafted styrene, respectively. We compared the relaxation behaviors in E*(ω) and O*(ω) of the copolymers in view of the compatibility of their component polymers. The E*(ω) of three copolymers displayed typical glass-transition behavior of amorphous polymers and apprehensible differences were not appreciated between the copolymers. For three copolymers, minute dispersion was observed in the lower frequency region of dominant tanδ peaks arising from minute phase separation of the components. With increasing MAH content in the copolymers, it was absorbed into the main α-distribution, which indicated improved cooperativity of chain relaxation between dissimilar polymer species. Contrasting with the similar mechanical properties, the optical properties, O*(ω), reflected a great sensitivity to the minute variation of chain relaxation. The optical relaxation spectra of three copolymers showed definite difference in quality, indicating unlike optical relaxation mechanisms. The characteristic differences among the copolymers were simulated by assuming a simple additivity rule of the O*(ω) of component polymers. The compatibility of the copolymers was discussed in light of a fractional contribution parameter, F_{ps}, which was derived from the simulation.
Keyword: Birefringence, Complex Young's Modulus, Complex Strain-optical Coefficient, Poly(carbonate-g-styrene) Graft Copolymer, Cooperativity, Polystyrene, Polycarbonate

1. Introduction

Amorphous polymers become anisotropic and birefringent under deformation. Strain-induced birefringence has been an important subject in the field of rheo-optics since it is strongly related to the stress[1]. For melts or concentrated solutions, the birefringence, Δn(t), is proportional to the stress, σ(t)

$$\Delta n(t) = C_R \sigma(t) \quad (1)$$

Here the proportionality coefficient, C_R, is called the stress-

optical coefficient (SOC). The relation holds valid even when the birefringence and the stress vary with time, t, as in the stress relaxation process. The rule is known as the stress-optical rule (SOR) and its validity have been confirmed for many polymeric materials[1].

A similar rule holds valid between the stress and the glassy birefringence produced in glassy polymers.

$$\Delta n = C_d \sigma \tag{2}$$

This relation is called photoelasticity (PE) and different from Eq. (1). It is valid only for instantaneous values of the birefringence and the stress on application of the strain. The coefficient C_d is called the photoelastic coefficient (PEC) and is not equal to the SOC. The origin of the birefringence of glassy materials is not well understood whereas it is well established that the birefringence and the stress in the rubbery and flow zones are attributed to the polymer chain orientation. In theories of birefringence, the Lorentz-Lorenz relation is usually used to connect the refractive index to the polarizability. The relation between the birefringence and the anisotropy of the polarizability, $\Delta\beta$, of units with molecular weight M may be described as follows:

$$\Delta n = \frac{2\pi}{9} \frac{(n^2+2)^2}{n} \frac{\rho N}{M} \Delta\beta \tag{3}$$

where n denotes the refractive index and ρ is the density. $\Delta\beta$ includes the intrinsic anisotropy of polarizability and the degree of orientation of the structural unit. The factor $\rho N/M$ represents the number of repeating unit per volume, with N being Avogadro's number.

In an dynamic elongation of polymeric materials, one can define the complex Young's modulus, $E^*(\omega)=E'(\omega)+iE''(\omega)$, as the ratio of the complex stress, $\sigma^*(\omega)$, to the complex strain, $\varepsilon^*(\omega)$[2]. Similarly, when one measures the birefringence, $\Delta n^*(\omega)$, one obtains the complex strain-optical coefficient, $O^*(\omega)$, defined as

$$O^*(\omega) = \Delta n^*(\omega)/\varepsilon^*(\omega) = O'(\omega) + iO''(\omega) \tag{4}$$

$O^*(\omega)$ is also proportional to $E^*(\omega)$ in the rubbery plateau and the flow zones and this is an example of the SOR applied to an oscillatory elongation[3].

Polystyrene (PS) and polycarbonate (PC) are excellent in optical transparency. PS contains a side phenyl group with polarizable anisotropy in the unit structure. Its birefringence caused by deformation is notably high and, C_R, is negative[4]. On the other hand, PC shows congenial optical property comparable to other polymers and good mechanical properties such as impact strength, creep-resistance, and dimensional stability. It bears phenylene groups in the main chain and its birefringence induced by deformation is positive and high[5]. Thus, a combination of PS and PC is expected to lead to a reduction of birefringence coming from the compensation of positive and negative birefringence induced by chain orientations of their constituent polymers. However, a homogeneous blend, if produced, is not stable and eventually becomes turbid[6]. The graft of PS chain on a PC chain is one of the methods to attain a homogeneous alloy[7].

In the present study, we examine the dynamic birefringence and viscoelasticity of three kinds of poly(carbonate-g-styrene) copolymers. They are favorably expected to be used for optical purpose, *e.g.* birefringence free compact-disk substrate. We will concentrate on the mechanical and optical relaxation behavior of the copolymers, and their birefringence behavior as a measure of miscibility.

2. Experimental

2.1. Materials

The copolymers used in this study were three kinds of PS-g-PC graft copolymer (Mitsubishi Gas Chemical, Japan). The molecular characteristics of graft copolymers were shown in Table 1. The copolymers were known to be composed of a polymer of PC main chain with PS graft body. For the two copolymers, coded as MGC2 and MGC 3, the constituent PS graft chain was modified with maleic anhidride (MAH).

For the measurement of viscoelasticity and birefringence, we prepared the films of the copolymers by press machine at 250°C. Before preparing films, the copolymers were purified for getting high optical transparency with the procedure that they were dissolved at 2 wt% in dichloromethane and dropped into a stirred excess methanol yielding bulk precipitation. The copolymers in bulk state were first dried at 120°C under vacuum for 2 days. Then they were compression-molded into films having a thickness of about 700 μm. The molded films were also dried

Table 1. Compositions and characteristics of the copolymers and hompolymers studied.

Polymers	PC wt%	PS wt%	T_g °C	M_n	M_w	MA/SMA wt%
MGC1	50.4	49.6	139,102	-	134,000	0
MGC2	50.9	49.1	133,115	26,000	116,000	10
MGC3	53.1	46.9	137,123	27,400	156,000	20
PS	-	100	100		270,000	
PC	100	-	-		160,000	

under vacuum for 24 hours prior to the measurements. The films remained transparent during the storage time and the measurements.

