ELSEVIER

Polymer 42 (2001) 765–773

polymer

www.elsevier.nl/locate/polymer

A dielectric study on the local dynamics of miscible polymer blends: poly(2-chlorostyrene)/poly(vinyl methyl ether)

O. Urakawa*, Y. Fuse[1], H. Hori[2], Q. Tran-Cong, O. Yano

Department of Polymer Science and Engineering, Kyoto Institute of Technology, Matsugasaki, Sakyo-ku, Kyoto 606-0085, Japan

Received 15 November 1999; received in revised form 27 March 2000; accepted 7 May 2000

Abstract

Dielectric relaxation of poly(vinyl methyl ether) (PVME)/poly(2-chlorostyrene) (P2CS) blends with a lower critical solution temperature (LCST) was investigated in the one-phase region over a wide range of temperature. Four distinct dielectrically active processes were observed and identified as α_1, α_2, β and γ relaxation processes. It was found that the β and γ processes were almost unaffected upon varying the blend composition, while their relaxation intensities were approximately proportional to the PVME content. Furthermore, there exist two peaks (α_1, α_2) corresponding to the segmental relaxation process of each component. By comparing this with the data obtained by small-angle X-ray scattering and differential scanning calorimetry, the experimental results are discussed in terms of dynamical heterogeneity of miscible polymer blends composed of two polymer components with a large difference in glass transition temperatures. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Miscible polymer blend; Dielectric relaxation; α-relaxation

1. Introduction

The feature of polymer dynamics is characterized by broad relaxation spectra spreading over a wide range of time and length scales. Relaxation processes of a homopolymer can be greatly modified by blending with another polymer component [1]. From the practical viewpoints, it is important to understand and control these relaxation processes because the mechanical as well as electrical properties of multi-component polymers are greatly affected by the mixing process. Most of polymers are not miscible with each other and undergo phase separation upon blending. The correlation between mechanical [2], dielectrical properties [3] and morphology of phase separated blends has been one of the central research subjects for polymer materials science in past decades because physical properties such as high impact strength, optical properties and so on are strongly dominated by their morphologies [1]. On the other hand, dynamics of miscible blends have also been extensively studied by several groups using differential scanning calorimetry (DSC) [4,5], NMR [6–9], dielectric [10–15], mechanical [16–20] and birefringence [16–18] measurements. From these studies it is obvious that polymer components in a miscible blend do not always share the same local segmental dynamics and the relaxation time distribution of the segmental motions is much broader than that of pure components. In some particular cases, a bimodal distribution of the α-relaxation processes can be detected even though the blend is in a single phase [12,13]. As a consequence, the appearance of two α-relaxation peaks for a given binary blend is not necessarily a criterion for determination of phase separation. The two distinct relaxation times observed in the α-process of miscible blends have been qualitatively explained in terms of the so-called “dynamic heterogeneity” arising from the intrinsic difference in mobility of chain segments and the effect of the composition fluctuations.

In this paper, we investigate the dielectric relaxation behavior of poly(2-chlorostyrene)/poly(vinyl methyl ether) (P2CS/PVME) blends. It has been known that this particular blend possesses a lower critical solution temperature (LCST) and its miscibility has been reported to be better than polystyrene (PS)/PVME blends [21,22]. Furthermore, these two polymers have a large difference in T_g and both of

---

* Corresponding author. Address: Department of Macromolecular Science, Graduate School of Science, Osaka University, 1-1 Machikaneyamacho, Toyonaka, Osaka, 560-0043, Japan. Tel.: +81-6-6850-5463; fax: +81-6-6850-5464.

E-mail address: urakawa@chem.sci.osaka-u.ac.jp (O. Urakawa).

[1] Present address: KOYO fine chemical corporation, Minamiku, Kyoto, Japan.

[2] Present address: Department of Macromolecular Science, Graduate School of Science, Osaka University, 1-1 Machikaneyamacho, Toyonaka, Osaka 560-0043, Japan.

0032-3861/01/$ - see front matter © 2000 Elsevier Science Ltd. All rights reserved.
PII: S0032-3861(00)00370-0

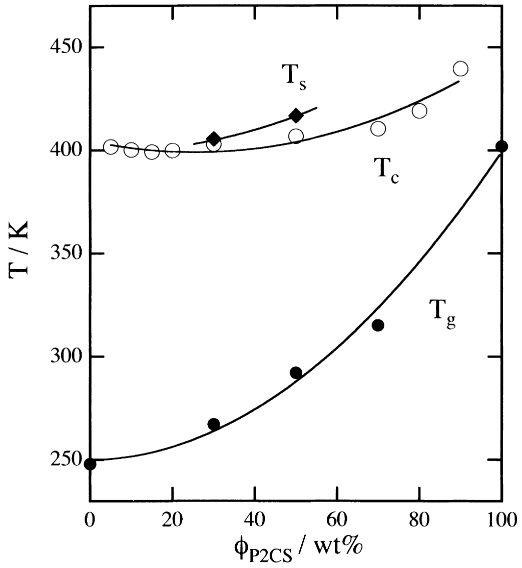

Fig. 1. Composition dependence of the cloud points (T_c), the spinodal temperature (T_s) and the glass transition temperature (T_g).

them have large dipole moments, providing a suitable system for studying dielectric behavior over a wide temperature range. First, the miscibility of P2CS/PVME blends was examined by using small-angle X-ray scattering and DSC. Subsequently, the dielectric relaxation of the blend and its homopolymer components was measured. The composition dependence of the relaxation processes was measured over a wide range of temperature. Finally, these experimental results were compared to other polymer blends such as PS/PVME, poly(vinyl ethylene)/polyisoprene (PVE/PIP) blends with a wide gaps between T_gs of the two polymer components and discussed in terms of dynamic heterogeneity.