2.2. Measurement

The apparatus for the dynamic birefringence measurement was reported previously[8]. An optical system was attached to an oscillatory rheometer (Rheology DVE 3, Kyoto, Japan). A Senarmont optical system was used to compensate the static birefringence induced by the load to maintain the sample: the He-Ne laser, polarizer, quarter-wave plate, analyzer, and photodetector were placed on an optical bench. The sample was placed between the polarizer and the quarter-wave plate with their axis at $\pi/4$ to the strain axes in the specimen. The amplitude oscillatory strain was typically 10^{-3} in the rubbery zone and 10^{-4} in the glassy zone. A slight tension of the order of 1 Pa was applied to prevent from the sample buckling. The signal from the photodetector was analyzed with a lock-in amplifier.

The measurements were performed under isothermal conditions at several temperatures over the frequency range 1~130 Hz. In order to avoid the effect of physical aging, the sample was preheated at Tg+15°C and kept at this temperature for about 30 min before the measurements. All measurements were performed at least 15 min after the temperature reached the required value.

3. Results and Discussion

3.1. The Young's Modulus and the Strain-optical Coefficient of Copolymer

Three graft copolymers investigated in this study are composed of bicomponent dissimilar polymers but their E* (ω)'s displays distinct typical glass-transition behavior much similar to those of amorphous polymers. Figs. 1 and 2 show the frequency dependence of mechanical and optical properties of MGC2 copolymer that is simultaneously measured in the glass-transition zone over 111~177°C, respectively.

As shown in Fig. 1(a), the frequency dependence of E' (ω) is very small at lower and at higher temperatures in the measured range, but it is drastically changed in the middle temperature range. At temperatures lower than 122 °C, E'(ω) reaches approximately a constant value of about 10^9 Pa with frequency. The E"(ω), standing for energy loss in dynamic test, decreases with decreasing temperature and increasing frequency, which is attributed to the restriction of macroscopic chain segmental motion at the low temperatures and corresponds to glassy zone of amorphous polymers. At higher temperatures above 156°C, E' (ω) is about 10^6 Pa and varies little with frequency. It's E"

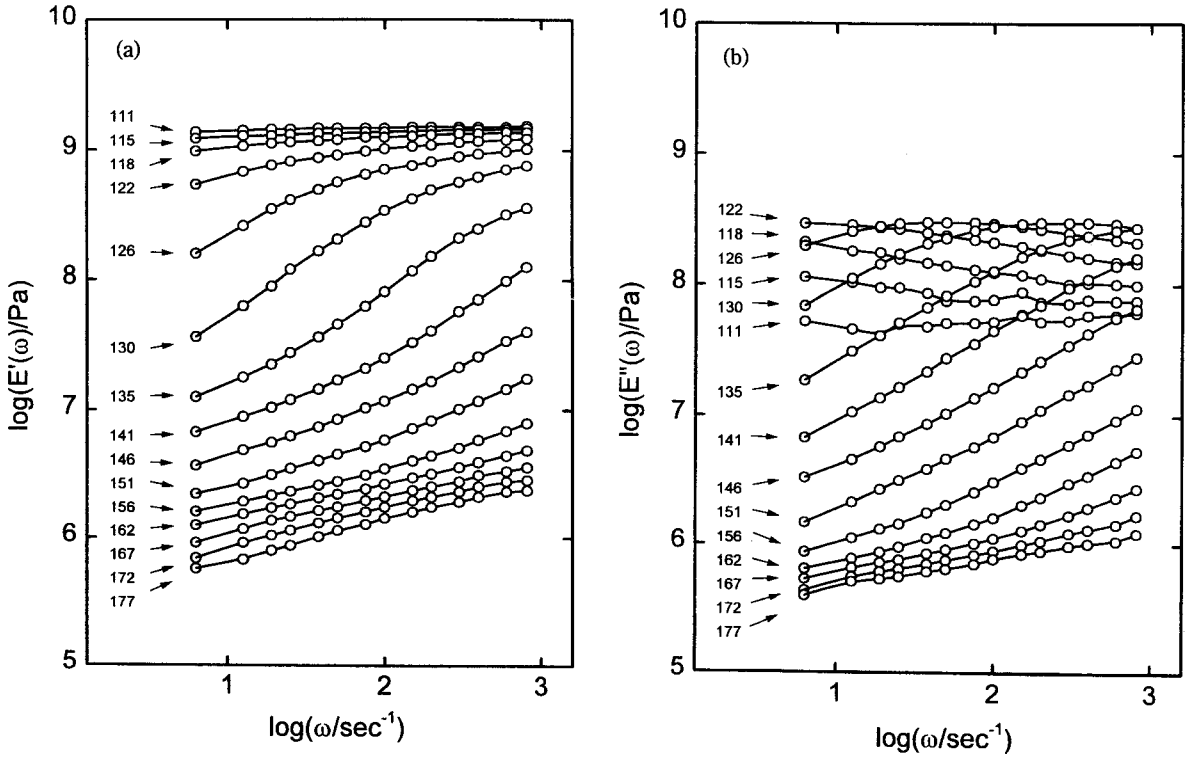

Fig. 1. Frequency dependence of the complex Young's modulus of MGC2. Temperatures in degree centigrade are indicated in the figure.

(ω) at the same temperature range in Fig. 1(b), is about 5 times smaller than E'(ω). These characteristics correspond to the rubbery plateau zone of amorphous polymers arising from highly entangled polymeric chains that behave like cross-linked rubber[9]. In temperature range of 126~151°C, variations in E'(ω) and E"(ω) increase rapidly with decreasing temperature and with increasing frequency at isothermal condition. Moreover, E"(ω) dominates over E'(ω) in the same region. These features are typical to the glass transition zone.