2. Experimental section

2.1. Samples

P2CS was obtained by radical polymerization of 2-chrolostyrene (Tokyo Kasei, Japan) in benzene at 60°C with α,α'-azobis (isobutyronitrile) as initiator. After polymerization, the polymer was reprecipitated once by using a toluene/methanol mixture and subsequently twice using a toluene/methylcyclohexane mixture to remove polar impurities.

PVME purchased from Scientific Polymer Products Inc. was precipitated twice using toluene/heptane mixtures. The weight-average molecular weights of P2CS and PVME are $M_w = 4.5 \times 10^5$ and 9.6×10^4, respectively. The former was determined from the intrinsic viscosity [23] measurements with toluene as a solvent at 30°C and the latter by gel permeation chromatograph equipped with a small-angle light scattering photometer (GPC, Tosoh Co., Model HLC-8011). Their molecular weight distributions M_w/M_n are, respectively, 2.5 and 1.6. The blends were prepared by casting the toluene solutions of these polymer mixtures on a Cr-plated brass electrode of dish shape. After drying under vacuum at 60–100°C for 2 days, the sample was sandwiched between two electrodes with a gap of ca. 50 μm and pressed under ambient pressure at the temperatures between T_g and the cloud point T_c of the blends.

2.2. Dielectric relaxation measurements

Dielectric measurements were carried out by using an LCR-meter (Ando Electrics, Japan) with frequency variable between 100 Hz and 100 kHz over a wide range of temperature between 15 and 410 K below the binodal temperatures of the blend. Cr-plated brass electrodes were used for measurements of P2CS/PVME blends and PVME homopolymer. For P2CS homopolymer, silver electrodes were made by vapor deposition onto the samples after solvent casting. Experimental temperatures were controlled with a precision of ±0.5°C.

2.3. Differential scanning calorimetry

Glass transition temperature (T_g) of the blends was measured using DSC (Mac Science, Model 3100) under nitrogen atmosphere with a heating rate of 5°C/min. T_g was determined as the midpoint of the transition on the DSC thermogram.

2.4. Light and X-ray scattering measurements

The cloud points of the blends with various compositions were measured by using a light scattering photometer at a fixed angle (ca. 20°) [24]. To eliminate the kinetic effects in the cloud point determination, the temperatures of phase separation was determined by extrapolating the scattering data obtained with three heating rates 0.1, 0.2 and 0.5 K/min to zero-heating rate, assuming the linear relationship between the cloud points and the heating rates.

Small-angle X-ray scattering using synchrotron radiation was carried out at the BL-10C beam line of the Photon Factory (National Laboratory for High Energy Physics, Tsukuba, Japan) for P2CS/PVME = 3/7 and 5/5 blends. X-rays with a wavelength of 1.488 Å selected from a 2.5 GeV storage ring were point focused on the 1D position-sensitive photon counter. The sample of 2 mm thickness was mounted on a sample holder and kept in a brass heating block whose temperatures were controlled with precision of ±0.5°C. The blend was sandwiched between two Mylar (PET) thin films with the thickness 5 μm. Prior to the data analysis, the scattering intensity was corrected by subtracting the absorption of the sample and two Mylar windows from the total intensities.

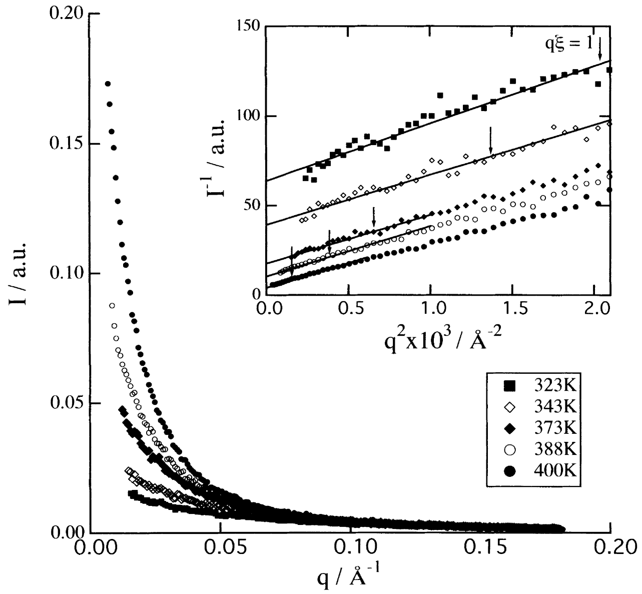

Fig. 2. SAXS profiles for a P2CS/PVME (3/7) blend at various temperature in the one-phase region. The inset shows Ornstein–Zernike plots with arrows indicating the location at $q\xi = 1$.

3. Results and discussion

3.1. Phase behavior and glass transition of P2CS/PVME blends

The composition dependence of the cloud points T_c obtained for P2CS/PVME blend is shown in Fig. 1. From these results, it is obvious that similar to the well-known PS/PVME mixture, this blend has also a lower critical solution temperature (LCST) and undergoes phase separation upon increasing temperature. In order to examine the phase behavior of P2CS/PVME blends in a quantitative way, small-angle X-ray scattering (SAXS) was used to determine the spinodal temperatures of the blend. Fig. 2 shows the typical SAXS profiles obtained for a P2CS/PVME (3/7) blend upon increasing temperature. Obviously, the scattering intensity increases with increasing temperature, revealing the existence of an LCST for the P2CS/PVME blend. The scattering function of the blend is well expressed by the Ornstein–Zernike function:

$$I(q) = I(0)/(1 + \xi^2 q^2) \qquad (1)$$

where q is the magnitude of the scattering vector given by $q = (4\pi/\lambda)\sin(\theta/2)$ where θ is the scattering angle and λ is the wavelength of the incident X-ray, $I(q)$ is the scattering intensity measured at an arbitrary angle with $I(0)$ corresponding to the intensity at zero-scattering vector and ξ is the correlation length corresponding to the wavelength of the concentration fluctuations.

The correlation length ξ was calculated from the ratio of the slope and the intercept of the Ornstein–Zernike plot as shown in the inset of Fig. 2. ξ obtained under various temperatures for P2CS/PVME (3/7) and (5/5) blends was summarized in Table 1. To estimate the spinodal temperature T_s, we assume that the critical behavior of this particular blend obeys the mean field theory and plot $1/\xi^2$ vs. $1/T$ in Fig. 3 for P2CS/PVME (3/7 and 5/5), where T is the absolute temperature. The linear relationship obtained from this plot justifies the validity of the mean field theory within the temperature range of this experiment. The spinodal temperature for a given composition of the blend was then obtained by extrapolating $1/\xi^2$ to zero. These T_ss are also shown in Fig. 1 along with the cloud points T_c. The spinodal temperatures situate just above the cloud points of the blend, justifying also that this blend has a LCST.

Fig. 4 shows the DSC thermograms of P2CS/PVME blends with various compositions including P2CS and PVME homopolymers. All the blends exhibit a single glass transition temperature (T_g). The arrows in the figure correspond to the midpoints of the transition that were taken as T_g of the sample. The composition dependence of these glass transition temperatures was shown previously in Fig. 1. The negative deviation from the linear relation between T_g and ϕ_{P2CS} has also been reported previously and was explained by the Kwei's formula with the attractive interactions between P2CS and PVME [22]. The gap in T_gs of the component polymers in the P2CS/PVME blend is 160 K, which is much larger compared to PS/PVME (130 K) and poly(vinyl ethylene)/polyisoprene (PVE/PIP) (64 K) [4] blends. It is, therefore, expected that the P2CS/PVME blends would exhibit a remarkable effect of dynamic heterogeneity in the relaxation behavior due to a large difference in the component dynamics.

3.2. Dielectric relaxation of P2CS and PVME homopolymers

Fig. 5 shows the isochronal dielectric loss ϵ'' for P2CS and PVME homopolymers measured at a frequency of 1 kHz. P2CS exhibits a β-relaxation peak around 400 K and a broad shoulder corresponding to the α-relaxation in the lower temperature side. It is known, from the literature, that tan δ of P2CS homopolymer has the relaxation

Table 1
Characteristic length of concentration fluctuations for P2CS/PVME = 3/7 and 5/5 blends

T (K)	ξ (Å)	
	(3/7)	(5/5)
323	22.1	
343	27.0	
353	29.8	
373	39.0	
380	46.3	
388	50.8	39.0
396	64.7	47.3
400	79.8	51.4
405		62.6

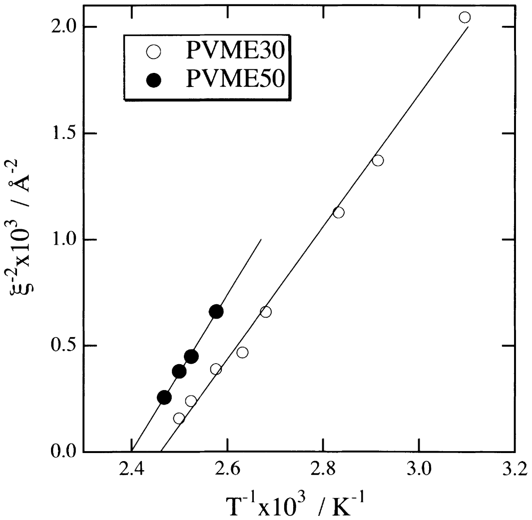

Fig. 3. Plots of ξ^{-2} versus reciprocal temperature T^{-1} for P2CS/PVME (3/7 and 5/5) blends.