Fig. 2 shows the frequency dependence of the real and imaginary parts of the complex strain-optical coefficient of MGC2 at various temperatures. Here, absolute values of O'(ω) and O"(ω) are plotted but negative values are shown with filled symbols. Contrasting to the systematic variation of mechanical properties with frequency in Fig. 1, strain-optical coefficients vary more complex with frequency and/or temperature. At the temperature range 156~177°C, both O'(ω) and O"(ω) are positive (n_{11}-n_{22}>0) arising from the orientation of the anisotropic links in polymer chain. n_{11} and n_{22} are refractive indices for light with electric vector parallel and perpendicular to the direction of extension, respectively. Further decreasing temperatures, the changes of signs are also observed in O'(ω) and O"(ω) at the range of 126~151°C. At 146°C and 151°C, O'(ω) in Fig. 2(a) changes sign from positive to negative with frequency, at frequencies around 30 and 250 sec^{-1}, respectively. |O'(ω)| shows a maximum with frequency at 135°C. At 126 and 130°C, it oppositely changes signs from negative to positive. The frequency dependence of positive O'(ω) is hardly observed at temperatures lower than 122°C, which is similar to that of E'(ω) at the same temperature. The characteristic behavior of O"(ω) with frequency in Fig. 2(b) is similar to that of O'(ω); with decreasing temperature, O"(ω) changes signs from positive to negative, shows maximum, and oppositely changes form negative to positive with frequency. The change of the signs of O"(ω) takes place at lower frequencies than that of O'(ω), being compared at the same temperature. This optical variation with frequency is closely related to the orientation of anisotropic segments[10]. For two other copolymers of MGC1 and MGC3, similar qualitative mechanical and optical variations are observed with temperature or frequency and they are not presented herein.

3.2. Characteristics of the Master Curves of Viscoelasticity, E*(ω)

It has been established that time-temperature superpos-

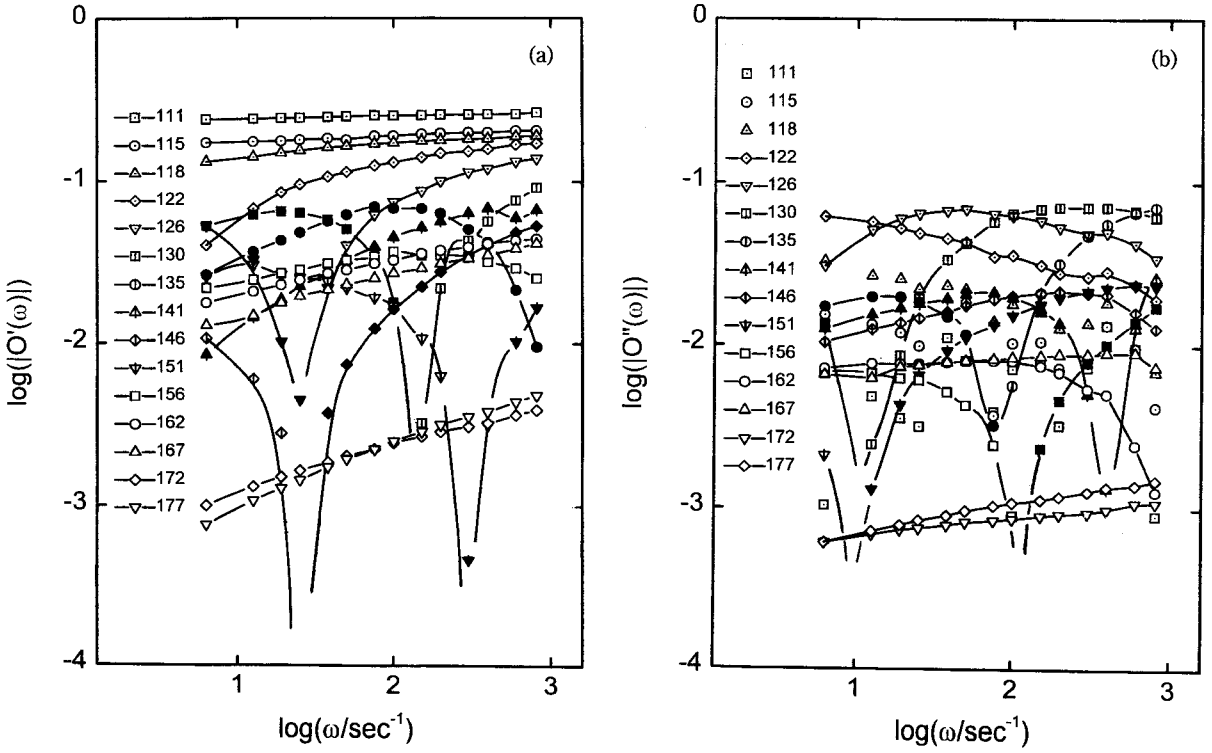

Fig. 2. Frequency dependence of the complex strain-optical coefficient of MGC2. Unfilled symbols represent positive values and filled symbols do negative values. Temperatures in degree centigrade are indicated in the figure.

ition principle[2] are well performed for $E^*(\omega)$ measured with frequency in a wide range of discrete temperatures. The master curve of $E^*(\omega)$ for MGC2 was constructed from the data shown in Fig. 1 with the time-temperature superposition principle. Attempt was also made for $O^*(\omega)$. The data of $O^*(\omega)$ are plotted against ω in log-log scale and shifted along the abscissa so that each quantity is laid on one composite curve as closely as possible. The same procedure was also carried out for two other copolymers, MGC1 and MGC3. Figs. 3 to 5 shows the constructed master curves of $E^*(\omega)$ and $O^*(\omega)$ of MGC1, MGC2, MGC3, respectively. The reference temperature, T_r, is chosen so that $E''(\omega)$ of each polymer is 10^8 Pa at $\omega=10s^{-1}$ in an isothermal measurement[11-14]. They are 116°C, 135°C, and 142°C for MGC1, MGC2, and MGC3, respectively. The curves were extended from rubbery plateau to glassy modulus. Firstly, we shall discuss the viscoelastic properties of the copolymers. In Figs. 3 to 5, one can observe the distinctive glass-transition behaviors of sigmoidal figures even though three copolymers are in heterogeneous state employed with dissimilar bicomponent constituents. As shown in Table 1, two glass-transition temperatures were found for all three copolymers in the DSC measurement, which means they are separated into two phases in the bulk state. However, the mechanical spectra of three copolymers give no indication of differences in characteristics between different species of the copolymers. This is presumably due to the assimilated cooperative relaxation of two constituents via a consequence of the attaches of PC and PS chains. Further, the frequency dependence of mechanical spectra is remarkably different in comparison with our previous study of the PS/PC blend with the composition of 50/50 wt%[6]. In a master curve of the blend, $E^*(\omega)$ displayed two step transition zones indicating separated two phases of constituents, PS and PC, which was ascribed to the independent relaxation of separated component phase of the PS/PC blend.