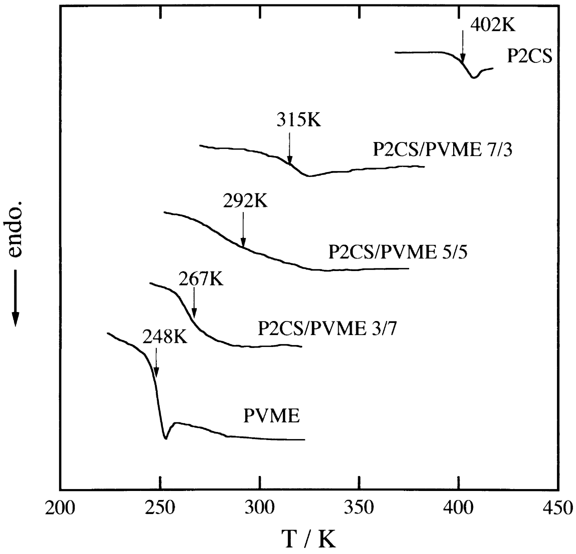

Fig. 4. DSC traces for the homopolymers and P2CS/PVME blends with various composition.

intensity in the order of 10^{-5} below 100 K [25]. However, within our experimental accuracy, no significant relaxation could be observed for P2CS below 200 K. On the other hand, PVME homopolymer shows three distinct peaks designated respectively as α, β and γ from the high-temperature side. The α-relaxation is related to the segmental motions of PVME whereas β and γ processes are related to the molecular motions of smaller scales. In order to assign the β- and γ-relaxation processes of PVME, Arrhenius plots of the frequencies corresponding to these peaks are shown in Fig. 6. The activation energies of these two modes are 5.6 and 1.3 kcal/mol for the β- and γ-processes, respectively. It would be expected that the rotational relaxation of the methyl ether groups is responsible for these local modes. To elucidate the origin of these local motions, the potential energy of the model compound 2-methyl ether propane illustrated in Fig. 7 was calculated as a function of the rotational angle ϕ_1 around the O–C bond by using a commercially available software CSChem3D Pro®. The dependence of the potential energy on the angle ϕ_1 is shown in the same figure. It was found that there exist two barriers corresponding, respectively, to the steric hindrance between CH_3(a)–H(a) and CH_3(a)–CH_3(b,b′) as shown in the potential map of Fig. 7. The energy barriers obtained from the calculation are 4.4 and 1.3 kcal/mol, which are very close to, respectively, the experimentally observed activation energies 5.6 kcal/mol for the β-process and 1.3 kcal/mol for the γ-process.

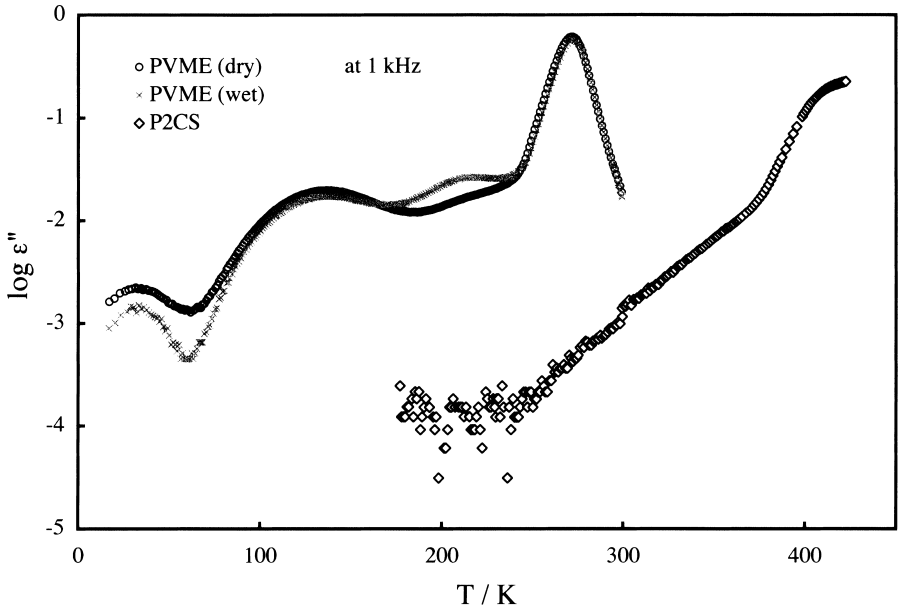

Fig. 5. Temperature dependence of the dielectric loss ϵ'' of P2CS and PVME (dried and treated under humidity).

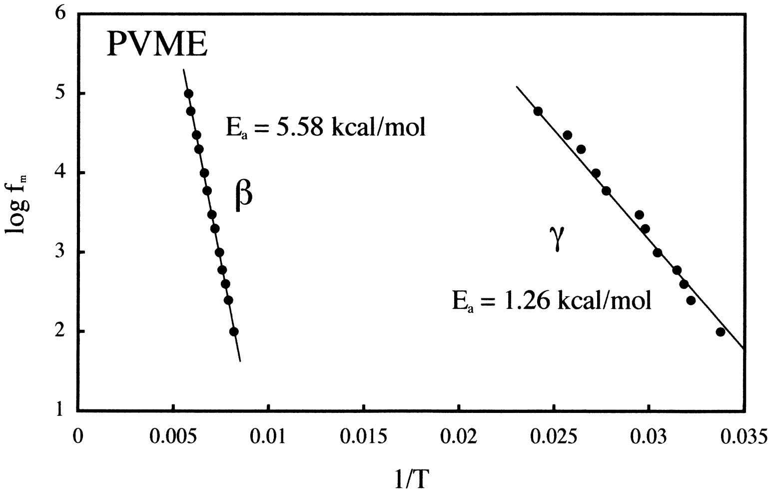

Fig. 6. Arrhenius plots for the β- and γ-relaxation processes of a PVME homopolymer.

These results suggest that the molecular motions corresponding to the β- and γ-relaxation of PVME can be assigned, respectively, as the free and restricted rotational motions of the methyl ether groups around O–C bonds (ϕ_1-rotation).

As seen in Fig. 5, between the α- and β-peaks, there exists a broad and minor relaxation whose intensity increases with the moisture content of the sample. In this figure, the temperature dependence of the ϵ'' for PVME samples treated under the atmosphere of 100% humidity was compared to a sample dried under the conditions described in the experimental section. It was found that the intensity of the peak appearing at 210 K greatly increases with the water content in the sample, indicating that moisture is responsible for the broad peak between the α- and β-relaxation processes.

3.3. Dielectric relaxation of P2CS/PVME blends

Fig. 8 shows the isochronal ϵ'' of P2CS/PVME blends with the compositions 10/0, 7/3, 5/5, 3/7 and 0/10 observed at the frequency 1 kHz. Below 200 K, the β- and γ-relaxation peaks of PVME component in the blends appear remarkably because P2CS has negligibly small dielectric response compared to PVME. It is obvious that the peak temperature of the β- and γ-relaxation processes remain unchanged regardless of the blend composition. The peak height, on the other hand, is approximately proportional to the PVME composition of the blends. Fig. 9 shows the Arrhenius plots for the β- and γ-relaxation observed in the blend.

These activation energies are almost unchanged with the blend composition. From these results, we conclude that the

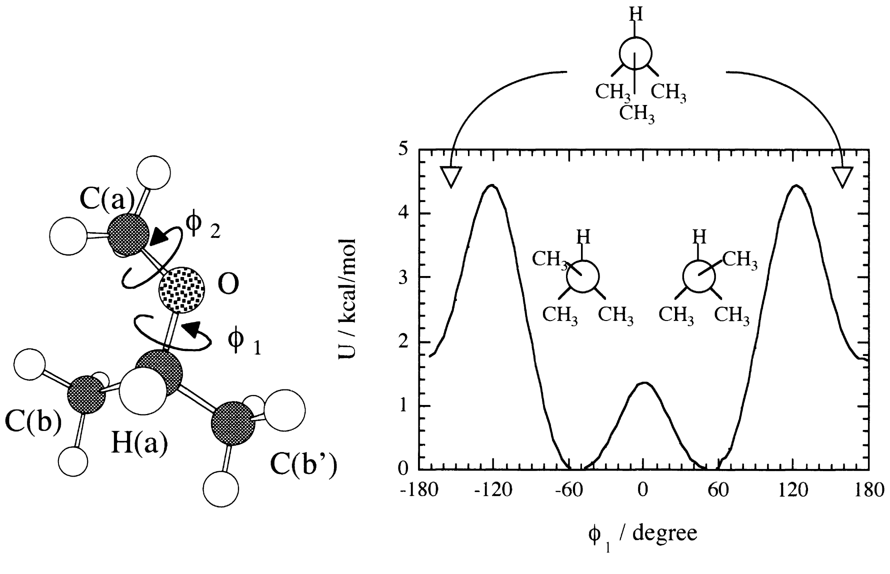

Fig. 7. Potential curves as a function of the rotation angle ϕ_1 with a fixed ϕ_2 (= 180°) calculated by using CSChem3D Pro®.

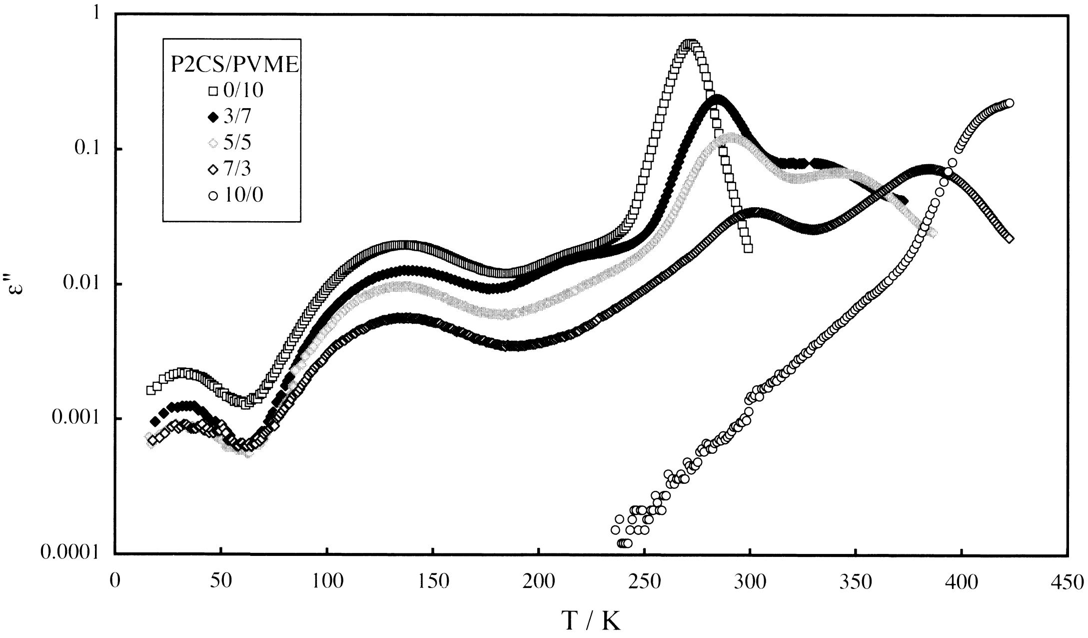

Fig. 8. Isochronal ϵ'' curves obtained at 1 kHz for P2CS/PVME blends with various compositions.

dynamics of β- and γ-relaxation processes of PVME is not affected by blending with P2CS. In other words, the time scale of the molecular motions involved in the β- and γ-relaxation is insensitive to the change in the environments upon blending and therefore the relaxation behavior of PVME remains as in the unblended state.