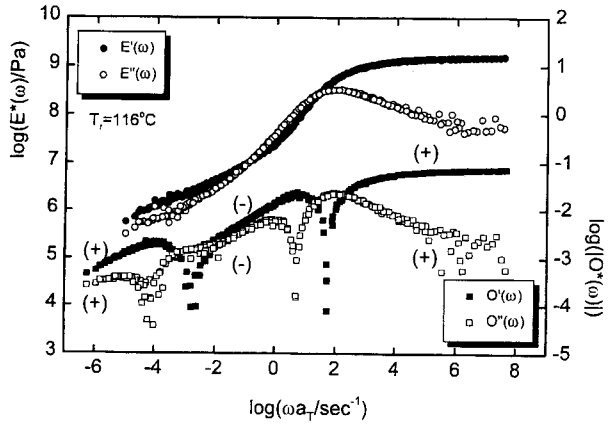

Fig. 3. Master curves of the complex Young's modulus and strain-optical coefficient of MGC1 constructed with time-temperature superposition principle. Reference temperature is 116°C.

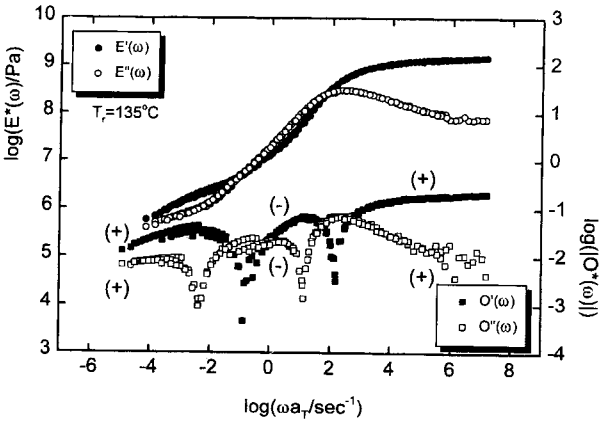

Fig. 4. Master curves of the complex Young's modulus and strain-optical coefficient of MGC2 constructed with time-temperature superposition principle. Reference temperature is 135°C.

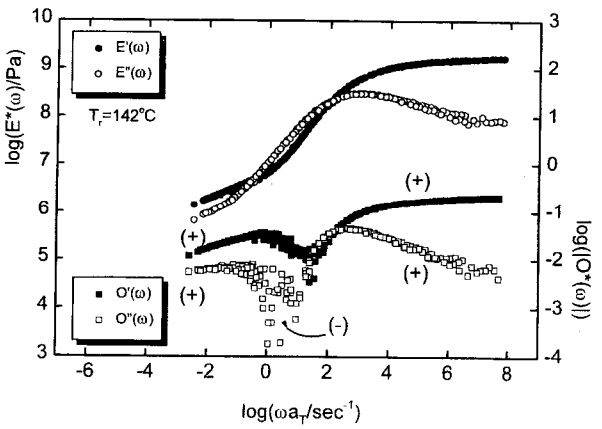

Fig. 5. Master curves of the complex Young's modulus and strain-optical coefficient of MGC3 constructed with time-temperature superposition principle. Reference temperature is 142°C.

3.3. Loss Tangent of the Copolymers

For the purpose of finding the minute difference among three mechanical spectra, we present the tanδ of three copolymers in Fig. 6. The tanδ's are calculated from the above master curves of $E^*(\omega)$ of three copolymers in Fig. 3 to Fig. 5. The apparent tanδ's of three copolymers show almost a single peak distribution implying a cooperative relaxation of the component polymers. The features are very similar to one another, as seen in that of the $E^*(\omega)$. For the comparison, tanδ of the blend of PS/PC, are displayed in a dotted line. One can see the definitely separated dou-

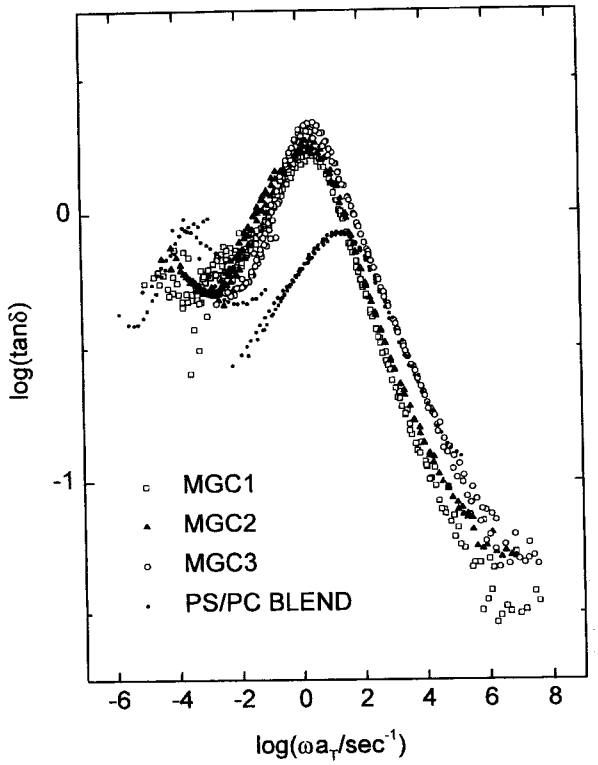

Fig. 6. Mechanical loss tangent of the copolymers of MGC1, MGC2, and MGC3. The properties of PS/PC blend (=50/50 by wt), previously reported[6], were also displayed for comparison.