On the other hand, blending apparently changes the α-relaxation as seen in Fig. 8. The unusual behavior is the appearance of two peaks (α_1, α_2) in dielectric loss ϵ'' for all the blend compositions, P2CS/PVME = 3/7, 5/5, 7/3 though these blends are in the one-phase region as revealed by SAXS measurements. Here α_1 and α_2 denote the α-relaxation peaks in higher and lower temperature sides, respectively. In order to examine the possibility of micro-phase separation, the dielectric relaxation of the blends containing P2CS with different M_w was measured and compared to those with P2CS of higher molecular weights because it is expected that P2CS/PVME blends with P2CS of low M_w has the wider miscible region [22]. The experimental results are shown in Fig. 10 where the P2CS/PVME blends with P2CS of $M_w = 61{,}000$ and 442,000 are used. The overlap of isochronal ϵ'' curves observed over a wide range of temperature 250–400 K for these two blends suggests that the appearance of the double α-peaks is the inherent feature of the blend and is not originated from micro-phase separation. Unlike the glass transition data obtained by DSC shown in Fig. 4, dielectric spectroscopy is able to resolve with high sensitivity the dynamics of polymer components in the blends.

Over the past decade, dynamic heterogeneity of polymer blends has been extensively studied, particularly for PVE/PIP mixtures [4,8,9,12,13,16–19]. It is well known that PVE/PIP blends are miscible in all compositions and the

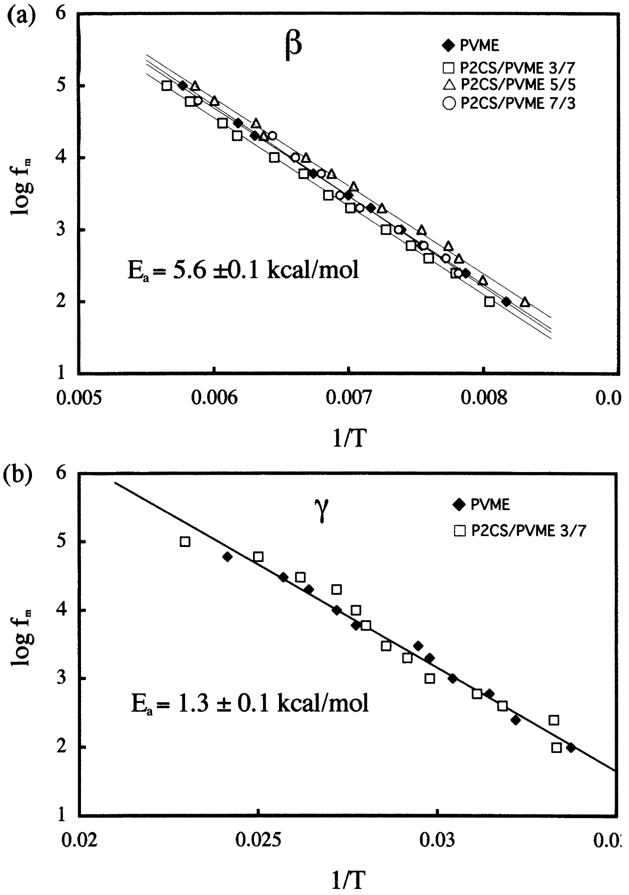

Fig. 9. Arrhenius plots for: (a) the β-relaxation; and (b) the γ-relaxation processes of PVME in P2CS/PVME blends of various compositions. The γ-peaks were not accurately measured for P2CS/PVME 5/5 and 7/3 blends because of the low intensity. Thus only the data of P2CS/PVME 0/10 and 3/7 are shown in the figure.

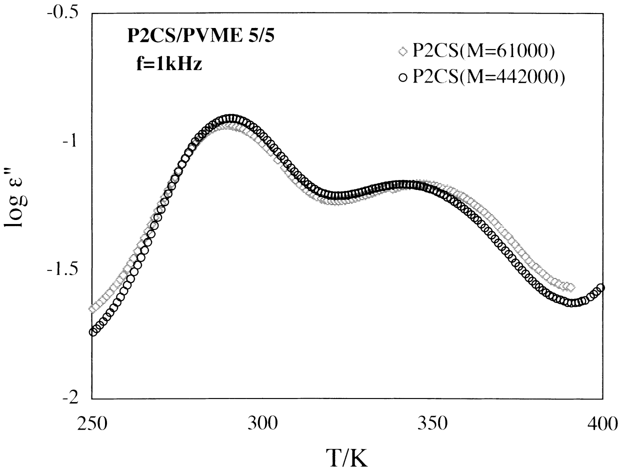

Fig. 10. Temperature dependence of the dielectric loss ϵ'' obtained at 1 kHz for P2CS/PVME blends (5/5) with P2CS of different M_w (6.1×10^4 and 4.42×10^5).

segmental interactions between PVE and PIP are nearly athermal [26,27]. In addition, the two components of the blend have a large difference in T_g ($\Delta T = 64$ K) which makes the dynamical inhomogeneity of the mixture significant: unusually broad width of the glass transition [19], breakdown of the time-temperature superposition principle [18,19] and the appearance of two α-relaxation peaks in dielectric loss [12,13]. However, miscible polymer mixtures exhibiting two separated α-peaks are not common, except the PVE/PIP blends, to the best of our knowledge. As shown in Fig. 8, the P2CS/PVME blend is another particular system having two α-peaks. It is noted that for the P2CS/PVME blend two α-peaks appear though attractive interaction between two components exists in contrast to PVE/PIP blend where the interaction is nearly athermal.

Shown in Fig. 11 are the dielectric loss for P2CS/PVME (5/5) and PS/PVME (5/5) blends for comparison. The β-relaxation process of PVME in these two blends is almost the same, whereas the α-relaxation of the PS/PVME is apparently different from that of the P2CS/PVME blend due to the absence of the α_1-peak in the higher temperature side. The small deviation between the two α-peaks at the low-temperature side of these two blends is probably due to the difference in the T_gs of PS and P2CS components. The significant difference in shape of the isochronal ϵ'' curves (double vs. single α-peaks) can be explained by the fact that P2CS has a larger dipole moment compared to PS. The peak of P2CS/PVME blend, which appears in the higher temperature side (α_1), can be assigned as the segmental motions of the P2CS component and the one observed in the lower temperature side (α_2), as that of PVME. At the detailed level, a small but not negligible shoulder exists on the ϵ'' of PS/PVME at ca. 340 K as shown by an arrow in the figure. This relaxation might reflect the segmental motions of the PS component. The small dipole moment of PS might be responsible for this small dielectric loss of PS/PVME blends.

Mixing two polymer components gives rise to the change in their segmental dynamics due to the coupled or cooperative motion between two kinds of segments. However, complete coupling in the segmental motions is hardly realized unless the different kinds of segments are connected via covalent bonds. In a miscible state, if the surrounding molecules around one particular segment can be approximately regarded as a uniform media in the mean-field sense, then each component dynamics being different in its pure state will become similar in the same surroundings. However, we believe that they cannot inherently take the same dynamics and independent nature for the segment dynamics remains because of the difference in chemical structures, i.e. difference in the segment size and in the degree of motional coupling with surrounding molecules.

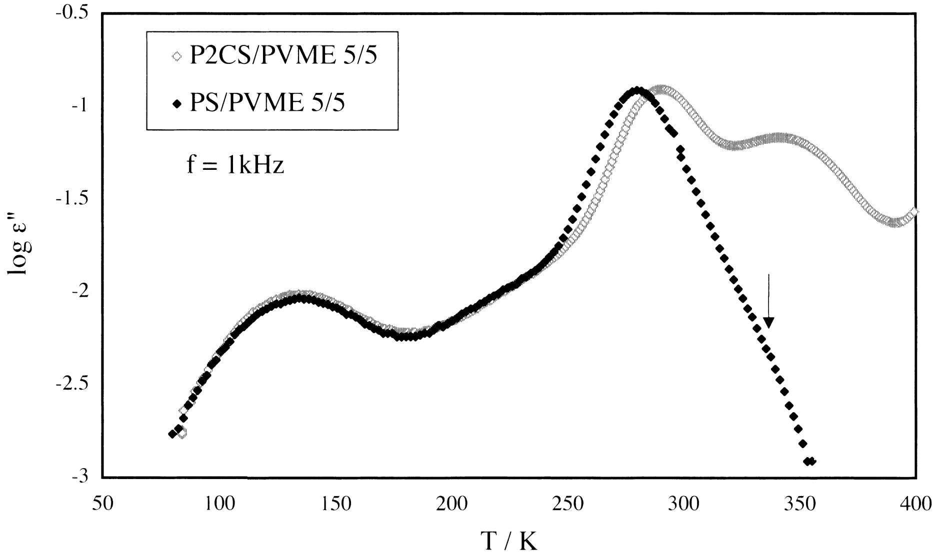

Fig. 11. Comparison of the isochronal ϵ'' observed at 1 kHz for a P2CS/PVME (5/5) and PS/PVME (5/5) blends.

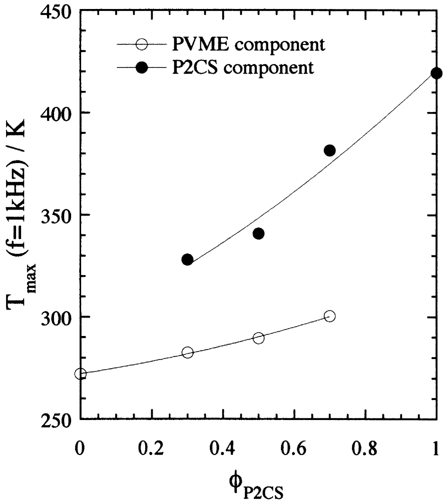

Fig. 12. ϕ_{P2CS} dependence of the maximum position of the two α-peaks of a P2CS/PVME blend observed at 1 kHz.

Thus we think that two time scales must exist more or less in the α-relaxation of any miscible polymer blends. Furthermore, it has been shown that the effect of composition fluctuations does not induce the two separate time scales in motions of two kinds of segments, but broadens the distribution function of the relaxation times [10,11], in the case that the time scale of the fluctuation is much faster than the segmental relaxation times. (If the segment size is larger than the correlation length ξ, such effect will no longer play an important role in α-dynamics.) Thus the appearance of double-peaks does not originate from the composition fluctuation effect but from the intrinsic difference of segment dynamics. From the static viewpoint, the fact that the SAXS profiles can be well fitted by the Ornstein–Zernike theory as shown in Fig. 2 whereas the ϵ'' of these blends exhibits two distinct peaks of α-relaxation, might be a reflection of the difference between the dynamic and static homogeneity. In other words the intrinsic difference in the segmental dynamics of each component does not disappear if the blends are statically mixed each other.