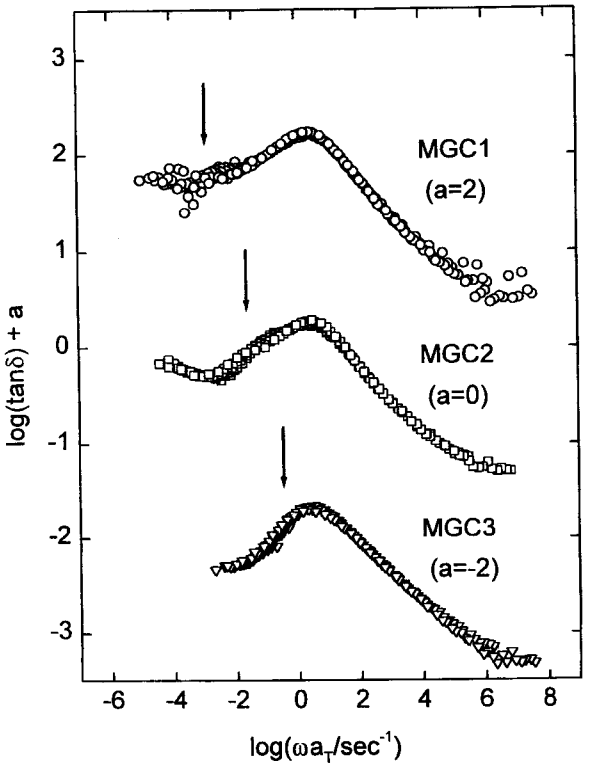

Fig. 7. Mechanical loss tangent of the copolymers of MGC1, MGC2, and MGC3. The curves were shifted in the vertical direction to avoid the confluence.

ble peaks and their relaxation strengths are almost the same. This implicitly reflects that the constituent polymers relaxed independently. A peak in lower frequency zone corresponds to the tanδ of the PC, and the other in higher frequency zone corresponds to the tanδ of PS. Three peaks of the copolymers are placed between double peaks of the blend in frequency axis. It must be a consequence that the relaxation's of constituents of the copolymers is dependent and behaves cooperatively each other. In comparison of three copolymers, distribution of the peaks in frequency zone over 10^2 sec^{-1} shifts toward higher frequency zone with increasing the content of MAH in graft PS. This may imply that the frequency dependence of PS constituent in the miscible state is constrained with increasing the MAH content. It means the relaxation modes of PS constituent of the copolymers come to be widely distributed over broad frequency range by MAH.

The tanδ's of three copolymers are redrawn in Fig. 7 with vertical shift for avoiding the interference in observation. A minute peak(arrowed distribution) is observed in the lower frequency region of the main peak of MGC1 and its strength is much smaller than that of main peak. In the curve of MGC2, containing about 5% of MAH, the minute distribution shifts toward the main peak. The distribution is almost merged into α-distribution in the curve of MGC3 that contains about 10% of MAH. This implies that the incorporation of MAH to the copolymers increases the compatibility of the polymers and the relaxation modes are significantly varied. That is, the relaxation modes of constituent polymers of the copolymers are assimilated by intermolecular cooperativity, and it is intensified with increasing the content of MAH.

3.4 Characteristics of the Master Curves of Optical Properties, O*(ω)

Contrasting to the similarity in mechanical characteristics of three copolymers, we can see the prominent difference among optical properties, O*(ω), in Fig. 3 to 5. First, one can find that the spectra lengths of the master curves of O*(ω) are longer than those of E*(ω) for respective copolymers. These features imply that the temperature dependence of O*(ω) is stronger than that of E*(ω), which has often been observed for various homopolymers [4-6,12-14]. According to the analysis of modified stress optical rule, two essentially different relaxation mechanisms, orientational and distortional modes, were contributing

to the relaxation modulus of homopolymers in the glass-transition zone[3,11-13]. Degrees of contribution of two modes to the relaxation modulus were different with the species of polymers. In addition, properties in optical relaxation mechanisms of the components are clearly different with each other. Thus, degrees of the contribution of the component mechanisms to the $E^*(\omega)$ and $O^*(\omega)$ are not the same and differences in temperature dependence of the $E^*(\omega)$ and $O^*(\omega)$ are consequently produced. The phenomena are more complex for the copolymers with bicomponent, because there may be at least 4 kinds of relaxation modes arising from two for each component polymer[6,15].

We redraw the $O^*(\omega)$'s of three copolymers in Fig. 8 for lineal comparison. The signs of $O^*(\omega)$ of three copolymers are positive (n_{11}-n_{22}>0) in the frequency zone corresponding to the glassy and the rubbery-plateau region. In the glass transition zone, the negative (n_{11}-n_{22}<0) signs of $O^*(\omega)$ are observed and its ranges in frequencies are different with copolymers investigated. The sign of $O^*(\omega)$ for MGC2 and MGC3 changes consecutively positive, negative, and positive with increasing frequency. The negative $O^*(\omega)$ regions of MGC1 are extended over 4.5 grades in frequencies. With increasing the quantity of MAH, the negative middle ranges of $O^*(\omega)$ are reduced to 3.5 grades

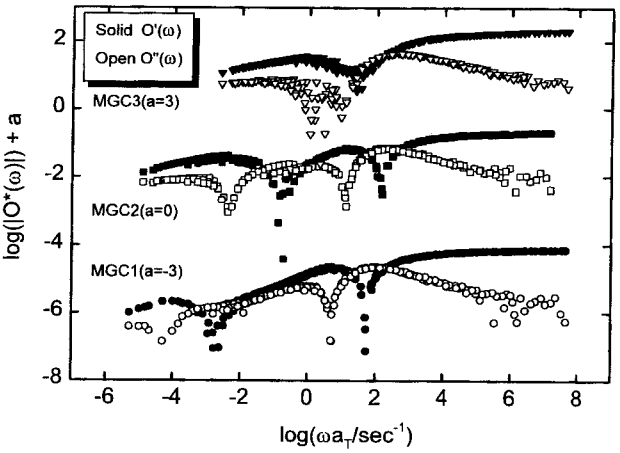

Fig. 8. Master plots of the complex strain-optical coefficient of MGC1, MGC2 and MGC3 in a frame. The plots were shifted in the vertical direction to avoid the confluence.

in MGC2 and to 0.5 grades in MGC3. Most discernible change is observed in $O'(\omega)$ of MGC3, which shows the positive values over the whole range of extended frequency. For MGC3, variation in narrow region of negative $O''(\omega)$, corresponding to glass-transition region, looks very complicated. Both properties are, however, systematically and steeply varied with frequency or temperature as shown in Fig. 9. This definite information leads to the conclusion