Two α-peaks as seen in Fig. 8 cannot always be detectable depending on the experimental method. The most powerful technique to detect these features is the usage of chemical labeling to the one component. Fig. 11 is the typical example showing that the dipole labeling (incorporation of chlorine) enables us to detect the two α-dynamics while deuterium labeling to one component is usually used for NMR or IR dichroism.

The dependence of the peak temperature, T_{max}, on the P2CS composition, ϕ_{P2CS}, observed at 1 kHz is shown in Fig. 12. Compared to P2CS, T_{max} of PVME does not depend strongly on the composition of the blend. Furthermore, the gap between the two T_{max}s, which reflects the dynamic heterogeneity of the blend, becomes larger as the P2CS composition increases. This may possibly suggest that the independent nature of the segmental dynamics for each component polymer will be enhanced as the increase of ϕ_{P2CS}.

4. Summary

1. Four dielectrically active processes were observed for a P2CS/PVME blend. From the low-temperature side, these are, respectively, the γ-relaxation resulted from the restricted rotational motions of the methyl ether group in PVME below 50 K, the β-relaxation originating from the free rotational motions of PVME side chains and the two α-relaxation processes that are assigned as the segmental motions of the PVME component (corresponding to the low temperature peak) and of the P2CS component (the high temperature peak).
2. The peak temperatures and the activation energies of the β- and γ-relaxation processes remain unchanged upon varying the blend composition, implying that the dynamical environment for the motional units involving in the β- and γ-relaxation in PVME are almost unaffected by mixing with P2CS.
3. The emergence of two α-peaks can be explained by the dynamic heterogeneity effect arising mainly from the intrinsic difference in mobilities of two kinds of segments.

Acknowledgements

We greatly acknowledge the financial support from the Ministry of Education, Science, Sports and Culture, Japan under a Grant-in-aid No.08751047 (to O.U.).

References

[1] Araki T, Tran-Cong Q, Shibayama M, editors. Structure and properties of multi-phase polymeric materials. New York: Marcel Dekker, 1998.
[2] Imagawa A, Tran-Cong Q. Macromolecules 1995;28:8388.
[3] Runt JP. Dielectric studies of polymer blends. In: Runt JP, Fotzgerald JJ, editors. Dielectric spectroscopy of polymeric materials, Washington, DC: ACS, 1997 (Chap. 10).
[4] Trask CA, Roland CM. Macromolecules 1989;22:256.
[5] Bershtein VA, Egorov VM. Differential scanning calorimetry of polymers: physics, chemistry, analysis, technology. Chichester: Ellis Horwood, 1994.
[6] Le Menestrel C, Kenwright AM, Sergot P, Laupretre F, Monnerie L. Macromolecules 1992;25:3020.
[7] Chin YH, Zhang C, Wang P, Inglefield PT, Jones AA, Kambour RP, Bendler JT, White DM. Macromolecules 1992;25:3031.
[8] Chung G-C, Kornfield JA, Smith SD. Macromolecules 1994;27:964.
[9] Chung G-C, Kornfield JA, Smith SD. Macromolecules 1994;27:5729.
[10] Fischer EW, Zetsche A. Polym Prepr (Am Chem Soc Div Polym Chem) 1992;33:78.
[11] Zetsche A, Fischer EW. Acta Polym 1994;45:168.
[12] Alegria A, Colmenero J, Ngai KL, Roland CM. Macromolecules 1994;27:4486.
[13] Alvarez F, Alegria A, Colmenero J. Macromolecules 1997;30:597.

[14] Rellick GS, Runt J. J Polym Sci Polym Phys Ed 1986;24:279.

[15] Rellick GS, Runt J. J Polym Sci Polym Phys Ed 1986;24:313.

[16] Zawada JA, Fuller GG, Colby RH, Fetters LJ, Roovers J. Macromolecules 1994;27:6851.

[17] Zawada JA, Fuller GG, Colby RH, Fetters LJ, Roovers J. Macromolecules 1994;27:6861.

[18] Arendt BH, Krishnamoorti R, Kornfield JA, Smith SD. Macromolecules 1997;30:1127.

[19] Roovers J, Toporowski PM. Macromolecules 1992;25:3454.

[20] Colby R. Polymer 1989;30:1275.

[21] Tran-Cong Q, Kawakubo R, Sakurai S. Polymer 1994;35:1236.

[22] Tran-Cong Q, Nakano H, Okinaka J, Kawakubo R. Polymer 1994;35:1242.

[23] Braudrup J, Immergut EH. Polymer handbook. 3rd ed. New York: Wiley, 1989.

[24] Tran-Cong Q, Nagaki T, Yano O, Soen T. Macromolecules 1991;24:1505.

[25] McCammon RD, Saba RG. J Polym Sci Part A-2 1969;7:1721.

[26] Tomlin DW, Roland CM. Macromolecules 1992;25:2994.

[27] Roland CM. J Polym Sci Part B Polym Phys 1988;26:839.