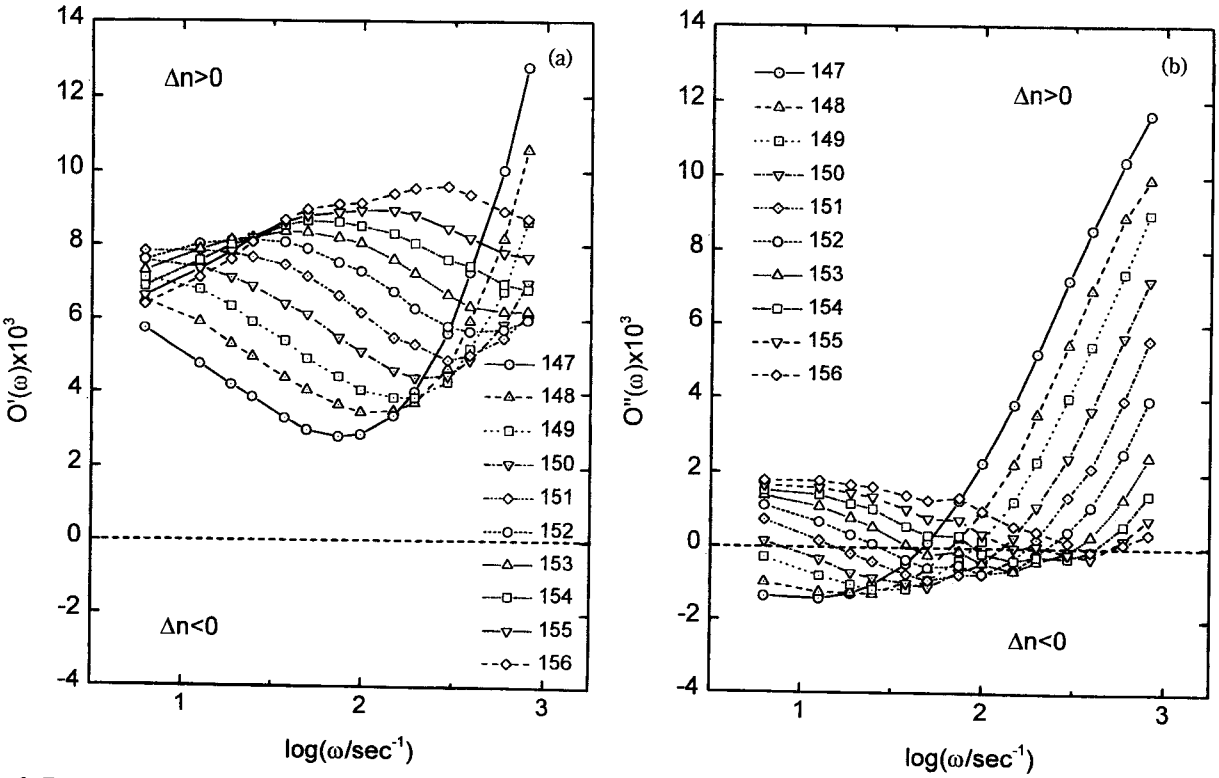

Fig. 9. Frequency dependence of the complex strain-optical coefficient of MGC3. Temperatures in degree centigrade are indicated in the figure.

that the optical and mechanical relaxation mechanisms of three copolymers are remarkably varied with MAH.

In our previous studies, PC homopolymer displayed positive birefringence over the observed whole frequency range[5]. PS homopolymer showed negative birefringence over the rubbery plateau to glass-transiton zone[4]. Hence, the negative values of O*(ω) of three copolymers, as shown in Fig. 8, are evidently caused by the orientation of PS chain in long-time relaxation region. Shortening of negative zone with incorporation of MAH is an evidence of the variation in chain orientational mode of PS. Increasing the compatibility of PS and PC component, both orientational modes are affected by each other. In the graft copolymers, the relaxation (disorientation under extension) of grafted PS chain will go ahead of the relaxation of main PC chain. Consequently, shortened negative O*(ω) of copolymers associated with decreasing the orientation of PS is easily predicted being compared with the blend. In our previous study of PS/PC blend[6], quite different feature of O*(ω) was observed being compared with that of the copolymers presented in this study. The negative range of O*(ω) of MGC1 is much wide among three copolymers. In the blend, however, more wide range of negative signs was discovered being compared with that of MGC1. The negative O*(ω) of the blend reflected the increased molecular motion of component polystyrene in the blend and it made us presume the poor dependency of PS and PC.

Furthermore, we can find that the contribution of PS chain to O*(ω) is decreased with increasing the quantity of MAH in the copolymers, MGC2 and MGC3. It is well known that the MAH will affect the compatibility between dissimilar polymers[7]. The incorporated quantity of MAH is employed to the variation of the optical relaxation mechanism of the copolymers. Hence, we are expecting to predict the compatibility of constituents of the copolymers from the optical variation with MAH contents.

3.5. Compatibility Prediction from O*(ω) of the Copolymers

Before looking into the compatibility of copolymers, we shall discuss the optical properties of constituent homopolymers. Fig. 10 displays the O*(ω) of PS and PC homopolymers measured in the glass-transition zone and had reported in our previous study[4-5]. PC includes the optically large anisotropic phenyl group in their main chain and PS has it as a side group. One can observe that the optical properties of both polymers are markedly different. The PC displays the positive and large O*(ω) in the whole

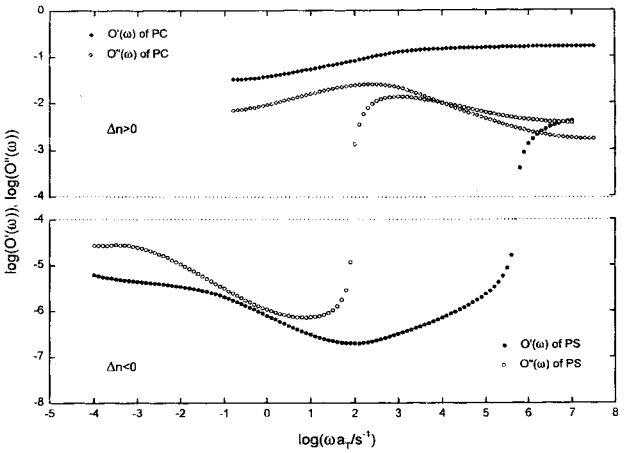

Fig. 10. Master curves of the complex strain-optical coefficient of PS and PC homopolymers.

range investigated, and its variation with frequency is monotonous. This feature of O*(ω) is commonly observed in the polymers containing phenyl groups in their main chain[11, 14]. On the contrary, the variation of O*(ω) of PS with frequency is remarkable and even shows changes in sign with frequency. This type of variation in O*(ω) has been frequently observed in the polymers that include anisotropic pendant side group such as phenyl or naphthyl[16]. These two different variation modes suggest that the local tilting or orientation of anisotropic side groups toward the directions of extension may be more complex than that of the anisotropic phenylene groups in main chain. In the long time relaxation of high temperature region, the birefringence is attributed to the long-range conformational rearrangements which are associated with the orientation and disorientation of main-chain segments. Optical properties are determined by the degree of orientation of anisotropic polymer chains with intrinsic birefringence[17]. Decreasing the temperature, the distortional change dominates over the orientational change in the shorter relaxation time region.

Intrinsic birefringence of polymers, Δn^0, can be determined by empirical measurements or theoretical calculation from the molecular structures of polymers[18]. For bicomponent polymer of A and B, the birefringence of the polymer may be described as the following relation

$$\Delta n = \phi_A f_A \Delta n_A^0 + \phi_B f_B \Delta n_B^0 + \Delta n_F \quad (5)$$

where ϕ is volume fraction and f is orientation function that is defined as $(3\langle\cos 2\theta\rangle - 1)/2$ where θ is the angle between the chain axis and the extensional direction. Δn_F is form birefringence which is assumed to be zero in the miscible state of bicomponent of the polymer, and is negli-

gibly small compared with orientational birefringence[19]. Thus, apparent birefringence of an alloy may be approximated by a simple summation of the birefringence contributions of constituents. As mentioned above, the cooperativity of constituent polymers of the copolymers will be varied with respect to the degree of compatibility. For a fully compatible polymer, relaxing cooperatively, one can assume the orientational and/or molecular relaxation motion of polymer A is similar to that of polymer B, *i.e.*, $f_A=f_B$. Hence, the birefringence free condition of Eq. (5) may be given by

$$\phi_A\Delta n_A^0 + \phi_B\Delta n_B^0 = 0 \quad (6)$$

Condition of Eq. (6) can be employed for achieving complete compensation of birefringence by alloying the positively and negatively birefringence polymers.

If there were a good miscibility between constituents of PS and PC of the copolymers, the degree of orientation of the optical anisotropic segments of constituents would be similar in the copolymers under the dynamic deformation. However, the constituents of three copolymers are not fully compatible as confirmed in the DSC measurements. Hence one can deduce that under extensional strain the orientation functions of the constituents will differ from each other with the degree of compatibility. The contribution of the birefringence of constituents may be expressed by the following equation as a first approximation with analogy of Eq. (5)

$$O^*(\omega a_T) = F_{PS}O^*_{PS}(\omega a_T) + (1 - F_{PS})O^*_{Pc}(\omega a_T) + O^*_f(\omega a_T) \quad (7)$$

where F_{PS} is the fractional contribution of PS, and ($1-F_{PS}$) is that of PC. The O^*_f is a form birefringence occurred in the interface of two phase but negligible compared to the strain-induced birefringence.

By using the $O^*(\omega)$ of PS and PC homopolymers shown in Fig. 10, the estimation of $O^*(\omega)$ for three copolymers was performed by above equation. As plotted in Fig. 11, the simulated results approximated to experimental figures of $O^*(\omega)$ in Fig. 8 by varying fractional contribution factor F_{PS}. On can find the characteristic birefringences are qualitatively very similar to each other. The fractional contribution, F_{PS}, estimated in the simulation are 0.85, 0.7, 0.6 corresponding to MGC1, MGC2, and MGC 3, respectively. Their respective weight fractions of PS to PC are almost the same as about 0.5. The weight fraction can be assumed to be equivalent to volume fractions because the density of PS is nearly equal to that of PC. As mentioned above, the degree of orientation of the two components will be similar in ideal mixing state of the copolymers. One can easily suppose that their volume fraction is employed to the bulk optical properties of the copolymers. Thus the calculated contribution fraction shall be equal to volume fraction and the ratio of contribution fraction to volume fraction becomes unity. If there is a deviation from the ideal mixing state, contribution fractions of component become dissimilar arising from the role of independent relaxation mechanism of components. From the above results, the ratios of contribution fractions to volume fractions are calculated as 1.7, 1.4, and 1.2 for MGC1, MGC2, and MGC3, respectively. The ratio getting close to unity may imply coming to ideal mixing state of the alloys. Hence, we can conclude that the mixing state gets better in the order of MGC1, MGC2, and MGC3. This is also consistent with the result inferred from the viscoelastic behaviors. Also we can see that the optical properties reflect a great sensitivity to the minute variation of chain relaxation of miscible alloys.

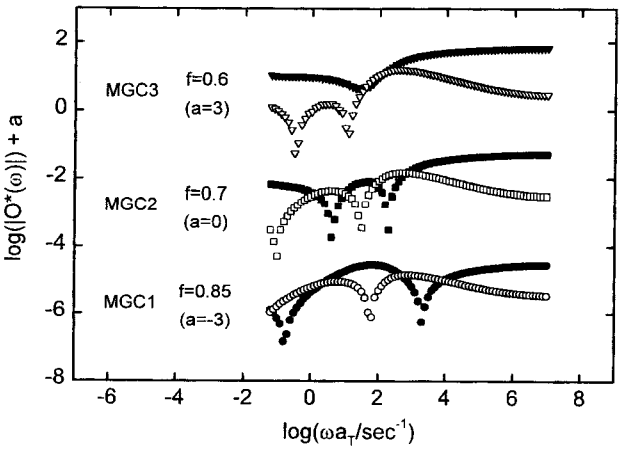

Fig. 11. Master plots of the complex strain-optical coefficient evaluated by simulating the MGC1, MGC2, and MGC3 with the first approximation of the Eq. (7). The plots were shifted in the vertical direction to avoid the confluence.

Morphology's of three copolymers were obtained using scanning electron microscope (SEM; S-510, Hitachi Co.) and displayed in Fig. 12. The fracture surface of the films were etched with styrene monomer. In the observations the protruding white domains are the PC particles. The PC domains of three copolymers are well ordered and homogeneous. In comparison of three copolymers, domains of MAH free MGC1 is crude and worst in dispersion. It is heterogeneous in size. Morphology of the etched surface of MGC2 in (B) shows fibrillar dispersion and it quite different from the others. We can see the phase morphology is appreciably affected by incorporating small amount of MAH. On the contrary, and MGC 3 in (C) exhibits sim-

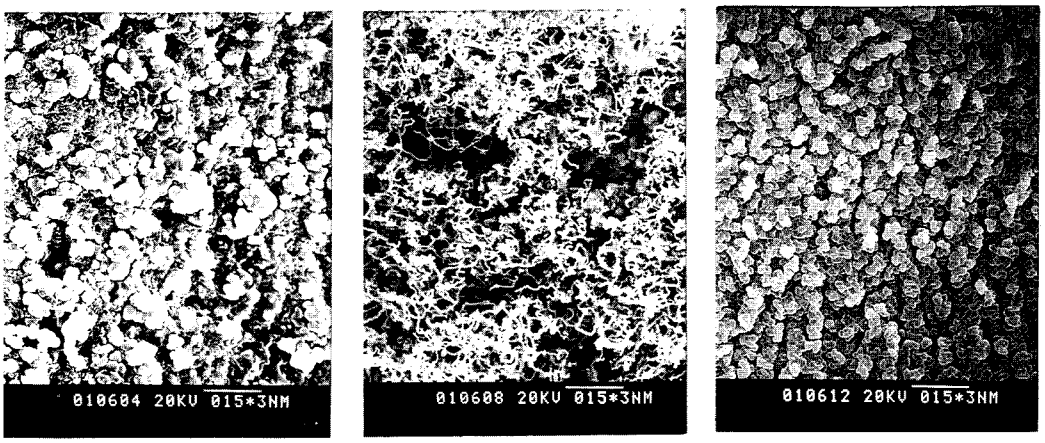

Fig. 12. Scanning electron micrograhs of the fracture surface of MGC1, MGC2 and MGC3 etched with styrene monomer.

ilar domains which is observed in (A). Its size is smaller and more even indicating better miscible state between PS and PC components.

4. Conclusion

We studied the complex Young's modulus, $E^*(\omega)$, and the complex strain-optical coefficient, $O^*(\omega)$, of three poly(carbonate-g-styrene) copolymers in the glass-to-rubber transition zone over a wide temperature range. Optical and mechanical properties were measured simultaneously. Two copolymers, MGC2 and MGC3, include 5 and 10 wt% of maleic anhydride (MAH) in their grafted styrene, respectively. In view of the compatibility, we compared the relaxation behaviors in $E^*(\omega)$ and $O^*(\omega)$ of the copolymers.

With all their heterogeneous bicomponent polymers, mechanical properties of $E^*(\omega)$ of three copolymers displayed typical glass-transition behavior of amorphous polymers and apprehensible differences among the copolymers were not found. Tanδ's of three copolymers showed almost a single peak distribution representing cooperative relaxation of component polymers, whereas in our previous study of PS/PC blend two isolated tanδ peaks, implying independent relaxation of constituents, were detected. For three copolymers, however, minute dispersion was observed in the lower frequency region of single peaks arising from minute phase separation of the components. With increasing MAH content in the copolymers, minute dispersion of lower frequency region was absorbed into the main α-distribution, which indicated the cooperative chain relaxation of dissimilar polymer species.

Contrasting to the similar mechanical properties among the copolymers, the optical relaxation spectra, $O^*(\omega)$, of three copolymers showed definite difference in quality, indicating unlike relaxation mechanisms. The optical properties reflected a great sensitivity to the minute variation of chain relaxation rather than the mechanical properties did. From the characteristic difference, we were able to simulate the $O^*(\omega)$ of the copolymers by assuming simple additivity of the $O^*(\omega)$ of component polymers. The fractional contribution, F_{ps}, evaluated in the simulation enabled us to predict the degree of optical relaxation contribution of component polymers to the $O^*(\omega)$ of copolymers. The conceptuality analyzed form the optical measurements corresponded to that from mechanical data.

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References

1. H. Janeschitz-Kriegl, "Polymer Melt Rheology and Flow Birefringence", Springer-Verlag, Berlin, 1983.
2. J. D. Ferry, "Viscoelastic Properties of Polymers", 3rd Ed., John Wiley and Sons, New York, 1980.
3. B. E. Read, *Polym. Eng. Sci.*, **23**, 835 (1983).
4. T. Inoue, H. Okamoto, and K. Osaki, *Macromolecules*, **24**, 5670 (1991).
5. E. J. Hwang, T. Inoue, and K. Osaki, *Polymer*, **34**, 1661 (1993).
6. E. J. Hwang, T. Inoue, and K. Osaki, *J. Soc. Mat. Sci., Japan*, **43**, 1546 (1994).
7. L. A. Utracki(Translated by Nishi Toshio), "Polymer Copoly-

mers and Polymer Blends(in Japanese)", Tokyo Kagakutoujin, Tokyo, 1991.
8. E. J. Hwang, "Dynamic Birefringence and Viscoelasticity of Amorphous Polymers in the Glass Transition Zone", Doctoral thesis, Kyoto University, 1994.
9. L. R. G. Treloar, "The Physics of Rubber Elasticity", 3rd. Ed., Clarendon Press, Oxford, 1975.
10. J. L. S. Wales, "The Application of Flow Birefringence to Rheological Studies of Polymer Melts", Delft Univ. Press, Delft, Netherlands, 1976.
11. Okamoto, H. Hayashihara, T. Inoue, and K. Osaki, *Nihon Reoroji Gakkaishi,* **19**, 220 (1991).
12. Inoue, E. J. Hwang, and K. Osaki, *J. Rheol.,* **36**, 1737 (1992).
13. T. Inoue, H. Okamoto, and K. Osaki, *Macromolecules,* **25**, 7069 (1992).
14. E. J. Hwang, T. Inoue, and K. Osaki, *Polym. Eng. Sci.,* **34**, 135 (1994).
15. E. J. Hwang, *The Korean J. of Rheology,* **9**, 87 (1997).
16. E. J. Hwang, T. Inoue, and K. Osaki, *Nihon Reoroji Gakkaishi,* **22**, 129 (1994).
17. R. S. Stein and G. L. Wilkes, "Structure and Properties of Oriented Polymers", Elsevier Applied Science Publishers, Barking, UK, 1975.
18. A. A. Askadskii, "Polymer Yearbook IV", **128**, 148 (1987).
19. S. Onogi, "Rheology for Chemist", Kagakutoujin, Tokyo, 1982.